# STUDIES
# on
# ALLOPHANE
# in
# SCOTTISH SOILS

Thesis

presented for the degree of
Doctor of Philosophy
in the
University of Glasgow
by
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Agricultural Section
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## SUMMARY

High amounts of allophane as measured by the sodium fluoride test were found in the brown forest soils and B horizons of podzols developed on basalt and basalt till. A hydrologic sequence of the Darleith association was examined and the soils' strong aggregation, high organic matter levels and phosphate retention were found due to their allophane content. Allophane was found also in the C horizons of podzols of other material.

C horizons flocculated on ultra-sonic vibration but were dispersed in ammonia. All horizons however, when vigorously peroxidised, behaved like allophane soils and remained flocculated in alkaline suspension. The relative tendency of a soil to flocculate appeared to depend on the number of aluminous sites exposed ie. on the amount of allophane and its $SiO_2 : Al_2O_3$ ratio. This correlation was supported by analysis of the alumino-silicate extracted with (a) cold 5% $Na_2CO_3$ (b) cation exchange resin (c) 1% citric acid, and by the rise in suspension pH on NaF treatment.

NaF released more Al, and $Na_2CO_3$ more Al and much more Si when added to dry soil than to suspensions, and this was attributed to energy provided by the heat of wetting.

Successful dispersion of flocs, as measured by mechanical analysis, was obtained for a New Zealand Tirau B horizon and the peroxidised Scottish soils by :

(1) Vibrating in HCl at pH 4.3. This was only possible for Tirau B, with negligible clay mineral present.

(2) Vibrating in zirconium or thorium nitrate solution and pH controlled at 4.3. Adsorption of the hydrolysis products (polycations) on the negative colloids, reversing their charge, was the dispersion mechanism.

(3) Shaking with Na-exchange resin, followed by hand shaking in ammonia. The resin took up large quantities of alumina and silica and some iron, in addition to bases.

(4) Vibrating in alkaline silica sol.

(5) Vibrating in sodium hexametaphosphate. Peroxidised Darleith soil dispersed in calgon. Tirau B was partially dispersed in $(NaPO_3)_6$ at pH 7.5.

(6) Repeated washing of alkaline flocs followed by shaking in NaOH (efficiency not yet measured).

(7) Dialysis at soil pH gave partial dispersion of Tirau B.

Alkaline flocculation of allophane could be explained in terms of (a) alumina groups (b) their capacity to adsorb hydroxyl (c) the presence of free electrolyte. Dispersion was achieved by any mechanism which interfered with one of these, viz. by:- masking alumina groups with organic matter or silica; 'destroying' hydroxyl with $H^+$ ions; or removal of electrolyte. This interpretation is inherent in Mattson's 1922 paper, in which adsorbed hydroxyl ions were shown to be flocculating agents, and a bridging mechanism dependent on electrostatic linkages between them and divalent cations in the free electrolyte was envisaged.

A review was made of the concepts of aggregation, coagulation and flocculation. Experiments showed the validity of the distinction between 'coagulation' by electrolytes and 'flocculation' by polyelectrolytes was unsubstantiated. It was suggested that aggregation could be interpreted in terms of the double layer Verwey-Overbeek theory, but flocculation required another explanation. Mattson's work, together with his postulate of the crucial role of the hydroxyl group should be reappraised.

The unusual cation exchange properties of allophane described in the work of New Zealand and Japanese soil scientists were re-interpreted in the light of Mattson's experiments with amphoteric colloids. Anomalies were explained in terms of the acidoid-basoid complex.

Sodium fluoride was used to extract allophane-held organic matter. Optimum conditions were established at pH 6 to 7. Approximately 30% of total polysaccharide was extracted, or allowing for non-humified cellulose, about 50% of soil 'combined' polysaccharide. It appeared to be representative in composition. Sodium fluoride extraction of soils high in allophane offers a technique for the systematic study of virtually unaltered organic matter.

N.B. Plastic artefacts interfered with organic matter studies: (a) Moist soils stored in plastic bags became impregnated with mobile hydrocarbons.
(b) Dialysis tubing dissolved out reducing substances. These gave high values to polysaccharide analyses and interfered with sugar chromatograms.

The Forestry Commission finding that spruce checked on basalt brown forest soils, and that the needles showed phosphate deficiency although the soils appeared to contain adequate phosphate, led the writer to postulate that aluminium toxicity was the cause of the phosphate deficiency. Large amounts of alumina were dissolved by 1% citric acid. Mattson and Hester (1933) showed that the pH of injury to wheat seedlings was raised in soils of low silica-sesquioxide ratio due to the greater mobility of aluminium. If the toxicity hypothesis were correct, the condition could be ameliorated by adding organic matter to mask aluminous sites and lower the pH of injury, or by liming. An alternative crop might thrive better than spruce. No allophane reaction to the NaF test was found on Darleith soils under hardwood, even where it was strong in the adjoining grassland.

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"Many anomalies will therefore be encountered but these are of value and should be studied as to their cause, for very often the most fundamental truths are thus established."

Sante Mattson.

# PREFACE

The work for this thesis was done in the Agricultural Chemistry Section of the Chemistry Department, University of Glasgow, while the writer was employed as an Assistant and then Temporary Lecturer, between October 1966 and February 1972.

The writer thanks all those who have aided her in these complementary tasks. In particular she thanks Dr. W.R. Rees, her former supervisor, for his inspiration, unfailing interest and trust; and his successor Dr. H.J. Duncan for the unstinted and generous way in which he was ever ready to assist, advise and discuss, and who in the last few months, took on more than his share of work in the Section, so that this thesis could be completed.

Thanks are due also to members of the Macaulay Institute of Soil Research; to Dr. R.C. Mackenzie and those in his Pedology Department who gave the writer hospitality for three weeks in the summer 1967, and to Mr. B.D. Mitchell for his help and interest and especially for his suggestion of South Drumboy as a demonstration catena, which led in the course of time to the present study. The writer thanks Soil Surveyors Mr. J.M. Ragg, Mr. J.S. Bibby and Mr. C. Bown, and also Mr. D.B. Patterson, Soil Survey Officer of the Forestry Commission, all of whose soil excursions have been invaluable to the writer and other members of this Section. She trusts they have been quoted correctly. She is particularly indebted to Mr. Patterson for a copy of the Fiunary Forest site survey report. Among those also whose assistance is much appreciated is Mr. James Young of South Drumboy Farm who has allowed his fields to be used for soil demonstrations every year.

Heartfelt thanks are expressed to Mrs. Maureen McIntyre for the patient and devoted way in which she typed an unwieldy minuscript; to Mrs. Ilsa Sobel whose reading from Mattson's 1922 German paper convinced the writer it contained the key to the allophane problem; and finally to Mrs. Helen Lee who prepared an exact translation of this long and important work and gave it to the writer as a gift.

# PART ONE

# REVIEW AND DISCUSSION

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# CHAPTER I : INTRODUCTION.

## 1. Origin of Study.

This study began as an investigation into the weathering of minerals. It was thought that the relative roles of complexing, acidity and the development of chemical potential by the interaction of plant, organic matter and soil solution with the rock minerals might be the object of the research. At the same time, it was decided to become familiar with the mineralogy of a hydrologic sequence of soils on South Drumboy, a hill farm in north Ayrshire. This was being used by the writer, and with the kind permission of the owner, Mr. James Young, for demonstrating soils in the field and in laboratory practice. It had been recommended as an excellent soil catena for the purpose, by B.D. Mitchell of the Macaulay Institute. In the event, the character of these soils posed a number of interesting questions and determined the direction of the research.

## 2. Soil Survey.

The area studied is an upland region on the southern edge of the Ballagioch plateau (600 - 1000 ft.)

Small hills, including South Drumboy itself, rise from the base of the plateau and the sharp changes in topography and micro-climate that are a feature of their slopes give rise to a hydrologic sequence of soil types. The solid rock is lava of Calciferous Sandstone age and comprised of basalt, porphyry and trachyte. It is overlain non-uniformly by glacial till. The ice which affected north Ayrshire flowed southwest from the Scottish Highlands, scouring the plateau and depositing its burden on the lee side of the hills, which is the situation of South Drumboy. The till has had a marked influence on soil type, but this has depended on its variable depth and texture, rather than on any difference in mineralogy, for, in general it is mainly derived from the local rock. The Drumboy soils however, have a sedimentary component of sandstone till.

The primary mapping unit of the Soil Survey of Scotland is the soil series, based on the morphology of the soil profile. Variations between one profile and another are largely governed by the drainage conditions within the soil. The soil series are then grouped into a major cartographic unit based on the parent material and called the Soil association. Soils developed on till derived from Calciferous Sandstone lavas have been assigned to the Darleith association (Mitchell and Jarvis 1956). This is widespread in central Scotland, particularly in the West. For example, it covers 103·2 square miles on the Kilmarnock sheet, very small areas are represented on the Kelso and Lauder sheet and the Haddington sheet, and it occurs in areas of Blairadam Forest. Due to high rainfall and altitude, the dominant land use is pastural, although some areas are being afforested.

On South Drumboy, the following soil types are represented:- (i) peaty podzol with thin iron pan (Baidland series), (ii) shallow, freely drained brown forest soil (Darleith series), (iii) imperfectly drained brown forest soil (Dunlop series), (iv) poorly drained surface-water humic gley (Amlaird series). (v) very poorly drained ground-water humic gley (Dunwan series), (vi) very poorly drained surface-water peaty gley (Myres series).

Hill farming is the agriculture of the district. The farms are small (South Drumboy has 322 acres) and marginal, and most of them appear to be poorly drained. They carry sheep and dairy cattle. The limiting factors are severe, both with respect to climate and soil.

Rainfall is high : Kilmarnock has a recorded 41·2 inches mean annual rainfall and the hill farms would receive more than this. Cloud cover is extensive : Kilmarnock's average bright sunshine is recorded as 1,255 days or only 28% of the possible. There is exposure to strong west and southwest winds and little shelter exists for the farms. Soils are limited either by shallowness due to outcropping rock, or by peat deposits, or by thick periglacial indurated layers, or by clay horizons developed from heavy textured till. Thus, much of the area would be considered class 4 or 5 in the land use capability classification (Bibby and Mackney, 1969).

## 3. Problems raised by the Darleith soils.

Despite these strictures, the brown forest soils of the Darleith association are inherently fertile. They are developed on base-rich material, and they have a particularly well-aggregated structure which allows good drainage despite climatic wetness. Ferruginous soils, world wide, are noted for their structural advantages and the firm and stable crumb structure of the Darleith have been attributed to their high iron oxide content (Mitchell and Jarvis, 1956). Since high rainfall and altitude make these soils in general unsuited to arable farming, it might be thought they would be among the better soils available to soft-wood forestry. This is not the case, however, for workers of the Forestry Commission have been disappointed to find that spruce checks badly on them and makes poor growth. The same problem has arisen with the similar potentially fertile tertiary lava soils of Mull and Fiunary Forest in west Argyll. At first it was postulated that the trouble might lie in phosphate unavailability, due to its fixation by the iron oxide (G. Pyatt, D.B. Patterson, pers. comm. 1969). Later it was discovered that although foliar analysis showed the spruce was indeed deficient in phosphate, acetic-soluble phosphate figures for the soil showed moderately good availability (D.B. Patterson, pers. comm. 1971).

The first discovery that raised doubts about the role of the iron oxides and suggested another interpretation for the soil properties was that three of the series in the sequence contained a high amount of allophanic material ie. of amorphous alumino-silicate. This could easily be seen in the field by the fluoride test (Fieldes and Perrott 1966). In this test a saturated solution of sodium fluoride is added to a soil crumb and the release of hydroxy groups displaced from the amorphous alumina by fluoride is made visible by having the crumbs arranged on filter paper pre-soaked in phenolphthalein. The B horizon of the peaty podzol and all horizons of the two brown forest soils, with the exception of Darleith S, stained the paper red. The gley soils and horizons gave no reaction. In the laboratory, the reactive soils suspended in saturated sodium fluoride solution reached pH values between 9•9 and 11•4 in forty minutes. The gley soils only rose within the range pH 7•7 to 8•9.

Several lines of enquiry were suggested by this information and these are summarised below, together with others that arose out of laboratory work.

(a) The high degree of aggregation might be due to allophanic clay rather than the iron oxide. The sand fraction indeed contained high proportions of hematite and pyroxene magnetite, but the sand-sized aggregates before dispersion were tightly bound by clay which was not necessarily ferruginous. The argument had practical relevance because if the allophanic material influenced the soil structure, this might be important in agricultural management. It might be recommended for example, that organic matter levels should be well maintained; or that a soil which appeared poor because of bad drainage, was potentially fertile and worth an economic outlay.

(b) If the soils were indeed susceptible to phosphate fixation, it might be the allophanic clay rather than the iron oxide which was primarily responsible. Liming the soil would improve phosphate availability in either case, but addition of organic matter and its preferential fixation on the aluminous sites, would inhibit the retention of phosphate by the soil. In view however, of the later discovery, by workers of the Forestry Commission, that phosphate was available in the soils but deficient in the spruce, the writer postulated that aluminium toxicity might be the cause of the deficiency and poor growth of the trees.

(c) Since allophane is well-known to have a pH dependent charge and thus a pH dependent cation exchange capacity, it was of interest to find out how far, if at all, the CEC of the mineral colloids was lowered by the acid pH. This was possibly of some importance since many farmers in the area (as indeed in other parts of Britain) were in economic straits and neglecting to lime. The pH of the surface horizons of the two brown forest soils ie. of the best pasture, varied during the period of study from 4•8 to 5•8 pH. Up until the summer of 1970, the Dunlop sward had not been limed for nine years.

(d) Routine mechanical analysis revealed that the $C_g$ horizon of the Dunlop soil could not be dispersed by the usual method of ultra-sonic vibration. Furthermore, when the other horizons, and also an Amlaird gley horizon were peroxidised and then given ultra-sonic treatment, massive flocculation followed. This unexpected discovery led to studies of the flocculation and dispersion properties of the soils, and also of a New Zealand allophane soil, with various reagents. It became of interest not only to find an efficient method of dispersion but in addition to understand the various mechanisms and interactions which induce flocculation and make allophane soils so difficult to disperse.

(e) Since allophane is associated with a high content of organic matter and is thought to inhibit humus decomposition, extraction with sodium fluoride was tried in the expectation that, if the pH were controlled at 7•0, this would turn out to be a mild but efficient method of dissociating the organic fraction from the clay in virtually unaltered form. It was decided to have a preliminary look at the polysaccharides, since these have been found important in soil aggregation.

(f) It was wondered why the allophanic material had not developed under gleyed conditions. The Amlaird and Dunwan gleys had a considerable amount of sedimentary material in the profile which would not be expected to give rise to alumino-silicate, but nevertheless they were mainly derived from basalt. It was asked whether the reducing conditions with mobile iron masked or inhibited the allophanic material from developing. So far no gley soils in Scotland have given a positive fluoride test (J.M. Ragg, pers. comm. 1971).

(g) Various technical difficulties produced some side-issues. The most important of these was the discovery of plastic artefacts. For example, (i) plastic bags leaked certain of their components into the wet soil collected in them when it was allowed to stand over a period of time. The saturation was such that a noticeable amount of hydrocarbon could be distilled from a gram of soil or even a spoonful of sand grains. (ii) dialysis bags leaked a large amount of a glycerol-like material which gave spuriously high results to polysaccharide analyses and spoilt sugar chromatograms. Hence, plastic was avoided both in soil sampling and in any laboratory work where the organic fraction was under examination. It was thought perhaps there might be other cases where the use of plastic could be detrimental or polluting and that situations where this might occur should be considered.

It will be seen that a rather wide spectrum of problems emerged, each of which deserved a special study, but all of which were connected with the presence of allophanic clay. Much of the work described in the experimental chapters is only exploratory. The writer has tried to indicate how it might be followed up, and to describe experiments generated by this exploration, part-devised but left undone, which stretch out like waves to the horizon.

# CHAPTER II : STUDIES OF ALLOPHANE.

## 1. The Nature of Allophane.

Allophanes are amorphous alumino-silicates. They are amorphous in the true sense, that is, they are not amorphous to X-rays or to an electron beam merely on account of small particle size, although the average size of New Zealand yellow-brown loam allophane has been found to be less than 50 Å (Fieldes and Swindale 1954). They are truly non-crystalline or "defined by a common property of structural randomness" (Fieldes 1966). This was established for allophanes of geological origin which were the first to be investigated (Ross and Kerr 1934; Adler 1950), and found to be (a) without definite crystal structure (giving no sharp X-ray nor electron diffraction maxima), (b) without definite index of refraction (varying from 1·472 to 1·496), (c) without regular molecular arrangement (giving no sharp infra-red maxima in the 600 to 3,500 kaysers region where characteristic spectra of many silicates appear), and (d) without definite chemical composition ($SiO_2$ 25·19 to 33·96%; $Al_2O_3$ 30·41 to 36·53%; $H_2O-$ 12·84 to 21·20%; $H_2O+$ 14·43 to 20·83%).

Allophanes also vary in their degree of order and the relative discreteness of their hydrous oxide phases. Those with one alumino-silicate phase have been distinguished as Allophane A and those with two discrete phases as Allophane B (Fieldes 1955). Allophane B is thought to be present in younger soils or in organic horizons where the development of the single alumino-silicate phase is inhibited by organic matter. Allophane A is thought to crystallise slowly under the influence of wetting and drying conditions to metahalloysite and finally kaolinite (Tamura and Jackson 1953; Fieldes 1955). Hence a pedogenic sequence has been proposed for allophane soils derived from rhyolitic or andesitic ash:-

allophane B → allophane AB → allophane A
→ metahalloysite → kaolinite.

Hence, allophanes may differ from each other in their chemical composition, the discreteness or interpenetration of their silica and alumina phases, and in their degree of organisation. They are distinguished from crystalline clays by their structural randomness and by the properties of their surface which has affinities with that of a hydrophilic gel.

## 2. Discovery of soil Allophane.

Down to the nineteen-thirties, soil colloids were assumed to be amorphous oxides and knowledge of them was obtained from chemical analysis and observation of their colloidal properties, culminating in the classic work of Sante Mattson. Discovery of the crystallinity of clay minerals by Hendricks and Fry (1930) and Kelly et al. (1931) using X-ray diffraction techniques, initiated a period of intense research into the correlation between clay crystal structure and the associated physico-chemical behaviour of the different minerals. The role of amorphous clays, meanwhile, was largely overlooked, not only because of the interest focussed on the micro-crystals, but because the amorphous material was difficult to isolate and characterise. It was usually present in small amounts and as an unwanted coating impurity on the crystal which had to be removed. For this reason, and owing to their small size, the amorphous colloids very often remained in the supernatant after centrifuging, and were poured down the laboratory sink.

In the past decade or so, techniques such as differential thermal analysis, infra-red spectroscopy, electron-microscopy and selective dissolution treatments have been applied successfully to the amorphous fraction. Most of the impetus behind the research is based on the belief that this is the most active fraction in soil and that it strongly influences soil properties even when present in very small amounts (Mitchell et al. 1964).

An amorphous colloid that could not fail to escape notice however, was allophane, because it was a major constituent, comprising up to 100% of the clay in some soils, and was not examinable by X-ray methods. Taylor (1933) first observed it in New Zealand during a study of soil processes on volcanic ash beds. Allophane soils were then discovered to be widespread in regions where there were relatively young rocks of volcanic ash and lava, notably in the central areas of North Island, New Zealand, and in Japan. An early study of the New Zealand soils (Birrell 1952) arose out of requests to report on the load-bearing capacity of the volcanic ash soils. Their suitability as foundations for buildings and dams and as construction material for embankments and airports was unknown, but it had been noted with some alarm that Mexico City had undergone settlements of great magnitude, due to the behaviour of the underlying volcanic ash clays.

Thus it came about that the first distinctive properties observed for allophane soils were their engineering properties. These included variation in moisture and compaction characteristics which depended on the history of the sample. The soils had a high initial water-holding capacity and shrank intensively on drying out, but did not readily wet up again, shown as strong hysteresis in the wetting and drying curves. In compaction tests, a variety of water content/dry density relationships were found, the curve for fresh soil showing no change in density as considerable water was lost, but that for a reworked soil showing a peak density for lower moisture content. Thus values for peak density and water content were controlled largely by the amount of pre-drying before re-wetting. Consolidation tests demonstrated that the soils were not compressed until the load intensity exceeded one to two tons/sq.ft., which was far above the pre-consolidation pressure due to the original overburden, but that thereafter the compressibility was fairly high. This led to the recommendation that load intensities ought to be decreased by spreading the foundations, in order to avoid the dangers of settlement if the critical pressure stage should be reached.

Birrell attributed the lag in moisture uptake to the vesicular nature of the grains. His laboratory tests showed that allophane affected the physical properties of soil by virtue of its extremely small particle size and its behaviour as a slowly reversible gel (Gradwell and Birrell 1954). Moreover, a small per cent exerted great influence, for Fieldes notes (1966) that a Puteraki subsoil with 10% allophane and 35% vermiculite "had all the engineering and field properties of allophane".

The second feature of practical interest which drew attention to the soils was in the effect of allophane on soil fertility. When the broadleaved forests of New Zealand were cleared in the last century for dairying, stock fattening and market gardening, the allophane soils were notable for their fluffy crumb structure, the free drainage and moisture storage capacity of their porous aggregates and their strong affinity for organic matter. Agricultural practice in some districts has produced soil changes. In the pasture areas, the fragile aggregates can withstand the use of heavy machinery for the occasional plough and resow, but in the market garden areas, fifty to one hundred years of continuous cropping have produced structural breakdown. Heavy machinery puddles the soil which then sets hard. In addition the soils have developed phosphate fixation. Both problems appear to be connected with loss of organic matter. The practice of cropping one to one and a half times a year, with four months dry fallow, and the unavailability locally of farmyard manure, has depleted the humus, so that the structure can only be nursed back with difficulty by reverting to pasture for several years, or by ploughing in barley. A few farmers have used poultry manure with good results and claim a reduction in phosphate fixation (Agric. Adviser, pers. comm., Pukekohe area 1968).

## 3. Modes of formation of Allophane.

Allophanes are found in rocks, in soils or they may be artificially prepared. In rocks they occur as linings to fissures and cavities and this suggests precipitation at low pressure and temperature from solutions containing hydrous alumina and silica. They were synthesised under similar conditions by Mattson (1928b, 1930a), in a series of studies on the co-precipitation of alumina and silica. In the soil they are found (a) as the weathering products of rocks produced by volcanic activity and (b) in the subsoils of podzols. This suggests two possible modes of origin, the first determined by the disordered structure of the rock mineral and the second controlled by a leaching process.

(a) The volcanic rocks giving rise to allophane are pre-eminently rhyolite or andesitic lava and contain an abundance of glass and andesine felspar. Fieldes (1966) points out that glasses are random-structured alumino-silicates and that the felspars have disordered structures due to rapid cooling. He contrasts these to sedimentary felspars, which when they weather, produce the micaceous sheets of sericite commonly observed under the microscope. Sericite is absent from New Zealand volcanic felspars and he suggests that this is due to the fact that these have no ordered Al-Si in the lattice capable of reorientating to produce mica sheets (De Vore 1957). Grinding of sedimentary felspars has been found to yield amorphous material with allophanic properties and this is assumed to be due to the production of disordered material (Fieldes and Furkert 1966). One might expect that rocks scoured by an ice sheet would show similar effects, and there is strong evidence for this. The Te Anau series from a New Zealand moraine contain allophanic material. In Scotland, certain upland and mountain soils give a positive reaction to the fluoride test and this has been found due to powdered felspar resting on the angular surfaces of sand grains which have been subjected to frost shattering and previous ice-action. (J.M. Ragg, pers. comm. 1971).

Fieldes also notes that the formation of allophane is not confined to acidic rocks but has been found in soils on basalts in, for example, Japan (Kanno 1964) and northern Ireland, and on dunite in New Zealand. In Table 1 he shows the mineral assemblages of three rocks and their derived soils, and suggests that the olivine, pyroxene and amphibole in the basalt would have contributed silica and alumina by dissolution and reprecipitation.

(b) Allophane, as diagnosed by the sodium fluoride test, has been found consistently in the subsoils of podzols, and this is considered due to the dissolution of silica and alumina from the upper horizons and their eluviation and reprecipitation as amorphous alumino-silicate in the lower horizons. The parent material has no influence upon this. The Soil Survey of Scotland now use the fluoride test as a routine indication of the 'degree of leaching' in soil. It provides a simple and effective method for detecting whether podzolisation is occurring. In the Darleith association soils, those on the eastern side of Scotland give only weak responses to the test, or none at all (J.M. Ragg pers. comm. 1971), while the Ayrshire soils on the west, as has been seen, give a

Table 1  Mineral assemblages in some New Zealand rocks and their derived soils.  (compiled from Fieldes 1966).

|  | felspar % | glass % | mica % | amphibole % | pyroxene % | olivine % | allophane % |
|---|---|---|---|---|---|---|---|
| Rhyolitic Ash | 60 | 30 | - | - | - | - | - |
| Yellow brown pumice soil | 45 | 5 | - | - | - | - | 15 |
| Andesitic Ash | 40 | 30 | - | - | - | - | - |
| Yellow brown loams | 15 | 15 | - | - | - | - | 30 |
| Basalt | 20 | 12 | 5 | 10 | 10 | 10 | - |
| Red loam | 1 | 5 | 0•1 | 0•1 | 0•1 | - | 50 |

very strong response. From this evidence, soil survey would classify the South Drumboy brown forest soils as "crypto-podzols" or "pseudo-podzols", thus distinguishing the eastern soils, where rate of leaching keeps pace with rate of weathering, from the western soils where rate of leaching is faster than rate of weathering. However, it seems unlikely that the South Drumboy allophanic material is solely due to podzolisation because of the positive response to sodium fluoride given by the Dunlop A horizon. This is further discussed, together with other considerations, in the experimental part(p.436).

Allophane thus persists in podzols due to the continuous replenishment of alumino-silicate by leaching. But random-structured materials like glass and allophane are not stable. They crystallise eventually, and in the yellow brown loams and pumice soils of New Zealand the allophane weathers to metahalloysite and finally kaolinite. Fieldes (1966) observes that crystallisation seems to be favoured by drying conditions so that as the gel loses water cross-linking of the alumina and silica occur, whereas persistence is favoured by relatively moist conditions where the gel never shrinks enough to allow re-arrangement.

In Scottish gleys however, allophanic material either does not persist or does not occur. Mitchell et al. (1964) note that

> "The occurrence of highly amorphous clays in surface soils also seems to depend on the permeability of the subsoil, since they have been observed, up to the present, only in soils with free internal drainage".

Since that time the total absence of allophane from Scottish gleys has been confirmed by Ragg, as mentioned above.

## 4. The Leaching Index.

The fluoride field test, described on p. 5 was devised and assessed by Fieldes and Perrott (1966), who roughly correlated the pH as measured by the phenolphthalein reaction, with known estimates of allophane in the soil. This is shown in Table 2, for subsoils. The authors note that topsoils yield organic acids which may neutralise some of the alkalinity produced and modify the response. In the laboratory, the standard test was described as 1g. soil suspended in 50ml. saturated NaF (which corresponds to IM NaF) for some standard time such as 30 minutes. This gives a better indication of the relative allophane content. It also

Table 2 Correlation of sodium fluoride field test with the allophane content of subsoils.

(compiled from Fieldes and Perrott 1966).

| Colour | pH value | allophane activity and content |
|---|---|---|
| none | 8·8 | little, less than 5% |
| pink, fading quickly or tending to fade | 8·8 - 9·0 | intermediate, 5 - 7% |
| red | 9·0 | strong, more than 7% |

shows that all soils respond, albeit weakly, to the sodium fluoride test, and this, together with the finding that all soils appear to contain some hydrous alumino-silicate which can be mobilised by alkali, has led to the conclusion that "amorphous materials characterised as allophane are present in all soils", (Birrell and Fieldes 1968).

## 5. Definition of Allophane.

This raises the problem as to what should be designated 'allophane' and what should be called 'allophanic material' or 'amorphous alumino-silicate' or 'non-crystalline alumino-silicate'. These materials are characterised by structural randomness, but otherwise they show a gradation of properties in their response to sodium fluoride, their dissolution in alkali and their water-holding capacity. They also show, as will be discussed later, similar properties of phosphate, humate and silica retention, and, evidence suggests, (Fieldes 1966) the same anomalous cation exchange capacities. Some difference can be made between allophanes on the basis of their DTA trace, as discussed later ( p.32 ), but there are reservations on this score also. A possible distinction might be in whether the allophane was present as discrete particles capable of isolation, or as coatings on clay minerals. The engineering properties of allophane soils for example, may depend more on their being a vesicular network of such particles than on the actual amounts of allophane present. Such a distinction however, might be difficult to test easily, and an engineering criterion might not be the best in an agricultural situation. Hence, for simplicity, and in view of the fact that the important properties of allophane to agriculture are in its effect on soil structure, fertility and plant nutrition, the writer proposes that in the context of this work, the criterion should be that of the 'amount present' as measured by the very simple sodium fluoride test, and that all alumino-silicates giving a strong response in the field, or arbitrarily, 9·5 pH after 15 minutes in the laboratory, should be described as 'allophane', and the rest as 'allophanic'. It is hoped to justify this criterion in what follows and to show that there must be some threshold of allophanic content above which its influence is strongly felt. The term 'allophane soil' will refer to a soil whose physical and engineering properties are determined by the presence of particulate allophane clay in the soil.

## 6. The composition of Allophane.

The silica : alumina ratios of soil allophane vary greatly. Within the range 0.5 to 2.0 artificial co-precipitates of alumina and silica show DTA effects resembling geological allophane. A ratio $< 2.0$ is regarded as due to amorphous silica and $< 0.5$ to amorphous alumina. ("Soils of New Zealand" 1968 2 p.47). Values ranging from 1.0 to 1.8 have been found for clay fractions of volcanic ash soils of rhyolitic or andesitic origin that have not been deferrated, or in which gibbsite has not been detected (Birrell and Fieldes 1968), and ratios 0.7 to 2.1 for Japanese volcanic ash soils (Kanno 1956). It was these silica : alumina ratios which first led Henderson and Ongley (1923) to predict the presence of allophane in New Zealand soils.

Structurally, allophanes are thought to be similar to the artificial silica-alumina cracking catalysts. These are formed by random crosslinking due to condensation between hydroxyls attached to silicon and/or aluminium. It is thought aluminium may be present in both 4- and 6- coordination (Thomas 1949). Similar conclusions have been reached for allophane (Fieldes 1955, Egawa 1964).

## 7. Techniques for investigation of Allophane.

Allophane has been investigated by a variety of methods, many of which depend on the indirect examination of its properties rather than direct observation. Techniques have been developed which diagnose:- (i) its structural randomness (X-ray and electron diffractometry, infra-red spectroscopy), (ii) its water holding capacity (liquid limit tests, differential thermal analysis), (iii) its pH dependent charge (cation and anion exchange capacities, flocculation and dispersion studies), (iv) its ready attack by certain chemical reagents (dissolution techniques with identification of the products and residues), (v) its particle size and shape (BET surface area measurements, electron microscopy), (vi) its affinity for organic matter (selective extraction procedures, uptake of organic material), (vii) its genesis, history and course of weathering (field studies, rock and soil thin section microscopy). It may be separated from other clay minerals by differential centrifuging, electrophoresis or by the addition of charged detergents. But separation may be either difficult due to its strong tendency to flocculate, or impossible if it is present as a surface coating. In this case the contribution of allophane to the soil properties can only be deduced by examining these properties prior to and after the removal of allophane.

A few of the techniques are outlined below in the following sections. Others are reserved for discussion in the relevant chapters.

### 8. X-ray powder diffractometry.

The lack of crystallinity in allophane is inferred from the absence of an X-ray or electron diffraction pattern. Nevertheless, White (1953)and Minato (1960) noted two X-ray diffraction halos at 3·34 and 2·25 Å for geological allophanes, and Yoshinaga and Aomine (1962) found these for soil allophanes, together with a diffuse band between 4 Å and 4·6 Å. On heating to 1000°C and 1200°C they obtained diffraction patterns for γ-alumina and α-alumina respectively.

### 9. Differential thermal analysis.

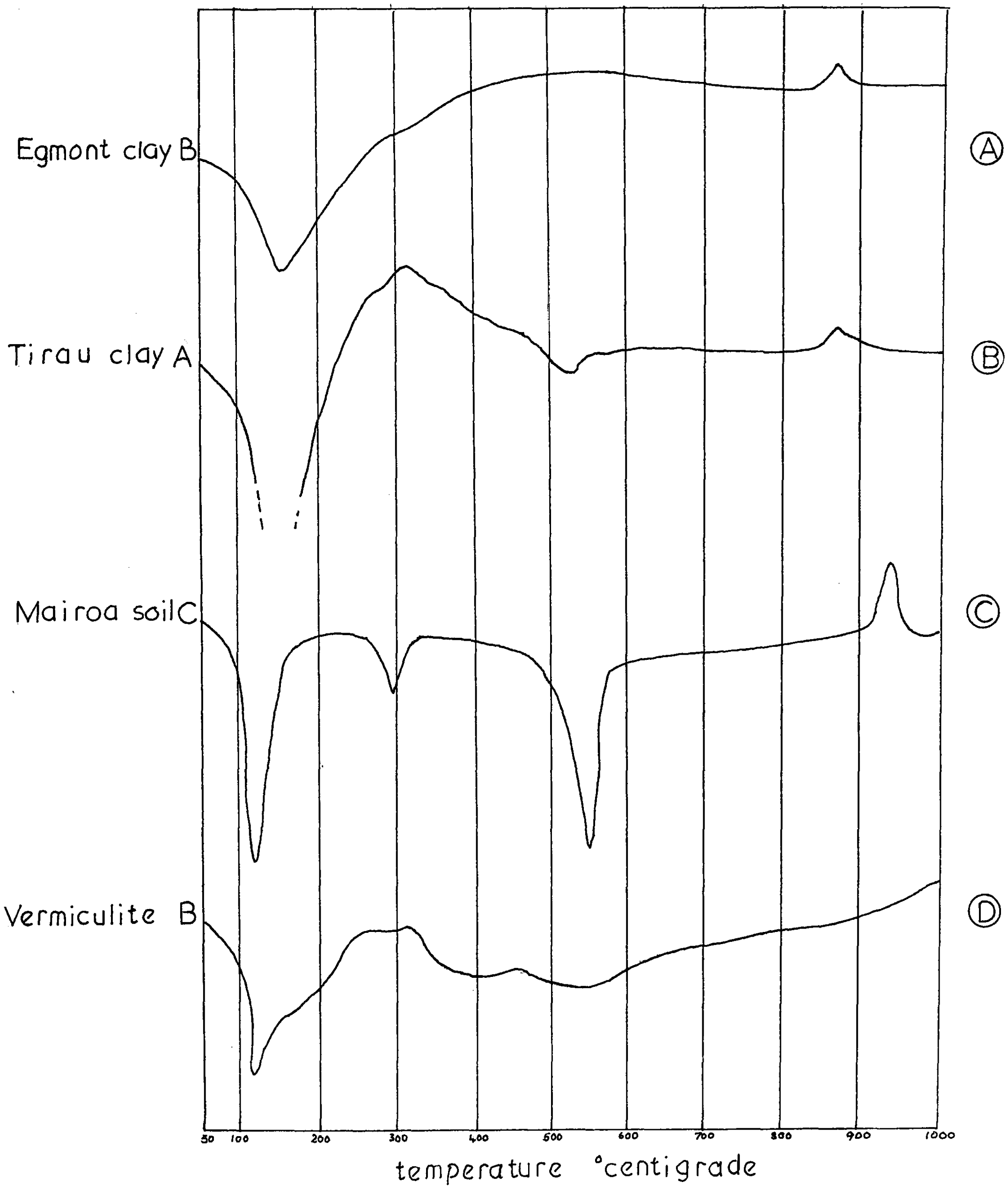
This technique offers one of the best means for identifying and characterising allophane. Its DTA curve consists of a large low-temperature endothermic peak, corresponding to considerable water loss; the absence of a dehydroxylation peak, consistent with its random structure; and a high temperature exothermic peak in the range 800 - 1000°C. Fig. 1 shows curves for three New Zealand clays and a whole soil. (A) Egmont clay is of allophane only, (B) Tirau clay is allophane, together with what is deduced to be a small amount of kaolinite, (C) Mairoa soil from deep subsoil shows metahalloysite and gibbsite, (D) clay from a yellow brown earth shows mainly vermiculite (Fieldes 1957). These curves are discussed below in relation to each region of temperature which gives rise to a transformation in the clay.

(i) The endothermic dehydration peak at low temperature records loss of water sorbed on the external and internal surfaces of the clay. Allophane peaks with maxima at above 150°C. are consistently larger than the corresponding peaks for the expanding clays montmorillonite and vermiculite, and indicate that allophane has a bigger internal surface from which water may be removed. This is consistent with a non-crystalline structure. The metahalloysite peak is sharper and the lower temperature of its maximum near 120°C. suggests a smaller internal surface and lower cation exchange capacity.

Mitchell and Farmer (1962) examined the DTA curves of clays that had been rehydrated after partial ignition. The clays were from soils developed on Ayrshire basalt and basalt till and which contained appreciable amounts of amorphous material, particularly in the surface layers. The clays showed a large hygroscopic peak at 120°C. Heating was continued to 600°C. and then the samples were cooled, re-equilibriated at 56% relative humidity for four days and their differential curves redetermined. It was found that the dehydrated peaks recovered 60 - 70% of their former area. When this precedure was applied to vermiculite, chlorite, illite and Tirau allophane, only the allophane and illite rehydrated significantly. Since the illite peak is comparatively negligible, the authors suggested the method might be useful in differentiating between crystalline and amorphous material in soil clays. These observations should be pondered while bearing in mind the apparently conflicting evidence that allophane soils, once dried, do not readily re-wet and have a much lower liquid limit than the original soil (Gradwell and Birrell 1968), and that oven-dried samples regain an appreciable amount of water from the atmosphere but additional water is taken up more slowly (P.G. Harris, pers. comm.). This is of interest to an understanding by farmer and engineer of the water holding properties of allophane soils in the field.

Fig. 1 DTA patterns for some New Zealand clays.

(Fieldes 1957)



The low temperature peak for clays is often a doublet or has a shoulder, and with crystalline clay these maxima are identified with layers of water held with progressive tightness to the clay's internal surface. The position of the peaks on the temperature scale reflects the energy with which the water is held and is determined by the cation species present. When allophane shows double maxima however, Fieldes (1955) has identified them as due to allophane B, with desorption of water from the discrete phase of amorphous hydrous silica at $<150^{\circ}$C. and from the discrete phase of the corresponding alumina at $200^{\circ}$C. This alumina peak appears in fig. 1 (D). A single broad peak, as illustrated in fig. 1 (A), between $150^{\circ}$C. is attributed to allophane A.

(ii) <u>The endothermic dehydroxylation peak</u> which normally occurs for clay minerals in the region 500 - $700^{\circ}$C. is absent in allophane. Its randomly arrayed hydroxy groups are lost progressively as the temperature is increased and thus no sharp energy change occurs. The metahalloysite peak in fig. 1 (C) at about $560^{\circ}$C. is similar to that for kaolinite. The peak at $300^{\circ}$C. is due to gibbsite. In fig. 1 (B), the small endotherm at $540^{\circ}$C. is consistent with kaolinite, and a small amount has been found in Tirau clay by X-ray diffraction.

(iii) The exothermic recrystallisation peak varies with allophane in position, sharpness, height, or whether it appears at all. Fieldes (1955) distinguishes allophane A as giving a strong exothermic peak between 850°C. and 1000°C., from allophane B showing no peak and intermediate material having it weakly developed. Support for this interpretation was given by the work of Insley and Ewell (1935) who experimented with mixtures of amorphous hydrous silica and alumina in an attempt to explain the kaolinite exothermic peak. They showed that wherever methods were used which allowed co-precipitation, sharp exothermic peaks below 1000°C. were obtained, but when the gels were merely mixed they were absent. Fieldes comments that since hydrous alumina and silica are oppositely charged colloids at soil pH, it was difficult to see why co-precipitation should not come about in wet soil, with production of allophane A. He postulates that this was inhibited by the binding of alumina in stable organic complexes.

Some doubt was cast in the validity of the distinction between allophane A and B by a discovery that considerable changes in the exothermic peaks could be produced by treatments often used prior to differential thermal analysis (Campbell, Mitchell and Bracewell (1968). These included dispersion in ammonium hydroxide and peroxidisation.

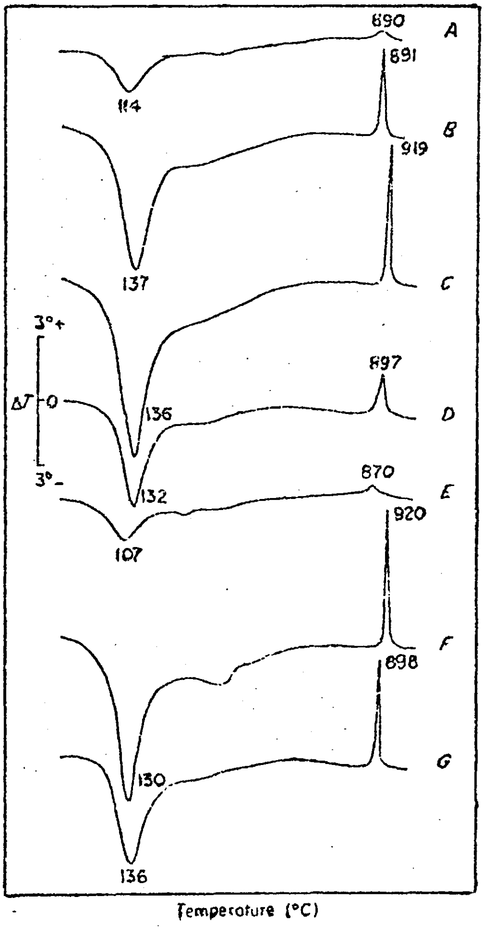
The clay the authors examined was from the C horizon of an 'Imogo' layer, from Kodonbaru, Japan. It was separated from the coarser fractions by repeated washings with distilled water, saturated with neutral ammonium acetate and subjected to the various treatments described in figs. 2 and 3 . The DTA curves give the following information:-

(a) The height and temperature of the exothermic peak increased with decrease in particle size.

(b) Increase in pH by addition of ammonium hydroxide to acid or water-dispersed clays caused considerable reduction in height and sharpness. The authors comment that this might have been due to flocculation, induced by ammonium hydroxide, increasing the particle size. But a clay flocculated by neutral ammonium acetate showed no such reduction. (curve not given). Alkali-dispersed clays brought to pH 5 with acetic acid regained the sharp exotherm. The authors go on to say: "this behaviour suggests that either the addition of acid causes a reduction in particle size, or that the height and sharpness of the

Fig. 2 The effect of particle size and pH on the DTA pattern of a Japanese allophane soil.

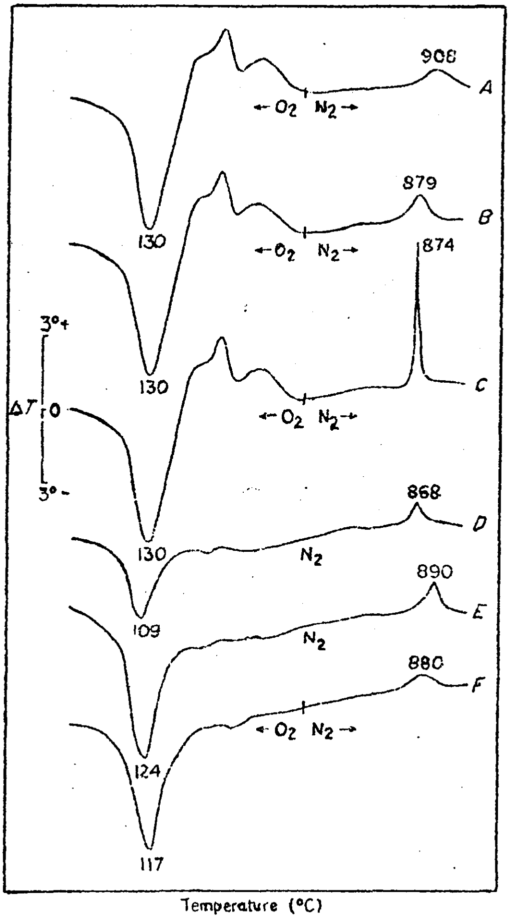
(Campbell et al. 1968)



Effect of particle size and pH. (*A*), (*B*) and (C). Total soil, coarse clay and fine clay respectively from dispersion with water at pH 5·7. (*D*) coarse clay treated with $NH_4OH$ at pH 9·0 after dispersion. (*E*) and (*F*) Residue and fine clay from dispersion with acetic acid at pH 5·0. (*G*) Clay (< 1·4μ) from dispersion with $NH_4OH$ at pH 9·0 Treated with acetic acid after dispersion. All curves were obtained in nitrogen atmosphere.

Fig. 3 The effect of organic matter on the DTA pattern of a Japanese allophane soil.

(Campbell et al. 1968)



Effect of organic matter. Coarse clay from water dispersion heated to 600° C in oxygen atmosphere, cooled, 0% (*A*), 2·5% (*B*) and 5·0% (*C*) by weight of charcoal added and reheated to 1000° C in nitrogen atmosphere, composite curves. Residue from water dispersion heated with 5% charcoal in nitrogen atmosphere (*D*). Coarse clay from water dispersion treated with peroxide to destroy organic matter, heated in nitrogen atmosphere (*E*), and heated to 1000° C in oxygen, cooled, 5% charcoal added and reheated in nitrogen (*F*), composite curve.

exotherm is pH dependent, and that this dependence is reversible".

(c) Removal of the organic matter associated with the clay also caused considerable reduction in the height and sharpness of the exotherm. If this removal was effected by burning it off in oxygen, the exotherm could be restored by adding 5% by weight of charcoal or other organic material and reheating in a nitrogen atmosphere (fig. 3 C). But if it had been removed by peroxidisation, then addition of charcoal could not restore the exotherm (fig. 3 F). Addition of charcoal lowered the peak temperature from 908°C. to 874°C., suggesting that it might have catalysed the reaction.

The authors conclude that the absence of allophane A could not be inferred from its DTA curve if the clay had been pretreated with an alkaline dispersion or with hydrogen peroxide, or if it had been heated in other than an inert atmosphere.

## 10. Infra-red spectroscopy.

Evidence for a random molecular arrangement in allophane is provided by its infra-red spectrograph. The most intense bands for silica, alumina and the silicates occur in the 800 - 1225 $cm^{-1}$ region. Fig. 4

(Fieldes et al. 1956) gives the spectra for trioctahedral vermiculite, halloysite, kaolinite and allophanes A and B. It is seen that while the crystalline clays give sharp maxima in this region, the allophanes show broad bands. Allophane B has a blunt peak at 800 $cm^{-1}$ corresponding to that for amorphous hydrous silica (Adler 1950, Fieldes 1955). In addition, the allophanes have broad bands in the 3500 $cm^{-1}$ region, corresponding to adsorbed water, whereas the crystalline clays give multiple peaks.

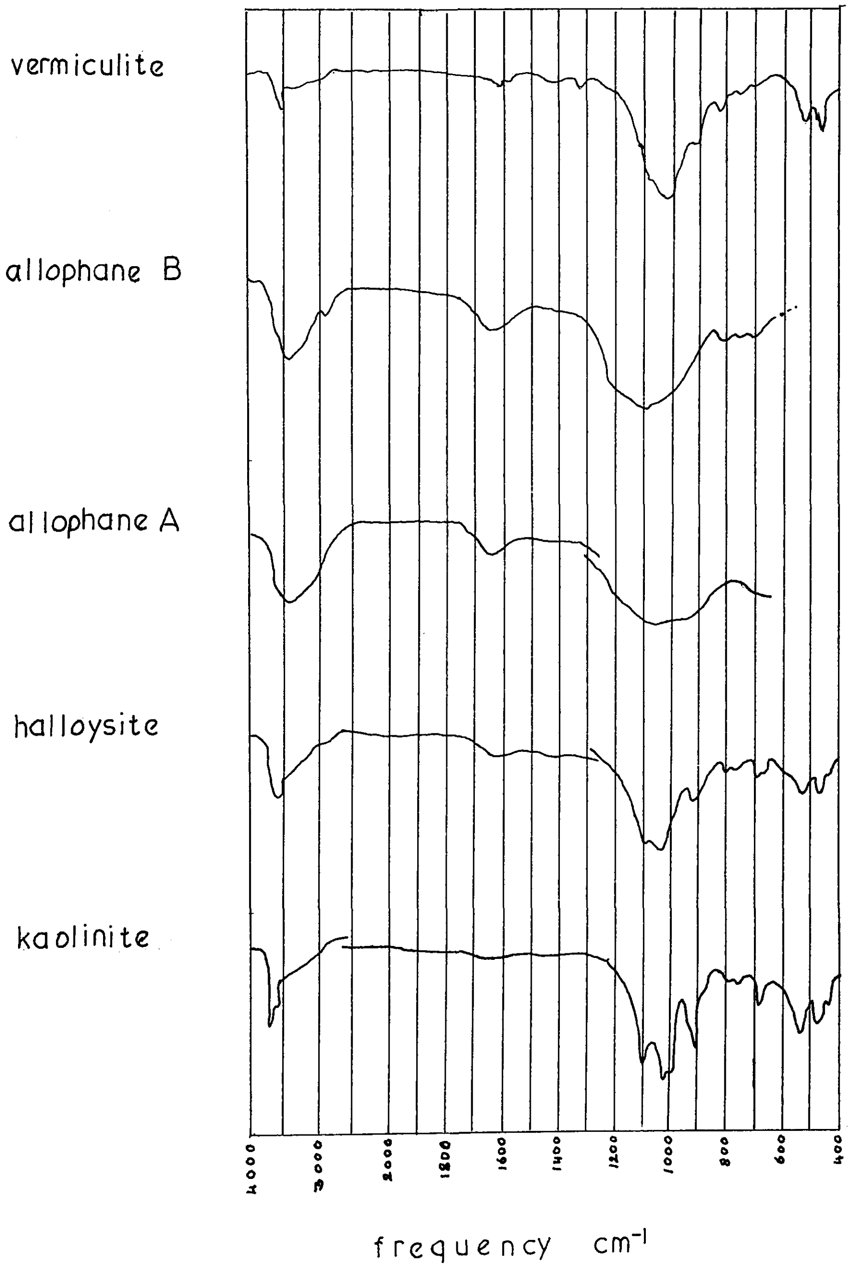
It will be seen that unless the clays can be fractionated, infra-red spectroscopy is difficult to use for identifying soil clays because of the masking effect they have on each other. In the experimental work that follows the technique has only been used to identify kaolinite, whose peak at 3698 $cm^{-1}$ is not masked by that of any other clay.

## 11. Optical microscopy of soil thin sections.

Thin sections allow the micromorphology of the soil profile to be studied in situ so that the position and orientation of the coarse grains and fine material in aggregates and throughout the network of interstices can be seen with the minimum of disturbance. An

Fig. 4 Infra-red absorption spectra of New Zealand soil clays.

(Fieldes et al. 1956)



important property of allophane is that it is isotropic under crossed nicols, while layered clay minerals are birefringent, and this allows the accumulation and deposition of allophane to be detected and interpretations of soil genesis to be attempted (Dalrymple 1964).

## 12. Dissolution of allophane by fluoride.

Fluoride reacts slowly with clay minerals with release of hydroxyl into the solution and for some years the mechanism was not understood. The following account of the ways in which this problem was solved is given both because of the intrinsic interest in retracing the steps of workers whose starting points were often very different, and because a close examination of their results helps to interpret aspects of the writer's experiments.

When Dickman and Bray (1941) demonstrated that large amounts of hydroxyl were released into solution when kaolinite was equilibriated with ammonium fluoride solutions at room temperature, it was logical to attribute this to anion exchange. Romo (1954) considered it was isomorphous substitution since fluoride and hydroxyl are interchangeable in the lattice of certain minerals, notably the micas eg. $KAl_2\ Al\ Si_3\ O_{10}\ (OH,F)_2$, and amphiboles. Samson (1952) however, concluded that fluoride complexed the clay aluminium and removed it in solution as $(AlF_6)^{3-}$ groups.

Romo and Roy (1957) sought to establish the correct explanation. Kaolinite, chrysotile, muscovite, boehmite and diaspore were saturated with concentrations of NaF ranging from 0•1 to 1•5 N at 25°, 60° and 100°C. and were investigated by three methods: (i) titration of the hydroxyl released and analysis of the fluoride taken up by the solid phase, (ii) measurement of the change in hydroxyl content of the mineral lattice by infra-red spectroscopy, (iii) X-ray diffraction analysis. The extracts were analysed weekly over a period of three months by titrating them with acid in situ, and sodium fluoride was added from time to time. The percent hydroxyl released by kaolinite, boehmite and muscovite was found to depend on temperature and sodium fluoride concentration. At the end of the period kaolinite suspended in 0•5 N NaF had released 15% of its lattice hydroxyl at 25°C and 22% at 60°C. The fluoride taken up by the solid phase was approximately stoichiometric with the measured hydroxyl released into solution and lost by the solid phase. The X-ray diffraction measurements showed no alteration in the lattice spacing consistent with isomorphous substitution, but this was not expected in view of the similarity of the two ionic radii. The important discovery was that sodium fluoaluminate, better known as the mineral cryolite, had formed in quantities that varied from a trace to ten per cent. This was not enough to account for all the hydroxide exchanged, but there was the possibility that much of the cryolite was fine grained and X-ray amorphous. The evidence was too inconclusive however, to decide which was the dominant reaction, postulated in the equations:-

$$Al_2Si_2O_5(OH)_4 + 6Na^+ + 6F^- = Na_3AlF_6 + AlSi_2O_5(OH) + 3Na^+ + 3OH^-.$$

$$Al_2Si_2O_5(OH)_4 + xNa^+ + xF^- = Al_2Si_2O_5(OH)_{4-x}F_x + xNa^+ + xOH^-.$$

So far, only crystalline minerals had been examined, but Wada (1959), in a study of phosphate uptake, found precipitation of a separate phase when he equilibriated allophane with ammonium phosphate solution at pH 4. He obtained the mineral taranakite ($(NH_4)_2O.3Al_2O_3.3P_2O_5.18H_2O$). Birrell (1961) experimenting on the same lines, tried to displace the phosphate from the taranakite by shaking it in 3M ammonium fluoride solution. After three hours, the solid residue was found to contain ammonium fluoaluminate, as detected by its X-ray diffraction pattern. The next step was to treat allophane with fluoride, and the formation of ammonium and sodium fluoaluminates was found much more rapid than the formation of taranakite. Birrell used neutral solutions of the fluorides and also accelerated the reaction by lowering the pH. A solution which was M/2 with the respect to NaF and HF produced cryolite from Tirau allophane within two days. Under these conditions, kaolinite, bentonite and halloysite showed alteration to cryolite in a few days, but gibbsite was resistant. At neutral pH however, the clay minerals reacted very slowly, and the results would probably be consistent with those found by Romo and Roy.

Huang and Jackson (1965) were apparently unaware of Birrell's work when they reinvestigated the mechanism of the interaction between fluoride and layer-silicate and oxide minerals. They used a similar procedure to that of Romo and Roy, in that they titrated the hydroxyl released and analysed for mineral-bonded fluoride in the solid residue, but differed in several respects which had important consequences for the results.

These were:-

(i) A wider range of materials was used, including allophane and soils.

(ii) Their extractions with 1N KF covered a maximum of 48 hours, but during this time the supernatant was removed at intervals and fresh additions of potassium fluoride made to the residue, thus displacing the equilibrium and re-initiating a high reaction rate.

(iii) The solutions were titrated separately from the residue.

(iv) The residue was recovered from a solution which was alkaline if much hydroxyl had been released.

(v) Aluminium and iron released into the supernatant by 1N $NH_4F$ was determined, after fusion of the evaporate and distillation of the fluoride.

A selection of their results is given in Table 3. It is seen that allophane and halloysite (which probably contained some allophane ) released large quantities of hydroxyl, 462·5 and 280·9 m.e. OH/100g. sample respectively; the layered clays and gibbsite released only small amounts. Still less was released by the iron oxide, and for quartz it was negligible. They correlated the hydroxyl released

Table 3 Titrable hydroxyl appearing in neutral 1N KF solution in contact with minerals and soils. (50ml. 1N KF / 100mg. sample was used) (compiled from Huang and Jackson 1965).

| Sample | pH of extract after 24 hrs. | m.e. OH/100g sample | | | |
|---|---|---|---|---|---|
| | | appearing in single 24 hr. | per hr. between 24 and 48 hr. without renewal of extractant. | per hr., with renewal of extractant at every 0·5 hr. after 24 hr. | |
| | | | | 1st. | 2nd. |
| kaolinite | 7·8 | 21·3 | 0·1 | 8·8 | 8·5 |
| montmorillonite | 8·5 | 37·3 | 0·0 | 9·6 | 7·7 |
| halloysite | 11·4 | 280·9 | 0·1 | 248·8 | 248·3 |
| allophane | 11·6 | 462·5 | 1·9 | 294·8 | 295·3 |
| quartz < 0·5μ | 7·5 | 3·4 | 0·0 | 0·0 | ... |
| hematite <20μ | 8·0 | 19·4 | 0·0 | 16·3 | 17·3 |
| gibbsite <20μ | 9·4 | 54·0 | 0·7 | 24·0 | 22·6 |
| Dodge soil B < 2μ | 9·6 | 41·2 | 0·2 | 30·0 | 30·5 |
| Alberni soil < 2μ | 11·1 | 130·6 | 0·2 | 55·5 | 54·5 |

with the aluminium and iron found (Table 4 ) and concluded from these results that the sesquioxides had been dissolved by complexing reactions, with the formation of fluoaluminate and fluoferrate.

No mineral bonded fluoride was found on the residue, nor did they find any evidence for potassium cryolite. They assumed that it had been removed with the water-ethanol washing owing to its solubility: 0·143 g/100g saturated solution (Seidell 1958), but did not consider the possibility that like $Na_3 AlF_6$, it was soluble in alkali, or whether it would have had time to form.

Two other points are of interest. The first is that Huang and Jackson displaced the equlibrium and re-initiated a high reaction rate by removing the reaction products. Displacement of the equilibrium in order to promote the reaction could also be assisted by:-

(i) maintaining a neutral pH and destroying the hydroxyl as it was formed. This was done by Romo and Roy when they titrated the suspension, and also by Birrell, who used neutral fluoride solutions or acidified them with HF.

(ii) maintaining a neutral pH to allow cryolite to precipitate.

Table 4 Comparison of HCl titrable OH appearing in neutral 1N KF to the aluminium and iron released in neutral 1N $NH_4F$ from minerals and soils.

(Huang and Jackson 1965)

| Sample | milliequivalents / 100g | | | |
|---|---|---|---|---|
| | Al | Fe | Al + Fe | OH titre |
| halloysite | 259·9 | 3·8 | 363·7 | 280·9 |
| montmorillinite | 33·4 | 8·1 | 41·5 | 37·3 |
| quartz | 4·1 | 0·0 | 4·1 | 3·4 |
| hematite | ... | 20·1 | 20·1 | 19·4 |
| Dodge soil B | 53·5 | 6·0 | 59·5 | 41·2 |
| Alberni soil | 109·8 | 19·5 | 129·3 | 130·6 |

50ml. 1N NaF / 100mg. sample was reacted for 24 hours.

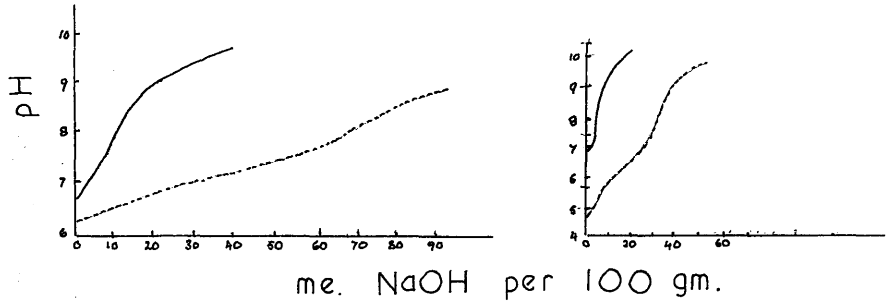
The second point is the observation of Huang and Jackson that when the residue was washed to remove potassium fluoride and reaction products, a drop in pH was noted, for example from 9•5 to 5•5, and when the residue was titrated with NaOH, it was found to be very strongly buffered (fig. 5 ). Their results showed that NaOH titrable donor groups had formed on the surface of the minerals in proportion to the aluminium and iron removed and hydroxyl released. These were comparable to the third buffer range for hydrogen-aluminium clays described by Schwertmann and Jackson (1963, 1964) and were interpreted as evidence that the mineral surfaces were disrupted by fluoride interaction. This was confirmed by electron micrographs of carbon replicas of mica crystals.

The surface acidity produced by fluoride attack on crystalline clays is characteristic of the allophane untreated surface. Allophanes have been compared to the synthetic silica-alumina catalysts used for cracking petroleum (Fieldes and Schofield 1960). A study of the mechanisms and reactivities of these was made by Hensley and Barney (1958), using sodium fluoride and their conclusions are relevant to allophane. They state:-

"Synthetic silica-alumina catalysts react with

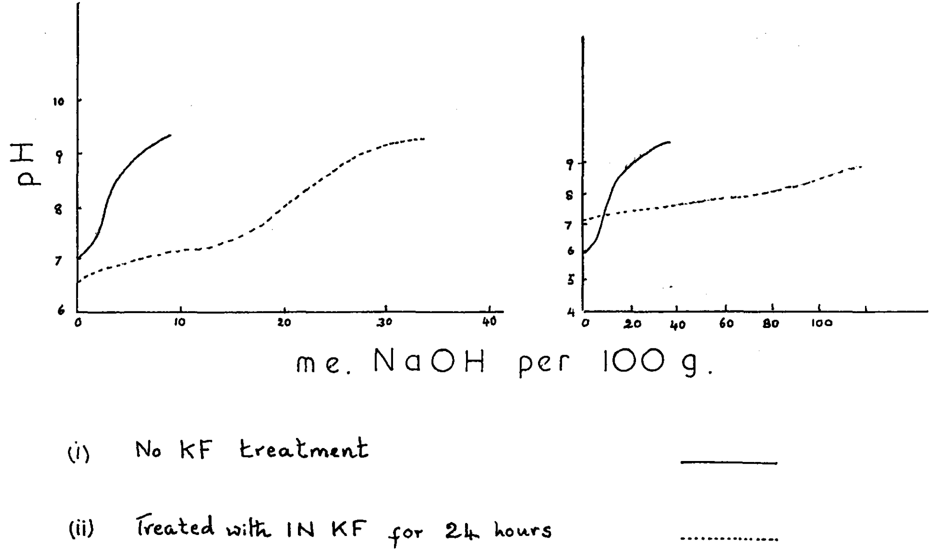
Fig 5 Potentiograms showing the effect of fluoride treatment on NaOH titration curves of clays suspended in 1N KCl.

(Huang and Jackson 1965)



a Alberni soil < 2μ

b Montmorillonite



c Gibbsite

d Halloysite

sodium fluoride in alkaline solution to liberate base; the reactive material, called reactive alumina, is probably the catalytically active alumino-silicate. Other constituents of the catalysts such as free alumina, silica and catalytically inactive alumina-silicate, react slightly or not at all"

No direct measurements of the cracking efficiency of ignited allophane have been made, but clay fractions containing allophane gave surface acidity values, when titrated in a non-polar solvent, similar to that of synthetic silica-alumina. Allophane B was less reactive than allophane A, and halloysite and kaolinite very much less so (Birrell and Fieldes 1968).

The simplicity and speed of the fluoride reaction make it an ideal tool for the detection of poorly ordered materials in soils. Bracewell et al. (1970) noted the accumulating evidence for their widespread distribution in Scottish soils and proposed the fluoride reaction be made a routine test; for these materials if present as a surface coating, might influence the water retention, nutrient balance and structure of the soil.

# CHAPTER III : STUDIES IN THE AGGREGATION AND DISPERSION OF COLLOIDS.

## 1. Introduction.

A primary aim of agriculture is the creation of good soil structure. The rotational systems, the timing of operations with respect to weather, season, soil, machinery and crop, and the skill and observation of the farmer in making use of these, constitute much of the art of husbandry. Plants, unless specially adapted, require soils to be well drained, well aerated and penetrable by roots and rootlets in search of water and nutrients. Similar demands are made by the microflora, insects and animals that inhabit the soil. At the same time, water must be available and nutrients retained against leaching. A crumb structure where large air-filled pores drain freely between the aggregates, and of small water-filled pores within the aggregates, is the ideal fulfillment of these requirements.

Soil structure is controlled by the degree and type of aggregation of the primary particles of sand, silt and clay, and the stability of the aggregates to water and pressure. Mineral soils high in calcium are well aggregated and resist deformation to pressure better than acid soils. Sodium soils disperse in water and set hard and clinkery when dry. Mull soils under grassland and deciduous forest, where organic and mineral matter is intimately associated, and in which high microbial and animal populations are supported, normally develop crumb structure. Poor soil structure may arise naturally, or as the result of mismanagement. If the organic matter level is allowed to fall too low, soils lose their range of soft consistency, and thus reduce their ability to hold water and to resist deformation or be stabilised against wind erosion. If such soils are high in fine sand or silt, they slake in water and settle out, on drying, to form an impermeable layer, such as a hard cap on the soil surface which resists the growing shoots of germinating seedlings, or as a pan below the root zone, which may be impenetrable to roots, or cause water logging, thus weakening or killing off the roots.

In arid regions, irrigated soils are liable to become sodium soils if the ground water level is raised too high; or downwash of silt and clay may lead to the formation of impenetrable pans, upon which saline marshes develop. In Britain, the use of bigger and heavier machinery, the risks taken in the timing of operations due to the dictates of delivery dates, the continuous cropping and intensification of grazing in response to economic pressures, have led to a breakdown of soil structure in some areas and awakened a concern for the future resource of soil.

Widespread observations on the deterioration of soil structure over the past twenty years and alarm at a fall in crop yields initiated a survey of soils in England and Wales by the Agricultural Advisory Council whose report (1970) gave a detailed account of the importance of soil structure in maintaining soil fertility, reappraised the neglected role of organic matter, and stressed the need for drainage, liming, careful management, and regular inspection of the subsoil for signs of pan formation.

Thus one of the major areas of soil research is in the investigation of soil structure, of the elements which control its development, and the ways in which it may be maintained or improved under agricultural systems. The aggregating mechanisms may vary from soil to soil, and depend on the crop or even the season. The study of these mechanisms may involve (i) dispersion of the soil into its primary particles, (ii) separation of the size fractions, particularly the colloidal fraction for individual study, (iii) examination of the physical properties of the aggregates and their effects on the bulk properties of the soil such as the voids and pore spaces on which depend its ability to hold oxygen and water, (iv) differential dissolution of colloids or aggregates so that the relative importance of calcium ion, ferric and aluminium oxides or complexes, allophane, crystalline clay, and organic material derived from plant, bacterial secretions, fungal tissue or animal excretions can be deduced; (v) correlation of these findings with the soil structure, vegetation, cropping history and season when the sample was collected.

In addition to the field and laboratory studies of soil, observations made on the behaviour of clay colloids in other industrial applications may be helpful. Examples include: water technology, where methods have been devised for inducing the settlement of slimes and sludges, and for removing colour and turbidity; extraction of minerals, and of mineral from gangue which is effected by techniques such as selective flocculation, dispersion and flotation dependent on surface properties specific to the mineral; oil drilling where muds must be made sufficiently well dispersed to seal the walls of boreholes against loss of drilling fluid, or offshore drilling where they must be protected against flocculation by salt water; and civil engineering, where the rheological properties of clay under load and the mechanisms of subsidence and landslip must be understood. Discoveries in any one such disparate field can prove of great practical use in another and can generate new conceptions of colloid behaviour.

In this chapter the experimental evidence which led to some general conclusions on soil colloid behaviour will be reviewed. A rather lengthy excursion has been made because in covering the literature it has become clear how often workers in one discipline were unaware of advances in another which might have helped their cause; and also because much of the work reviewed contains threads of evidence which have helped the writer to formulate interpretations and try new experiments.

## 2. Clays as hydrophobic and hydrophilic sols.

Clays in this context, are defined by particle size. This is usually taken to be $<2\mu$ or, as in the experimental text $< 1.4\mu$ equivalent settling diameter. They are complex colloids in that they show both hydrophobic and hydrophilic behaviour. As charged particles they act like hydrophobic sols whose stability is governed by the "rules" of electrokinetic behaviour. But the oxide and hydroxide groups on the surface of the particles give the clays hydrophilic properties, and furthermore encourage non-specific van der Waals interactions between themselves and other molecular species to occur.

Precipitation of clay colloids depends on a variety of mechanisms including (a) effective collisions between similarly charged particles (b) isoelectric flocculation (c) co-precipitation (d) flocculation by polyelectrolytes. Dispersion of particles may depend on their electrostatic repulsion, or on the protection of oppositely charged particles from mutual loss of charge by sorbed polyelectrolytes. The following discussion outlines the applications of this varying behaviour and traces the ways in which the mechanisms have been deduced.

## 3. Coagulation and dispersion by electrostatic interaction.

Hydrophobic sols are kept in suspension and their free fall prevented by the brownian motion. They are fundamentally unstable and will coagulate in time, but they may remain in a metastable ie. a dispersed state for long periods. This metastability reflects the competition between the kinetic energy of the moving particles promoting coagulation, and the mutual repulsion between their charged surfaces promoting dispersion. Collisions between colloidal particles are governed by diffusion rates and an effective bimolecular collision takes place when two particles approach close enough to be within the range of the forces of chemical attraction. These are thought to be van der Waals forces which although individually small, of the order 5 kcal./mole, are additive for atom pairs on the surface of the colloid. Collisions are inhibited by the long range forces of electrostatic repulsion between the particle surfaces. This repulsion is modified by the nature of the adsorbed layer of counter ions and by the dielectric constant of the medium. Attempts to quantify these modifications have been made in the various forms of double layer theory, particularly in that developed by Verwey and Overbeek (1948) but the complexity of the equations defy calculation. The essentials of the theory depend upon the fact that the counter ions decrease the electric potential of the particle surface and thus reduce the work required for a second particle to approach close enough for chemical interaction. If the ions are tightly held, the double layer is compressed and the electric potential on the clay surface reduced; with chemisorbed ions it is virtually zero. If the ions are weakly held and the double layer extended, the electric potential on the clay surface is large and particles are effectively repelled. The thickness of the double layer in water is a function of ion species and ion concentration.

Its thickness as a function of ion species has been shown to depend on the surface charge density and hydration of the ion as illustrated in the Hofmeister series for cations. This places them in descending order of coagulation power:-

$$La^{3+} > H^{+} \simeq Ca^{2+} > Mg^{2+} > Cs^{+} > NH_4^{+} > K^{+} > Na^{+} > Li^{+}.$$

The hydrated radii for univalent cations given in Table 5 provide a partial explanation for this behaviour.

The thickness of the double layer as a function of electrolyte concentration depends on certain threshold limits that determine the coagulating power of uni-, diand trivalent ions and has been expressed in the Schultze - Hardy rule (Hardy 1900). Concentrations can be visualised in terms of 'time spent' by the oscillating cation close to the colloid surface, so that there are critical concentrations for all cations above which coagulation will occur. These concentrations are given numerical values in Table 5 column 2 (van Olphen 1963) and relative values in column 6.

Double layer theory has been successful in the use and interpretation of the four basic electrokinetic phenomena : electrophoresis, electro-osmosis, sedimentation potential and streaming potential. The electrophoretic mobility of a colloid system is a particularly important measurement in clay chemistry since it gives an indication of the stability of the dispersion. Counter ions that are held tightly to the surface of the particle move with it when the particle is placed in an electric field, thus reducing its charge and velocity towards the anode. Counter ions oscillating more freely are attracted to the cathode so that the electronegativity of the particle and its velocity towards the anode are increased.
Many colloid chemists describe the system in terms of its zeta potential rather than electrophoretic mobility, ie. in terms of the work required to bring unit charge from

Table 5 **Data on the behaviour of cations in sols.**

**(columns * compiled from Jenny and Reitemeier 1935).**

| Valency of saturating ion | Threshold limits mmole/l | Ion | * Hydrated Radius Å | * Migration velocity $\mu$/sec/V/cm. | * Flocculation value with KCl |
|---|---|---|---|---|---|
| uni- | 25-150 | $Li^+$ | 10·03 | -3·45 | 21·6 |
| | | $Na^+$ | 7·9 | -3·31 | 11·2 |
| | | $K^+$ | 5·32 | ... | 7·8 |
| | | $NH_4^+$ | 5·37 | -3·48 | 5·4 |
| | | $Cs^+$ | 5·05 | -3·02 | 5·6 |
| di- | 0·5-2·0 | $Mg^{2+}$ | ... | -3·18 | 2·9 |
| | | $Ca^{2+}$ | ... | -3·27 | 3·0 |
| tri- | 0·01-0·1 | $Al^{3+}$ | ... | ... | ... |
| | | $La^{3+}$ | ... | -2·74 | 0·86 |

some infinite point in the solution to the shear layer or boundary of adsorbed water molecules moving with the particle. The zeta potential $\zeta$ is computed from the electrophoretic mobility v using the Helmholtz - Smoluchowski equation:-

$$\zeta = \frac{4\pi\eta v}{\varepsilon \vec{F}},$$

Where $\eta$ is the viscosity, $\varepsilon$ the dielectric constant and $\vec{F}$ the applied field strength. Modern water chemists tend to reject this mathematically derived paramater in favour of the measureable electrophoretic velocity (Table 5 ) but it is still widely used in practice (Baker 1967).

Double layer theory can be applied to soil situations. Rainwater is low in electrolytes and may peptise surface clay which is then washed into pores and fissures to create an impermeable subsoil. Hence liming the soil improves its drainage. Sodium and to some extent magnesium are known as peptising ions and calcium and hydrogen as flocculating ions. The anomalous position of univalent hydrogen is thought to be due to its release of aluminium from the clay lattice. Nevertheless, acid soils are not as well aggregated as calcium soils so that some other factors must be taken into account. A vivid example of the practical consequences of double layer effects is illustrated by the sequence of events when sea floods the land. The retreated sea leaves a soil with a well flocculated crumb structure. Rainfall leaches out the excess sodium chloride and the soils disperse and then set hard when dry. Gypsum is added to correct the structural breakdown, and through time the sodium soils become calcium soils and crumb structure returns. Thus the electrokinetic interpretation can be applied to the management of saline soils, of arid soils with high salt subsoils, of soils reclaimed from the sea and raw soils derived from sulphurous shale bings, whose sulphides have weathered to sulphates; and it can assist in understanding drainage. There are many situations however, where the theory is of small applicability, and these are next examined.

## 4. Isolectric flocculation and coagulation.

Isolectric precipitation may occur by (i) collisions between oppositely charged particles, (ii) by oppositely charged edges and faces or random molecular groups mutually flocculating the same colloid, (iii) by the colloid losing charge in the region of its isoelectric point.

In passing, one should note that colloid chemists such as La Mer (1967) and Matijević (1967) lay stress on the difference between coagulation, brought about by collisions between diffusing particles and flocculation produced by cross linking or bridging of particles. Particles coagulating in process of free fall are said to sediment. Their velocity is governed by Stokes' Law and they form a compact coagulum difficult to filter. Flocculated particles undergo 'hindered settling' and subsidence can be followed as a sharp line between the flocs and supernatant liquid. These settle to a loose three-dimensional structure, which is easily filtrable. The two mechanisms are often easily identified, but there are occasions on which the distinction is blurred.

### (i) Collisions between oppositely charged particles.

When negative sols of layered clays or organic matter extracts are added to positive sols of alumina, ferric hydroxide or allophane a precipitate is readily obtained. The isoelectric point of these positive colloids is very often above field pH ie. it may lie in the region 6•6 to 8.0. Hence it is logical to assume that the same mechanism applies in soil and that the crumb or nutty, porous structure found in allophane soils and in the Darleith soils is due to their high alumina, ferric oxide or alumino-silicate content interacting with the layered clays and organic matter by a purely electrostatic mechanism. There must be much truth in this interpretation, although it will be necessary to modify its simplicity.

### (ii) Edge-face and edge-edge flocculation.

Clay edges carry a pH dependent charge, due in the main to the hydrolysed alumina on the broken edge. In acid suspensions the edge-positive charge on layered clays may react with their face-negative charge to give edge-face flocculation. Striking evidence for the positive charge was demonstrated by Thiessen (1942) who mixed a kaolinite sol and a negative gold sol and obtained an electron micrograph which showed the gold particles adsorbed on the edges of the hexagonal clay plates. Prior treatment of the kaolinite with a trace of sodium pyrophophate reversesthe edge charge and the gold particles are dispersed from the edges of the plates (Marshall 1964). Schofield and Samson (1953) confirmed the view that positive edges could account for the flocculating behaviour and anion uptake of kaolinite by measuring its chloride adsorption in acid suspension. This was of the order 0·2 m.e./100g clay. Flocculation experiments in which anions were added to or removed from clays, showed how the positive sites could be blocked, thus leading to phosphate fixation in the field and deflocculation in the laboratory (Schofield and Samson 1954). In most soils, clay edges are neutralised or made negative by adsorbed silicate, phosphate or humate anions. The same effect has been deduced to account for the negligible or negative charge carried by some iron oxides, which would have been expected to be positive at field pH (Deshpande et al. 1968).

Interest in edge-face and edge-edge flocculation and the formation of 'card house' structures has chiefly arisen among civil engineers and workers in clay technology. Micrographs of thin sections of sediments can interpret soil stability under load stress. Close packed sediments are normally stable, although under low shear stress, face-face orientation may promote instability, because repulsive forces still allow the grains to slip over one another. Sediments containing card house structures have micro-voids and hold more water and thus tend to subside under stress.

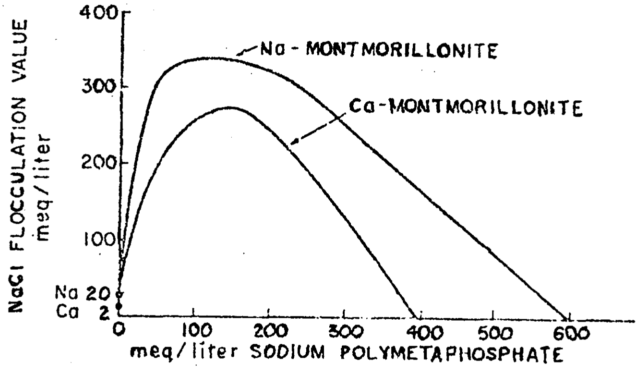
In clay technology, edge-face association is of fundamental importance and rheological studies of change in viscosity, yield stress and turbidity can follow its development. In dilute suspensions the viscosity is decreased and in concentrated suspensions the formation of continuous linked card house structures produces a gel in which the Bingham yield stress is a measure of the number and strength of the links in the card house (van Olphen 1963). Such a gel is the basis for a thixotropic paint, but the elimination of edge-face or edge-edge links is often desirable when it is necessary to get concentrated suspensions sufficiently fluid to be poured or pumped. This is achieved by reversing the charge with a peptising anion. A stiff clay suspension can be turned into a freely flowing liquid with the addition of a few tenths of one per cent of sodium tetrapolyphosphate or organic anion such as tannate.

Charge reversal rather than charge neutralisation is inferred from the large increase in salt flocculation values, together with an increase in electrophoretic mobility. The polyanion is assumed to be adsorbed on the reactive aluminium sites and its excess valence accounts for the excess negative charge. This gain in suspension stability is far greater than any gain that would be due to the conversion of a calcium clay to a sodium clay. As shown in fig. 6 the flocculation value for such a substitution is increased from about 2 to about 20 me/1 NaCl, but in the presence of polymetaphosphate it is raised to about 300 me/1. The explanation lies in the fact that the flocculating power of an electrolyte on a sol is determined by its activity, rather than its concentration, and the activity of the $Na^+$ is much reduced by the polyanion (van Olphen 1963). This may account too, for the finding that although clays are peptised with alkali, as in the standard practice for soil dispersion, the peptisation is not so effective as with polyanions.

The selectivity of the processes involving different clay substrates, anions and cations in the stability control of clay suspensions is illustrated here by two examples.

Fig. 6 Comparison between the dispersing effect of the $Na^+$ ion and the polymetaphosphate ion on montmorillonite suspensions.

(Van Olphen 1963)



Peptization of a sodium and calcium montmorillonite suspension with sodium polymetaphosphate.

The first example is in the conditioning of drilling fluids (van Olphen 1963). Polyphosphate peptisers are used to disperse the clays in the fluid and also in the clay formations passed through by the drill, so that the bore walls are plastered and sealed off against loss of fluid. More subtle properties are wanted in the oil producing zone where the mud must not be so dispersed as to impregnate the rock and stop the flow of oil. In this case the fluid is conditioned with tannate, which unlike polyphosphate, will not flocculate clay at high concentrations of electrolyte. Controlled amounts of alkali can thus be included in the 'red mud' to reduce the degree of dispersion. In deeper bores the mud stiffens with the higher temperature, but again it can be thinned by incorporating calcium hydroxide. The mechanism of this is obscure but it may be that calcium ion promotes some face-face aggregation, lowering the number of particles and reducing the tendency to gel.

The second example is from some recent work on laponite, a synthetic hectorite (Neumann and Sanson 1970). This formed gels at low concentrations (2%) in the presence of electrolyte. On adding polyphosphate, clear sols were produced and the clay concentration could be increased to 10% before breaking down to a gel. The observation that the sols formed more readily in hard than in soft water led to the discovery that additions of suitable amounts of certain cations such as $Ca^{2+}$, $Mg^{2+}$, $Li^{+}$, $H^{+}$, $Al^{3+}$ increased the stability of the sol, while others such as $NH_4^+$, $K^+$, $Na^+$ had a deleterious effect. The stabilising cations turned out to be those with a charge density $Z/r^2$ of more than $2 \times 10^{16}$ (where Z is the valency and r the radius in cm.). The explanation put forward was similar to that given by van Olphen for the lime red muds: such cations caused some face-face aggregation and reduced the number of particles available for card house formation and gelling.

### (iii) Isoelectric weathering : control of charge by ions in the colloid complex.

Some of the most outstanding work on soil colloids was done in the nineteen twenties and thirties by Sante Mattson in his studies of the electrokinetic behaviour of iron and aluminium systems. The observations that he made and published in a series of papers in those years are a gold mine of discovery, yet both they and their skilled interpretation have been strangely neglected.

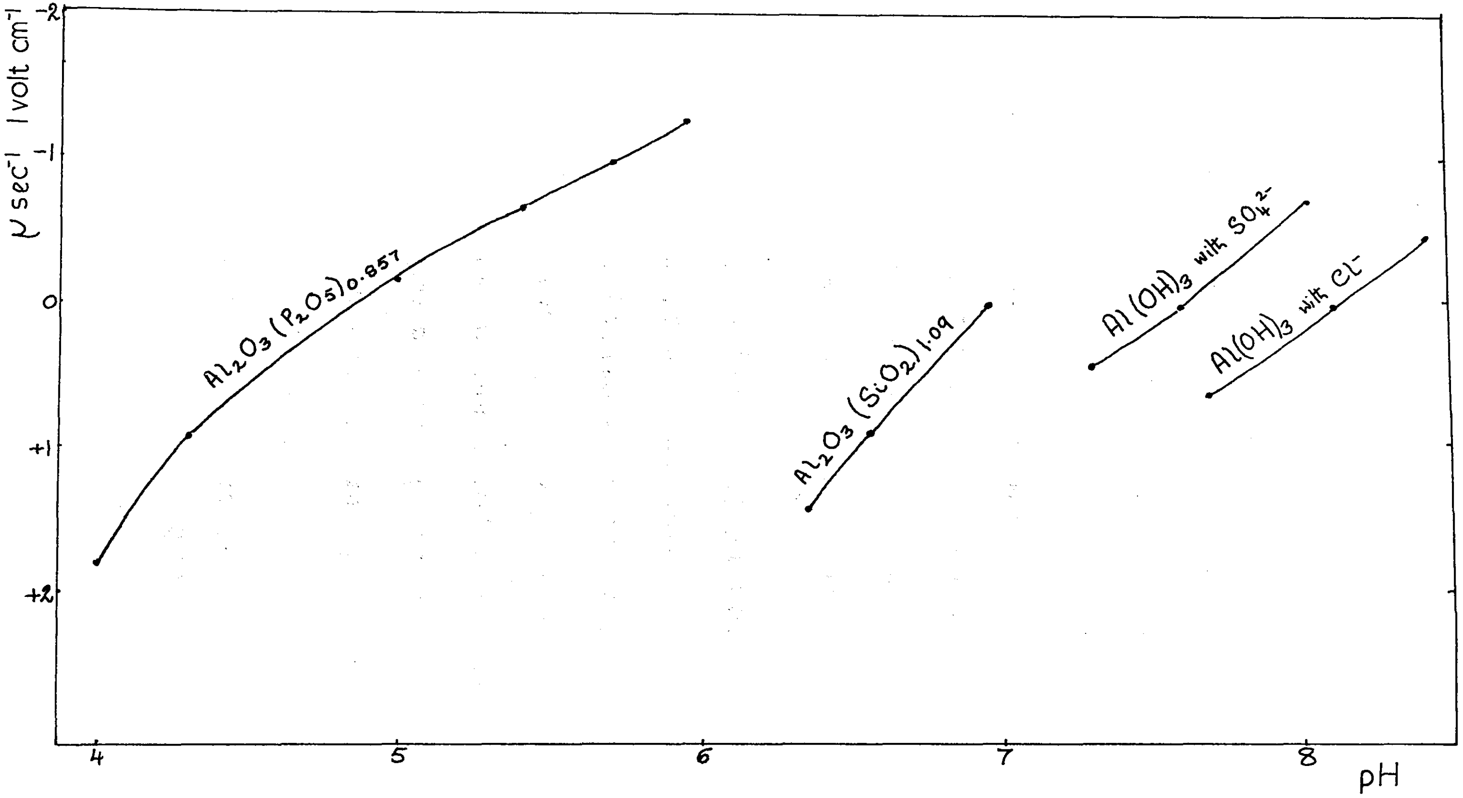
Mattson's interest was in what would now be called the amorphous fraction of the soil. He prepared iron and aluminium oxides, silicates, phosphates and humates and examined the effects of pH and of ion valency and concentration on their flocculation, floc composition, dispersion and electric charge. From these observations he put forward a theory of 'isoelectric weathering', arguing that it was the soil colloids of humus, silica and sesquioxides which "by flocculation and deposition in one layer and by dispersion and migration in another layer, give rise to the development of soil horizons". (Mattson 1930a).

Colloids with a pH dependent charge such as the sesquioxides and alumino-silicates lose their charge when the adsorption of cations or anions from the solution balance. This might be expected to be controlled by $H^+$ and $OH^-$ ions as with the precipitation of proteins, but Mattson showed that the floc composition of the colloid, its isoelectric pH, charge and electrophoretic mobility was a continuing process affected by the supply of silica, alumina, phosphate, humate and other ions in the solution. Some of his findings are outlined below and in figs. 7 to 9 which are either taken directly from his papers or compiled from the tables that he gave (Mattson 1928b, 1930a,b). Figs. 7 and 8 in which the systems were prepared from $AlCl_3$ or $Al_2(SO_4)_3$ and NaOH; $AlCl_3$ and $Na_2SiO_3$ or $AlCl_3$ and $Na_2HPO_4$ with additions of HCl and NaOH where it was necessary to control pH, show the influence of anion: $Al_2O_3$ ratio on the properties of the floc. Fig. 9 shows the same situation for the humates. The concurrent experiments with iron oxide are not generally given, but they are as illuminating as his work on alumina and the alumino-silicates or allophanes. The results and their interpretation are summarised as follows:-

(a) Fig. 7 shows the alumina systems and illustrates the rule that the more associating the anion the lower the pH of the isoelectric point. Thus, alumina precipitated from $AlCl_3$ had an IEP of pH 8.1 and this was lowered to 7.6 by the more strongly held sulphate ion. The displacement of the IEP to the acid side by silicate and phosphate was in proportion to the amount which had entered the complex and their relative displacing power. The reason for this behaviour is that the stronger the presence of the anion in the complex, the greater its contribution to negative charge and the more the cations dissociate. Hence, to achieve

Fig. 7 <u>The acidoid : basoid complex : influence of the anion on the flocculating zone of alumina systems</u>.

(Compiled from Mattson 1930a)



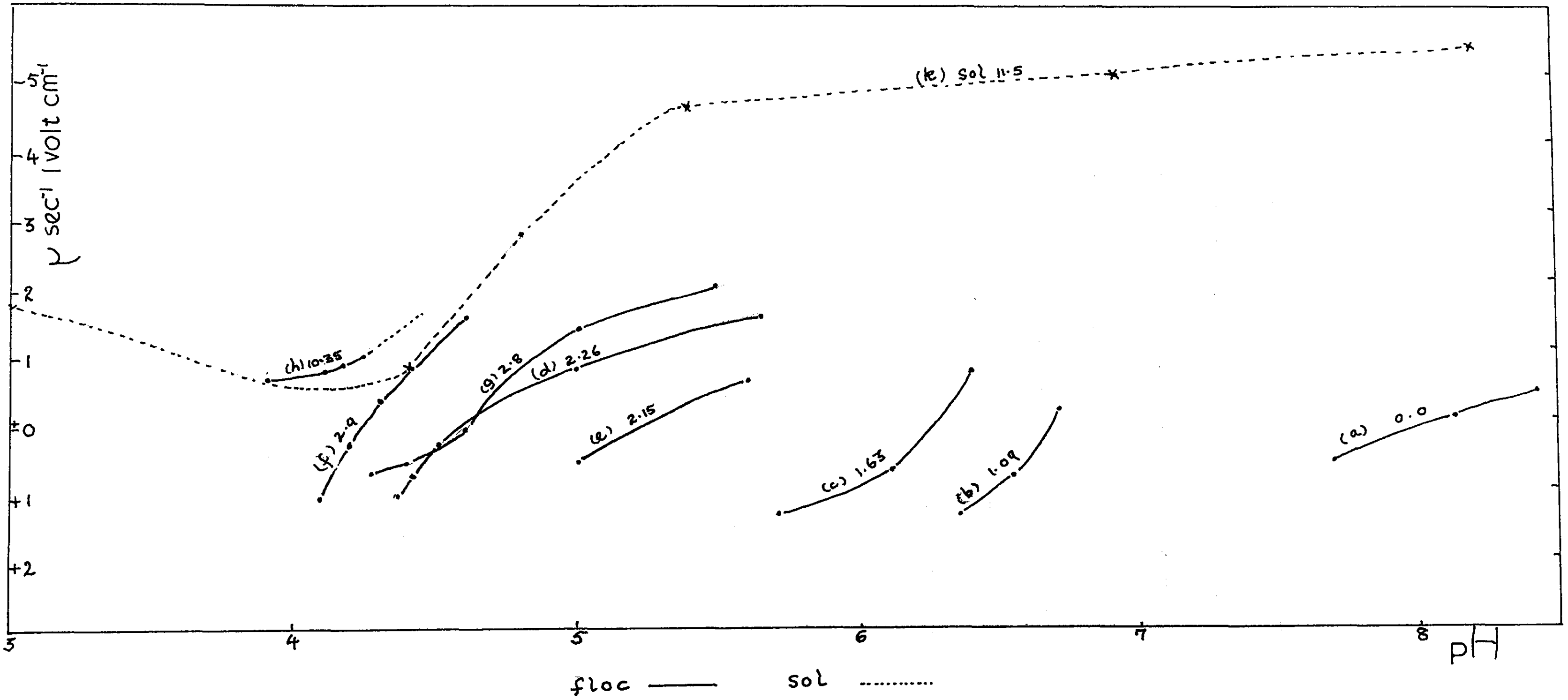
the isoelectric condition when the adsorbed cations and anions balance, positive charge due to the alumina must be proportionately increased by a lowering of pH.

Similarly from fig. 8 it is seen that the lower the $SiO_2 : Al_2O_3$ ratio, the higher was the pH of precipitation of the floc. This follows because the higher the pH the less electropositive the aluminium oxide and the lower the amount of electronegative silica with which it will combine. For a ratio of 2•9, the isoelectric point was pH 4•25, while for a ratio of 1•09 it was pH 6•6. In the context of soil development it is interesting to note that if the pH of the medium surrounding the floc rises, silica will be released, and if it falls, silica will be taken up.

(b) The results predicted that no matter how high the $SiO_2 : Al_2O_3$ ratio in the solution mixture, an isoelectric floc would form of composition less than 3•0 provided the system was sufficiently dilute (fig.8e,g). Under these conditions, the reaction must be between single ions, for mutual flocculation of positive and negative sols could hardly maintain such regularity in composition ratio. Siliceous allophanes, of ratio $>$ 3•0 were prepared in three ways: from concentrated solutions, from colloidal silica, and from solutions containing

Fig. 8 The flocculation zone and isoelectric floc composition of alumino-silicates under varying conditions (Table 6 p.78).

(Compiled from Mattson 1930a, 1928b)



divalent cations. (Table 6 f, h, l respectively).

(c) Concentrated solutions containing the same mixture ratios as dilute solutions precipitated an isoelectric floc with a higher $SiO_2 : Al_2O_3$ ratio and at a lower pH. This is shown in fig. 8f where a concentrated solution of ratio 10 precipitated a floc of composition 2•9 at pH 4•20, while an identical but dilute solution precipitated a floc of composition 2•15 at pH 5•6. (fig. 8 e) Mattson comments that there must be some critical point where free silica flocculates with the complex, and recalls an earlier paper (Mattson 1928b) in which the mixture ratio had been 8•0 but the solution concentration had been higher, and a negative floc had precipitated with a composition ratio of 4•27. The same paper had shown that if the sol was sufficiently electronegative and providing the diffusible ions were monovalent, no floc would precipitate. This is illustrated in fig. 8k where a sol prepared from a concentrated solution of ratio 11•5 reached a minimum charge with eletrophoretic mobility -0•8 $\mu$/sec. at pH 4•8, corresponding to the maximum electropositive activity of the alumina, and thereafter increased its negative charge so that no floc precipitated.

(d) Mattson noted that in the higher concentrations silica showed by itself a tendency to flocculate when sodium silicate was slightly acidified. Fig.8g,h is of an experiment in which acid was added to the $AlCl_3$ before mixing with $Na_2SiO_3$, and added to the $Na_2SiO_3$ before mixing with the $AlCl_3$ and the results compared for identical dilute mixtures of $SiO_2 ; Al_2O_3$ ratio 14. The isoelectric floc ratio was 2·8 at pH 4·7 for the acidified $AlCl_3$. For the acidified $Na_2SiO_3$ the floc ratio was 10·35, precipitation began at pH 4·25 and the floc remained negative to the end of the experiment at pH 3·9. The acid had changed the silica to a partly colloidal condition so that free silica aggregates precipitated with the complex.

The colloidal silica is interesting. In the parallel experiment with ferric chloride and acidified sodium silicate, the zone of flocculation was narrowly confined to pH ~ 4·2. The silica exerted a protective, peptising action on iron, confirming the work of Reifenberg (1927). Thus, in a single experiment, Mattson both anticipates the discovery of the water chemists that colloidal silica promotes flocculation in acid conditions (pp.92,93 ) and the finding that it can be used as a dispersing agent, as discussed in the

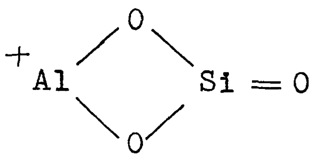
Table 6 <u>The flocculation of synthetic alumino-silicates under varying conditions</u>.
(compiled from Mattson 1930a and 1928b)

| System | Solution mixture | Isoelectric floc | | Supernatant as mmole oxide | | Ref. system |
|---|---|---|---|---|---|---|
| | $\frac{SiO_2}{Al_2O_3}$ | $\frac{SiO_2}{Al_2O_3}$ | pH | Si | Al | (1930a) |
| (a) $AlCl_3$ + NaOH | .. | .. | 8.0 | .. | .. | 3 |
| (b) $AlCl_3$ +($Na_2SiO_3$ + NaOH) | 1.43 | 1.09 | 6.6 | 0.83 | trace | 13 |
| (c) $AlCl_3$ + $Na_2SiO_3$ | 2.68 | 1.63 | 6.25 | 2.64 | 0.1 | 11 |
| (d) ($AlCl_3$+ HCl) + $Na_2SiO_3$ | 6.66 | 2.26 | 4.7 | 10.21 | 0.04 | 9 |
| (e) Dilute $AlCl_3$ + $Na_2SiO_3$ | 10.0 | 2.15 | 5.6 | 7.87 | 0.02 | 25 |
| (f) Concentrated $AlCl_3$ + $Na_2SiO_3$ | 10.0 | 2.9 | 4.2 | 26.84 | 0.08 | 27 |
| (g) ($AlCl_3$+ HCl) + $Na_2SiO_3$ | 14.0 | 2.8 | 4.7 | 14.14 | 0.05 | 29 |
| (h) $AlCl_3$ + ($Na_2SiO_3$ + HCl) | 14.0 | ⊕10.35 | 4.15 | 5.64 | 0.11 | 31 |
| (i) ($AlCl_3$ + $Na_2SiO_3$) + $Ca(OH)_2$ | 3.84 | 1.83 | 6.0 | .. | .. | (1928) |
| (j) $AlCl_3$ + $Na_2SiO_3$ | 8.0 | ⊕ 4.27 | <4.9 | .. | .. | " |
| (k) ($AlCl_3$ + $Na_2SiO_3$) + HCl | 11.5 | no precipitation | | | | " |
| (l) ($AlCl_3$ + $Na_2SiO_3$) + $Ca(OH)_2$ | 11.5 | ⊕5.65 | n.d. | .. | .. | " |

⊕ electronegative floc

experimental part of this work (Chapter XIII ).

(e) Mattson observed that aluminium appeared in increasing quantities in the solution with a lowering of pH (table 6 ) and suggested that it was present, not as free metal ion, but as a complex cation thus:-



.

The positive charge was deduced because in an earlier experiment he had found that when orthoclase was electrodialysed, aluminium appeared together with silica in the cathode chamber after the pH of the felspar had been reduced to a certain value by the removal of potassium. He had also confirmed the discovery of Oden (1927) and Wiegner and Palmann (1929) that silica migrated to the cathode when soil was electrodialysed.

(f) As long as monovalent ions such as $Cl^-$ and $Na^+$ were the only diffusible ions present, flocculation was confined to a narrow zone on either side of the isoelectric point. If the reacting solution contained divalent cations, then the range of flocculation was extended to the negative side of the isoelectric point and the composition ratio could be much more than 3·0.

Table 6 shows the influence of $Ca^{2+}$ in producing an excessively siliceous floc. Mattson's explanation was that divalent cations allowed the precipitation of excess silica by substituting for aluminium in the silica valencies. Such a floc would cease to be amphoteric as the alumina component dwindled. Moreover, no matter how strongly electronegative the sol might be, it would flocculate at once if enough $Ca(OH)_2$ were added.

(g) If the reaction solution contained di- or trivalent anions, the range of flocculation was extended to the positive side of the isoelectric point and the composition ratio $SiO_2 : Al_2O_3$ was reduced by the displacing anion. Mattson (1930b)in Part IV of "The Laws of Colloidal Behaviour" conducted a series of experiments to show how the aluminous floc composition and properties were affected by the competition of phosphate and humate, silicate and humate, phosphate, silicate and humate, and also of the other important ion $OH^-$. The order of displacing power seemed to be:-

humate $> OH^- > HPO_4^{2-} > SiO_3^- > SO_4^{2-} > Cl^-$.

Phosphate was slightly displaced by humate; an isoelectric floc of $P_2O_5 : Al_2O_3$ ratio 0·769 was reduced by the addition of 2 mmoles Na-humate (with respect to Na ) to 0·742, but the pH was lowered from 5·6 to 3·9, reflecting the strong electronegativity of the humate. Silica was powerfully displaced; an isoelectric floc of $SiO_2$ : $Al_2O_3$ ratio 2·2 precipitated at pH 6·25 was reduced to a ratio 0·83 by the addition of 2 mmoles Na-humate and the pH of precipitation fell to 5·5. Mattson also notes that the silicate ion did not displace the phosphate ion to any apparent degree, but that the presence of silicate in the floc caused more of the phosphate to combine, an anomaly which is discussed later (Chapter VII 2 p.310).

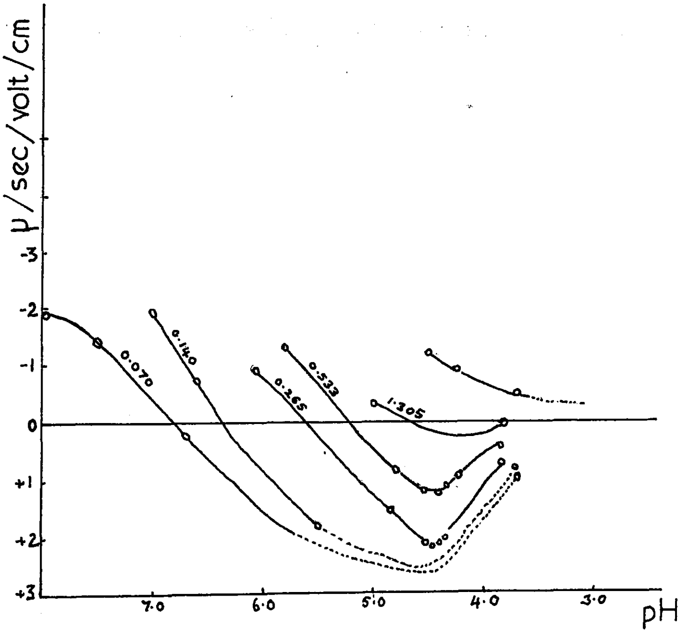
The strong displacing power of the humate explains the field and laboratory observations that allophane has a great affinity for organic matter and is capable of building it up to high levels. The displacement order also suggests that in the absence of organic matter, phosphate retention may be strong. Hence Mattson's experiments are very relevant to the discussions on phosphate and organic matter in Chapters VIII and VI . He does not mention these aspects however. He interprets the displacing power of humates as showing that humus desilicates the soil complex in podzolisation.

(h) In a study of iron and alumina-humates in the same paper, Mattson categorised alkali humates as very dispersible, alkaline earth humates as less so, and iron and aluminium humates as amphoteric precipitates, dispersible with increasing positive or negative charge. These humates are illustrated in fig. 9 . The dotted lines represent dispersion and the solid lines precipitation. It is seen that there is an electro-positive maximum on the acid side of the isoelectric point. This behaviour differs from that of the silicates and phosphates, in that the humus is colloidal and the electropositive contribution of the sesquioxides is enhanced. Where the proportion of humus is high, the alumino-humates show two isoelectric points, and where it is low they show zones of dispersion at low pH. This is between pH 5·8 and 3·7 for the humus: $Al_2O_3$ 0·070 complex. The corresponding ferric-humate disperses below pH 3·7.

These results may be relevant to the discussion of the mechanical analysis dispersion of soils.

(i) Mattson illustrates the significance of his findings by applying them to explanations of soil development. In tropical regions soil colloids are often low in bases and silica. High temperatures prevent the accumulation of organic matter so that the soils are fairly neutral; silica is thus removed, together with

Fig. 9 The relation between the pH, sign of charge, migration velocity and ratio of gram humus to millimol $Al_2O_3$ in a series of aluminium 'humates'. (Mattson 1930b)



the bases, by intensive leaching. In temperate regions soil colloids may be low in bases, moderate in silica ; the accumulation of organic matter and its acidifying influence protects silica from the heavy leaching which removes the bases. In arid regions, silica and bases accumulate together with the sesquioxides.

(j) Mattson also discusses the effects of the alumino-silicates on cation exchange capacity, but a review of this part of his papers is left over to another chapter (Chapter VII).

## 5. Hydrolysis products of hydrous oxides : their use in coagulation and dispersion.

### (i) Problems of coagulation in water treatment.

In 1884 Austen and Wilbur reported on the effectiveness of aluminium sulphate as a coagulant for purifying drinking water, and from that time it has become established in water treatment processes. Since the aim of the water chemist is to select conditions which will give maximum removal of impurities at minimum cost, many empirical studies have been made of the optimum alkalinity, pH, concentration of aluminium, choice of salt and use of activators. Similarly, the mechanism of its action upon the water-borne colloids has been investigated with a view to making water technology a predictable science. Conflicting views and evidence on this mechanism have been on (a) whether the coagulating agent was the aluminium ion, the hydrolysed positively changed polymer or aluminium hydroxide and (b) whether the nature of the suspended material had any influence on the course of the coagulation. However, it was well accepted that there was an optimum aluminium sulphate dose for the removal of colour or turbidity from any particular water, and at higher or lower doses the process became less efficient. In general it was thought that this depended on the pH or chemistry of the water rather than on the suspended material.

The discovery that the organic colloids in water had a negative charge (Blitz and Krohnke 1904) suggested that the efficiency of aluminium as a coagulant could be explained in terms of the Schultze - Hardy rule. However, plant operators found that optimum coagulation occurred in the range pH 5•8 to 7•5 (Hatfield 1922) or 4•8 to 8•5 (Baylis 1923). These workers were the first to stress the advantage of pH control.

The mechanism of coagulation was investigated by Mattson as part of a systematic investigation into the electrokinetic behaviour of dispersed systems. He was concerned to show the practical importance of electrophoresis, and to this end he had designed a microelectrophoretic cell which was used to illustrate the application of his technique for the purifying of milk and molasses, the preparation of pigments and the treatment of river water (Mattson 1928a)

Optimum conditions for the coagulation of a colloid clay by aluminium chloride were explored. 0•2g/1 electrodialysed Sharkey clay with a cation exchange capacity of about 79 me/100g (Mattson 1931) was treated with varying amounts of $AlCl_3$. The mixture became isoelectric with 1•5 me/$AlCl_3$ and the effect of pH was examined by adding this amount to clay which had been made acid or alkaline with HCl and NaOH respectively. The results are shown in fig. 10. Mattson's findings can be summarised as follows:-

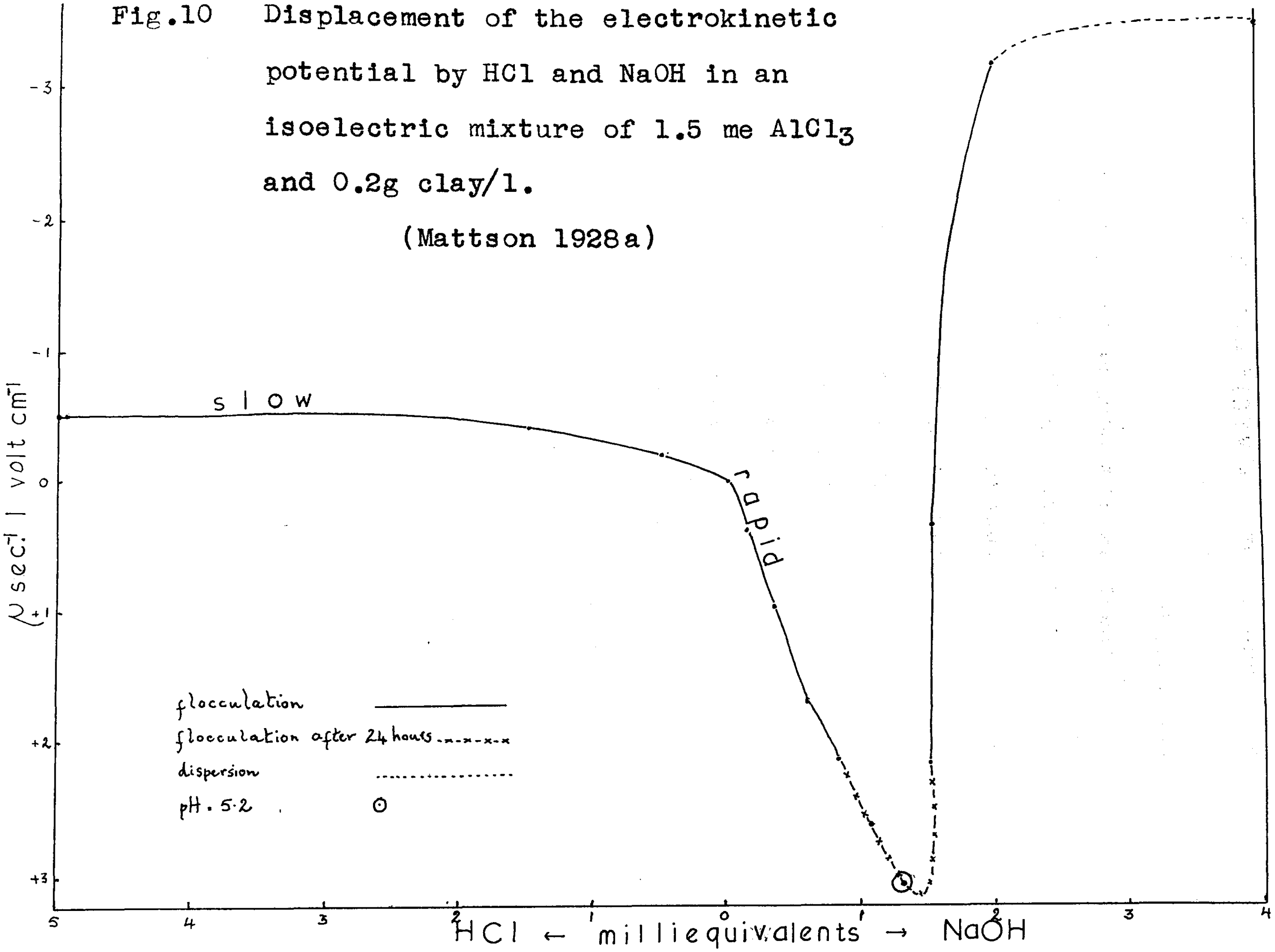


Fig.10 Displacement of the electrokinetic potential by HCl and NaOH in an isoelectric mixture of 1.5 me $AlCl_3$ and 0.2g clay/1.

(Mattson 1928a)

(a) There were two zones of rapid coagulation. The first was at low pH shortly after charge reversal. It was followed by a zone of metastability with the electrophoretic mobility reaching a maximum of +3·1 $\mu$/sec. at pH 5·2. The clay was dispersed but precipitated slowly over 24 hours. The positive charge declined until a narrow zone of coagulation appeared in the region of the isoelectric point, probably corresponding to a suspension that was near neutral. Excess of alkali created a stable dispersion which did not coagulate.

(b) On the acid side there was weak coagulation produced by the trivalent ion, but this was incapable of reversing the charge or even attaining the isoëlectric point. Mattson (1922) had already noted that it was "not the trivalent ion but the products of hydrolysis of aluminium which were responsible for the electrical neutralisation and flocculation of colloids." The hydrolysis products thus reached maximum electropositive activity at pH 5·2, lost their charge as $Al(OH)_3$ developed, and in alkali medium became strongly negative, redispersing the system.

(c) By adjusting the pH of the $AlCl_3$ with NaOH prior to adding it to the suspension, Mattson increased the concentration of electropositive polymer and found that by this means three times less $AlCl_3$, or only 0·5 me/l, was required to make the clay isoelectric. An additional improvement was that the flocs so produced were much more stable to washing than those precipitated by $AlCl_3$ alone.

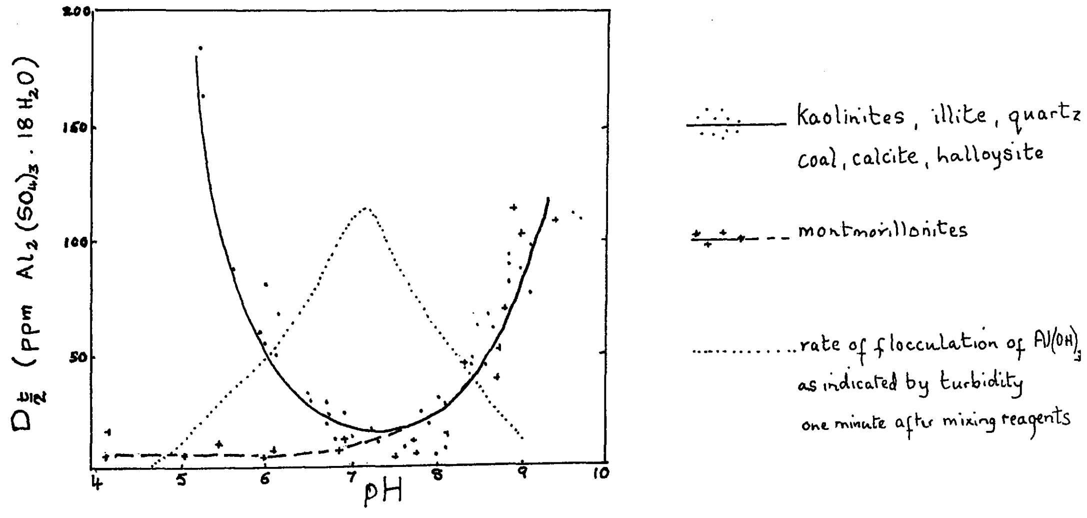
(d) Mattson assumed that the required ratio of $AlCl_3$ : NaOH would vary with the electronegativity of the colloid and recommended that the guiding parameter for coagulation with $AlCl_3$ should be pH 5·2, for it was at this point that the hydrolysis products had their maximum electropositivity. Since there did not seem to be a zone of metastability with the lower concentration of $AlCl_3$, he did not appear to consider it necessary to discuss the possibility of dispersion by positive charge reversal. Nor does he discuss whether the second isoelectric point, due to flocculation of $Al(OH)_3$ might be useful.

Mattson's paper was neglected. For the next thirty years plant operators continued to work empirically, while the relative merits of aluminium ion, its hydrolysis products and $Al(OH)_3$ as a coagulating agent were unresolved. The use of the micro-electrophoretic cell was at last revived by Pilipovich et al. (1958) who concluded that hydrolysis products might play the dominant role, but differed from Mattson in finding only one isoelectric point. Packham (1959) reviewed the theories of water works coagulation and made a systematic search for optimum conditions in which minimum coagulant was used for maximum coagulation. He reported that this coincided with the pH of the most rapid settling of aluminium hydroxide. This is illustrated in fig. 11 where the coagulant dose $Dt/_2$ required to halve the turbidity was plotted against pH for a variety of colloids and river suspensions and compared with the rate of flocculation of $Al(OH)_3$. It is seen that the most rapid settling of $Al(OH)_3$ is at pH 7·1 to 7·2, while the $Dt/_2$ curves have a minimum between pH 6·8 and 7·8. Further experiment showed that the curves varied systematically with the flocculation of $Al(OH)_3$ when studies were made in the presence of added anions that extended the coagulation zone to the acid side. Montmorillonites alone behaved differently and this was thought to be due to edge-face flocculation of very fine clay.

Packham concluded that the mechanism for these optimum results was co-precipitation or enmeshment of the colloids with the rapidly flocculating $Al(OH)_3$ rather than mutual coagulation of the clay with the hydrolysis products, as postulated by Mattson. "For if the mechanism were mutual coagulation, the minimum quantity of coagulant would be required between pH 5·35 and 6·0 where the aluminium hydroxide sol is relatively more stable and presumably has a higher zeta potential." (Packham 1960). He suggested his results were consistent with the coating of the clay particles by $Al(OH)_3$ and then binding them together by $Al(OH)_3$ precipitated in the bulk of the solution.

Fig. 11 Variation of $D\frac{t}{2}$ (the coagulant dose that halves the turbidity) with final pH for 50 ppm mineral suspensions.

(Packham 1965)



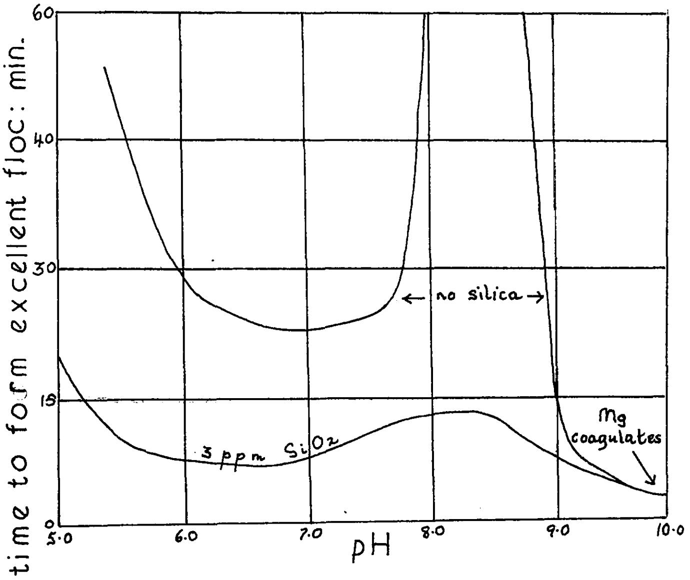
### (ii) Silica activation.

One further aid to the flocculation of water colloids by aluminium sulphate must be mentioned . The discovery of 'silica activation' stemmed from research into the ways in which the pH range of optimum flocculation could be widened in order to eliminate the rather specific conditions required by pH control. It was thought at first that the addition of sulphate salts, which laboratory trials had found effective in widening the pH range, would be suitable, but this failed on a plant scale. Baylis (1936), however, noted that there was a constituent in some natural waters which was giving the desired effect, and he set out to discover what it was by adding various amounts and combinations of constituents to distilled water. One of these was silica solution made up from an old sample of sodium silicate which had become carbonated because the stopper did not fit the jar. It gave considerable aid to flocculation, whereas solutions made from fresh sodium silicate gave none. This indicated that the sought constituent was colloidal silica. Graf and Schworm (1937) independently made the same discovery when they were trying to prevent after-precipitation of aluminium by treating the waters with sodium silicate. They found that a mixture of aluminium sulphate and sodium silicate gave such impressive coagulation, it was plain they had stumbled on a new aid.

The use of activated silica in water treatment was reviewed by Wheaton and Walker (1950), soon after its introduction to Britain in 1947. It has extended the range of pH over which the aluminium sulphate is effective (fig. 12), giving excellent coagulation above pH 5·5, with increased rate of coagulation and the production of tougher more filterable flocs. This has meant that the capacity of existing plants could be increased and that new plants could be built with smaller settling tanks and fewer filters. The silica can be prepared in various ways including those described for a 'Baylis sol' and a 'Graf and Schworm sol'. Doses vary with the conditions but a 1:10 $SiO_2 : Al_2(SO_4)_3 . 18H_2O$ has normally been found sufficient. It is believed to be in a highly hydrated colloidal form with a strong negative charge and to encourage floc development by augmenting the supply of negative colloids reacting with the aluminium hydrolysis products. The method has been found applicable not only to water purification but to treatment of sewage, and white water from paper mills, and to the removal of petroleum from water.

Fig.12 The effect of varying pH value on the coagulation of Lake Michigan water with alum and alum plus activated silica.

(Baylis 1936-37; rep. Wheaton and Walker 1950)



### (iii) Dispersion of colloids by positive charge-reversal.

Packham, in his review (1958) questioned the findings of a minority of workers (Miller 1925, Langelier and Ludwig 1949) of two zones of coagulation separated by a zone of dispersion, and did not refer to Mattson's (1928a) metastable zone. Mattson, and Langelier and Ludwig had assumed that the character of the suspended material would have some influence on the coagulation. This was shown in studies by Black and Hannah (1961) who used the micro-electrophoretic technique to study the coagulation of kaolinite, Fuller's earth and montmorillonite with base exchange capacities of 8•7, 26•5 and 115 me/100g respectively. Figs.13,14 and 15 show the mobility and residual turbidity curves for aluminium sulphate doses of 0,5 and 15mg/l. It is seen that charge reversal giving dispersed sols occurred as the concentration of the coagulant was increased, and that the lower the base exchange capacity of the clay, the lower was the concentration required to bring this about. A very high dose of 100mg/l reversed the charge on all three clays but dispersion at pH 4•5 was then followed by coagulation long before the isoelectric point.

Table 7 and a re-examination of Mattson's and Packham's graphs (figs. 10 and 11 ) allow an explanation

## The effect of aluminium sulphate on the coagulation and dispersion of clays of varying cation exchange capacity.

(Black 1966)

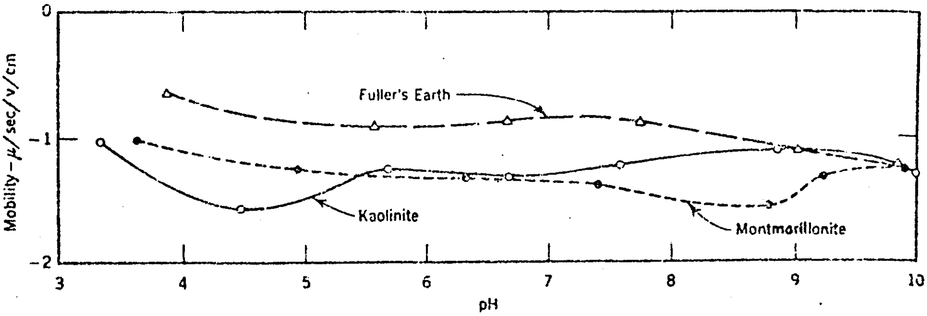


Fig. 13 MOBILITIES OF CLAYS WITHOUT ALUM.

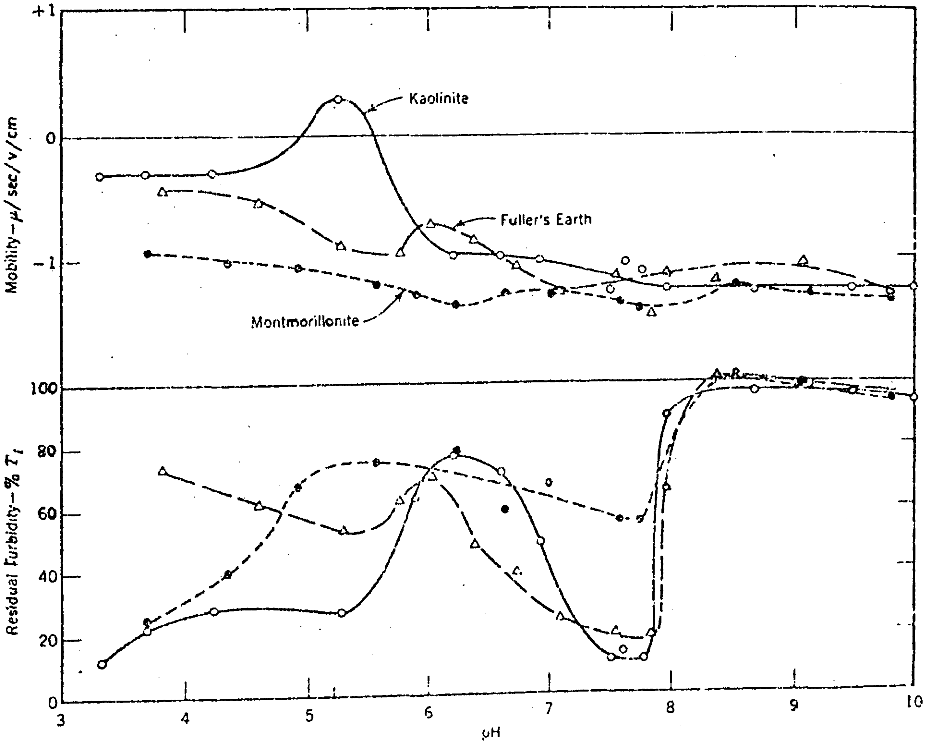


Fig. 14 COAGULATION OF THREE CLAYS WITH A DOSAGE OF 5 mg/l ALUM.

Contd/

## The effect of aluminium sulphate on the coagulation and dispersion of clays of varying cation exchange capacity.

(Black 1966)

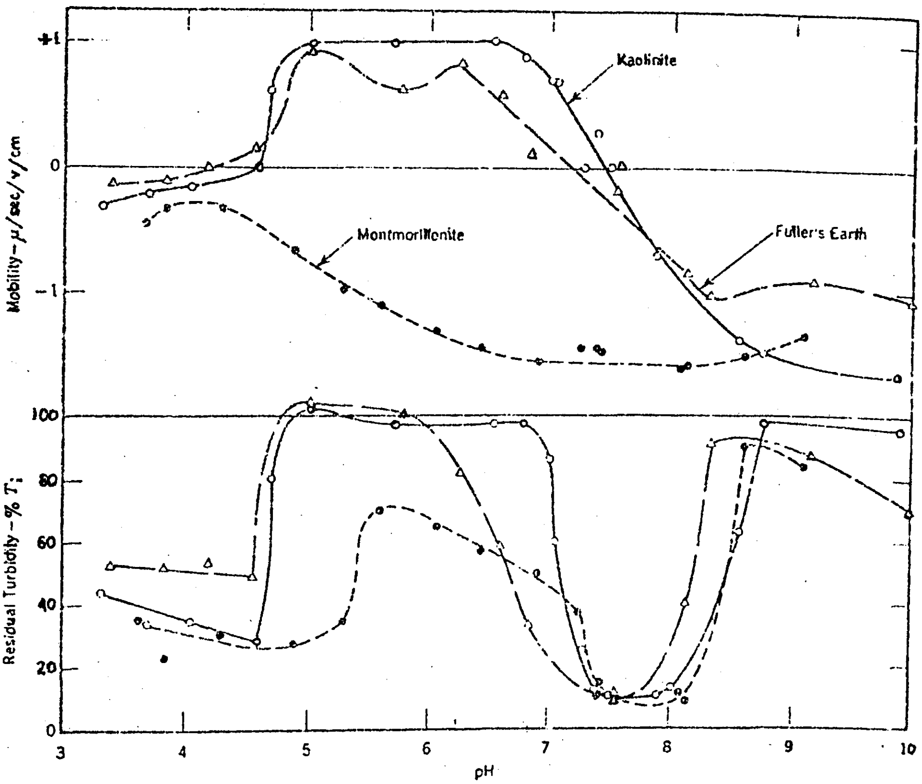


Fig. 15 COAGULATION OF THREE CLAYS WITH A DOSAGE OF 15 mg/l ALUM.

Table 7 The effect of aluminium sulphate concentrations on the charge reversal of clays of varying base exchange capacity.

| Workers | $Al^{3+}$ me/1 | clay dispersed | BEC me/100g | Mobility max. $\mu$/sec/V/cm. | pH at max. mobility. |
|---|---|---|---|---|---|
| Black and Hannah (1964) | 0·5 | kaolinite | 8·7 | + 0·4 | 5·2 |
| | 1·5 | kaolinite | 8·7 | + 1·0 | 5·0-6·5 |
| | 1.5 | Fuller's earth | 26·5 | + 0·9 | 5·0-6·2 |
| | 10·0 | kaolinite | 8·7 | + 0·8 | 4·5 |
| | 10.0 | Fuller's earth | 26·5 | + 0·7 | 4.5 |
| | 10.0 | Montmorillonite | 115·0 | + 0·6 | 4.5 |
| Mattson (1928) | 0·5 | Sharkey clay | 79·0 | flocculation | |
| | 1·5 | Sharkey clay | 79·0 | + 3·1 | 5·2 |
| Packham | 0·1 | kaolinite | 3-15 | + 0·3 | 6·2 |
| (1960,1967) | 0·4 | kaolinite | 3-15 | + 1·1 | 5·3 |
| | 0·4 | montmorillonite | 80-140 | flocculation | |
| | 4·0 | montmorillonite | 80-140 | flocculation | |

in terms of the concentration dose. Packham's curves showing a decrease in floccability below ~pH 6·8 suggest that charge reversal for kaolinite and the other colloids was tending to disperse the clays, while keeping his montmorillonites coagulated below ~pH 7·8. This was because his highest dose was only about 4me/l in aluminium. Similarly Mattson's metastable zone for a clay of 79me/100g base exchange capacity disappeared when the aluminium concentration was lowered from 1·5 to 0·5 me/l.

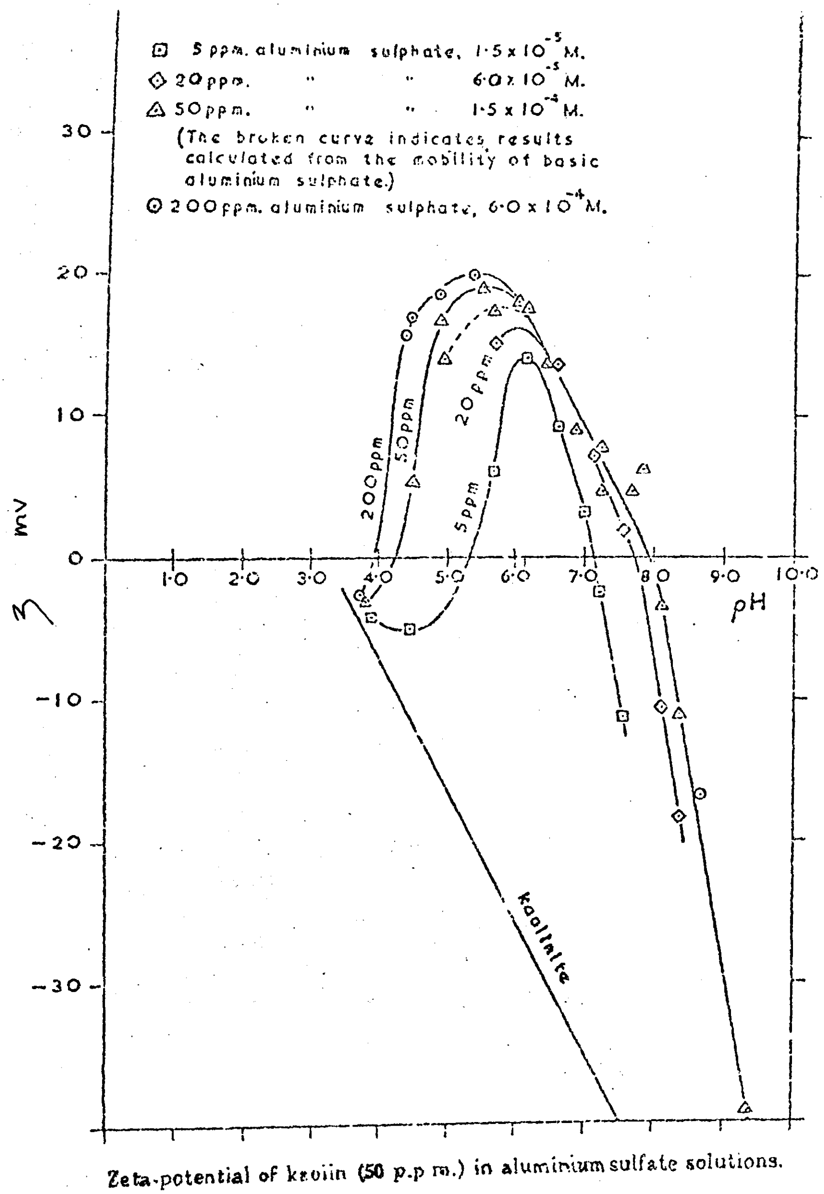
Further curves were constructed for river colloids, which varied with coagulation dose in the same way. It was concluded that : "The characteristics of clay particles; namely, the base exchange capacity, size and charge may influence the coagulant dosage but not the basic mechanisms of coagulation for a particular coagulant." (Black 1967).

Thus was confirmed Mattson's evidence and his interpretations of 1922 and 1928.

The major conclusion drawn from these results was that overdosing a water with aluminium sulphate could produce dispersion unless the pH was controlled between ~ 6·8 - 7·8 or activated silica introduced; and that

Fig. 16 Variation of charge (converted to zeta potential) with pH for kaolinite in aluminium sulphate solutions.

(Packham 1967)



Zeta-potential of kaolin (50 p.p m.) in aluminium sulfate solutions.

electrophoretic measurements, which were now being widely used in water works laboratories, could be a valuable guide to the efficiency of the dose. At the same time Black, and other workers who contributed to the discussion (Faust and Hunter 1967) expressed the need for caution: it could not be assumed that measurements of charge reversal always correlated with sol stability. Other mechanisms such as polymer bridging might be involved. Packham (1967) illustrated this in fig. 16 where optimum coagulation with 25 mg/l $Al_2(SO_4)_3$ at pH 7·1 corresponded with a zeta potential of +10 mv. He stated that no reasonable coagulation had taken place at any of the isoelectric points shown on the graph. Electrokinetic measurements were recommended as a guide and not a magic formula.

### (iv) The domains of charge reversal.

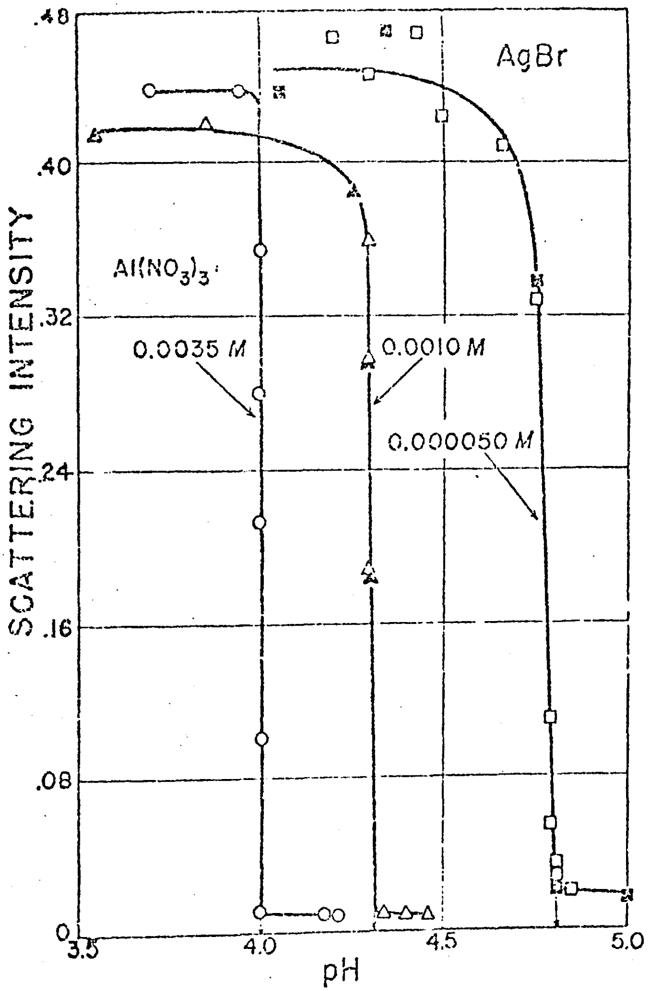
The reversal of charge on hydrophobic colloids by hydrolysed metal ions was studied systematically by Matijević and his colleagues (1960 - 1967). Using silver halide negative sols, they established the metal ion concentration - pH domains of stabilisation by carefully controlled electrophoretic and turbidy measurements. The metals chosen were iron, aluminium, thorium, zirconium and zinc, and their research showed that each of the ions was capable of reversing the charge on colloid particles under certain concentration - pH conditions that were characteristic for each ion. They put forward the view that the charge reversal was due to adsorption of hydrolysed metal ionic species containing hydroxyligands, and was governed by the concentration of these species in the suspension ie. by the degree of hydrolysis. This is illustrated in fig. 17 (Matijević et al. 1964). At low aluminium nitrate molarities and at low pH the hydrolysed species coagulated the sol. When their concentration was increased, by raising either the molarity or the pH, the sol was redispersed. The transition was abrupt. Electrophoresis measurements confirmed that stabilisation accompanied charge reversal. Fig. 18 plots the boundaries between coagulation and dispersion. Milliequivalent values have been inserted for comparison with the stabilised clay sols.

Similar metal ion concentration - pH domains of stabilisation and coagulation were constructed for the other polyvalent metal ions investigated (Matijević et al. 1960, 1961, 1962, 1964, 1967).

These measurements in themselves give no indication as to the mechanism by which the hydrolysed ion species

Fig. 17 The dependence of the dispersion of a silver bromide sol by charge reversal on the concentration of hydrolysed aluminium species as governed by $Al^{3+}$ molar concentration and pH.

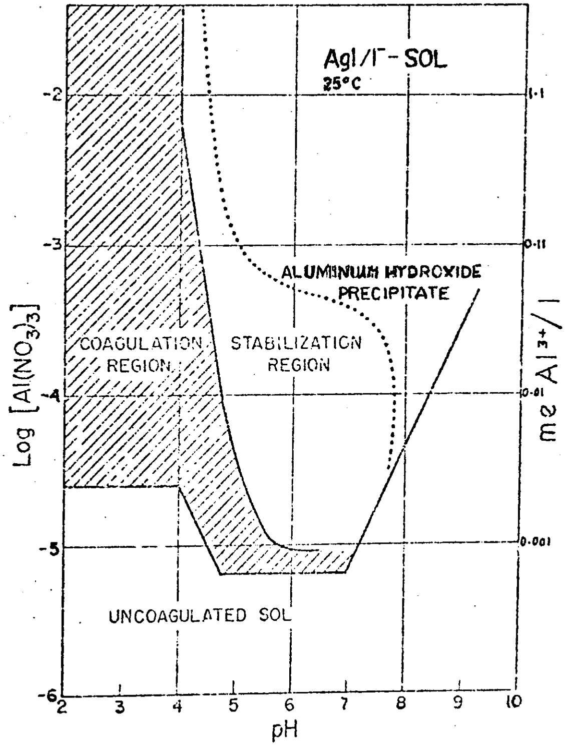
(Matijević et al. 1964, Matijević 1967)



Scattering intensity vs. pH of a silver bromide sol *in statu nascendi* in the presence of three different concentrations of aluminium nitrate. Concentrations: AgBr: $1 \times 10^{-4} M$; excess KBr: $1.9 \times 10^{-5} M$; $Al(NO_3)_3$: $3.5 \times 10^{-3} M$ (○), $1.0 \times 10^{-3} M$ (△), and $5.0 \times 10^{-5} M$ (□).

Fig. 18 The domains of coagulation and dispersion for a silver iodide sol suspended in aluminium nitrate solution.

(Matijević et al. 1964, Matijević 1967)



THE ENTIRE LOG $[Al(NO_3)_3]$ -pH DOMAIN FOR A AgI SOL ($1 \times 10^{-4}$ M AgI, EXCESS KI $4 \times 10^{-4}$ M) at 25°C. Below the lower solid line the sol remains uncoagulated. Above the upper solid line the sol is stabilized due to reversal of charge. Coagulation region is indicated by hatching. The dotted line indicates the formation of $Al(OH)_3$ precipitate in absence of AgI.

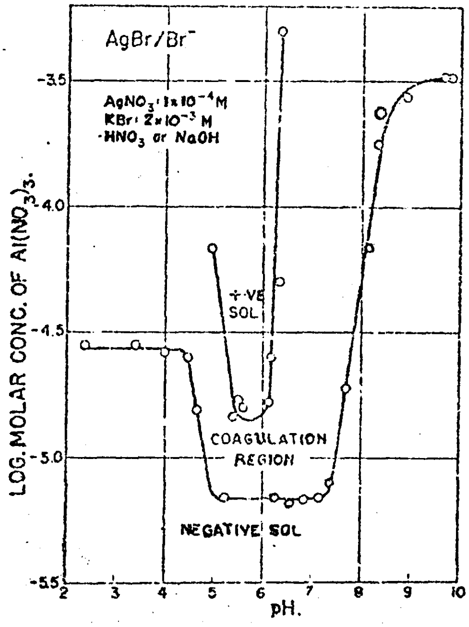
are adsorbed and the colloid's charge reversed. Most of the compounds active in charge reversal, such as the polycations, hexols and diol-complexes contain hydroxy groups, and the authors surmised that it was these which were responsible for the strong adsorption and that charge reversal was due to the relative tightness of the polymer's bonding to the colloid rather than the charge per se. They noted that hydrolysed aluminium was non-exchangeable when adsorbed on ion exchange resin (Hsu and Rich 1960). In an early study on thorium (Matijević et al. 1960) they found that "at lowest pHs, where the counterion appears to have the highest charge, (ie. as $Th^{4+}$ or $Th(H_2O)^{4+}$ H.J.F.), its ability to reverse the charge of sol particles completely disappears. Thus the charge or valency of the counterion itself cannot be considered as solely responsible for the reversal of charge effect." This of course was Mattson's finding for aluminium (1928 b) as shown in fig. 10, but at that stage the authors appear to have been unaware of his work. They concluded:

> "Thus we believe that hydroxyl groups in soluble counterion species are responsible for their adsorption on sol particles, which in turn causes the reversal of charge."

Further understanding might be achieved if composition of the polyions were known. This could be worked out if any two of the three parameters (a) OH : metal ion ratio (b) charge and (c) degree of polymerisation were determined. It had been attempted in various ways by many workers. The OH: Al ratio was found to be 2.5 from potentiometric measurements and was confirmed by the slope of the log $Al^{3+}$/pH graph in fig. 18. Matijević et al. (1961 a ) calculated the charge from their coagulation curves on the basis of the Schultze-Hardy rule. Fig. 19 shows the "critical coagulation" concentration of the aluminium as a function of pH. It was constant up to ~ pH 4 and its value of $2.5 \times 10^{-5}$ mole/l was consistent with the threshold limits of $10^{-5}$ to $10^{-4}$ M for trivalent ions. Between pH 4 and 7, the critical coagulation concentration dropped sharply to a second plateau equivalent to $7.2 \times 10^{-6}$ M, the threshold limit for quadrivalent ions. Thus a value of 2.5 for the OH:Al ratio and a charge of 4 fixed the polymer composition as $[Al_8(OH)_{20}]^{4+}$. This was the species believed to be in solution by workers using different techniques. Further hydrolysis appeared to take place above pH 7, leading to the formation of lower charged species, and a levelling off of the

Fig. 19 Plot of the critical coagulation concentration (lower curve) and stability limit due to the reversal of charge (upper curve) against pH for silver iodide sols in aluminium nitrate solution.

(Matijević et al. 1961a)



coagulation concentration (3 x $10^{-4}$ M) at pH 9 to 10 corresponded to a divalent counter ion whose composition could be $[Al_8(OH)_{22}]^{2+}$.

The hydroxyl : metal ratio, charge and degree of polymerisation was worked out in the same way for the other ions, including the zirconium ion, which will be referred to in the next Chapter when the use of zirconium nitrate as a dispersing agent for allophane soils is discussed.

## 6. Surfactants.

Surfactants, or detergents can be used as precipitants, emulsifiers, dispersing agents or as collectors in foam separations. They may be charged or uncharged. Charged surfactants are organic salts, usually of long chain and low valence, which are capable of coagulating sols at much smaller concentrations than would be required by the Schultze - Hardy rule, and at higher concentrations, of dispersing them by charge reversal.

The cationic detergents are quaternary ammonium salts such as cetyl pyridinium ammonium bromide (cetab), or hexadecyl dimethylammonium bromide (EHDA-Br). When added to a negative sol such as a clay suspension or organic matter extract, the ammonium cation is preferentially taken up by the exchange complex and at the same time the hydrocarbon chains displace the adsorbed water so that the sol precipitates. It is this dewetting process which diminishes the competition of the inorganic cations, and regardless of disparity in charge, allows the surfactants to be strongly adsorbed. Once the exchange complex is saturated, the colloid is dispersible in a non-polar solvent such as oil, and can be used as an emulsifier. At higher concentrations of surfactant, and providing the chain length is long enough, a second layer of hydrocarbon adsorbs by van der Waals bonding to the first, and its ionised groups project into the water phase. The particle-surfactant complex then acquires a positive charge and is redispersed.

Anionic detergents are normally fatty acid salts, such as sodium dodecyl sulphate, and they behave similarly, coagulating positive sols and redispersing them by reversal of charge at higher concentration. Non-ionic detergents are polyglycol ethers of alkylated phenols and esters of sucrose with higher fatty acids. This combination of polar and non-polar groups gives them their emulsifying properties.

The ionic surfactants are ideal in the laboratory for quick tests of colloid charge. They are useful in biochemical separations, as for example, in the selective precipitation of proteins or organic acids, the unwanted detergent being subsequently 'scrubbed off' by shaking in excess lithium chloride. Van Olphen (1951) has suggested that cation exchange capacities could be determined from measurements of the optimum emulsifying power of clay-quaternary ammonium complexes.

Although ionic surfactants have been widely developed in clay technology as for example in the preparation of drilling fluids and clay based greases, they do not appear to be much used in soil chemistry. The writer suggests they might afford a method of separating positively charged clays such as allophanes and oxides from layered clays. Simple addition of the surfactant to the dispersion is not effective because of the enmeshment of the stabilised particles with the flocs of the coagulating ones. Some method of flotation would be necessary. Foam separation of clays was first used by Hopper (1945) for the clarification of water, and has been studied by Grieves (1966) and Crandall and Grieves (1968), but their interest was non-selective. It is predictable that the clay minerals themselves could be separated on the basis of selective flotation techniques such as are used in mineral processing. The well-known flotation of sulphide minerals by xanthate chemisorption has been followed in recent years by the development of a wide range of surfactant collectors for the flotation of the oxide minerals, such as corundum, hematite, quartz and the alumino-silicates. The art of selectivity in mineral dressing is in the choice of suitable depressants, activators, pH- modifiers and frothers which will allow the surfactant to concentrate the mineral in question. In most cases the depressants and activators are ions which are in or added to the suspension. It is conceivable therefore, that the clay minerals could be similarly concentrated, on plant or laboratory scale, by selective methods which can exploit the differences in cation exchange capacity and other surface properties of the clays.

## 7. Polymer bridging.

In the past twenty years high molecular weight polyelectrolytes like starches and polyacrylamides have been widely introduced as flocculants, particularly in the mining industry. At the same time, recognition that there were many different mechanisms involved in dispersion, coagulation and flocculation has encouraged intensive research, in the hopes that this would assist the planning of the concentration process. New developments have become particularly urgent as the exploitation and depletion of mineral reserves call for expertise in the winning of low grade ores and as pollution of water resources demands the removal of finely divided waste from water supplies. The following example is given as an illustration of the discovery of polyelectrolyte flocculation and the way in which this affected the thinking of colloid chemists.

In 1951, the United States Atomic Energy Commission required an efficient method of preparing phosphate slimes for uranium extraction (La Mer 1967). The slimes were the waste product from the grinding of rock phosphate fertiliser and consisted in typical clays finely dispersed. They contained however, 0·1 - 0·01% uranium and at that time were stored in artificial lakes to avoid contamination of rivers. The extraction of the uranium was important both in terms of augmenting the supply and of removing a radio-active hazard. It was also widely desirable to develop a good method for the settlement of slimes, because slimes account for considerable mineral losses and settling ponds are space demanding and costly.

The project was undertaken by La Mer and his colleagues at Columbia University. Their original plan was to use the calculations of double layer theory to coagulate the slimes in the most efficient manner. It was essential however, that the dispersions should be precipitated in such a way as to be rapidly filtrable so that the chemical engineers could extract the $U_2O_3$. It was found that when precipitated with $CaCl_2$ or $Ca(OH)_2$ the particles formed a compact coagulum which did not filter well. Filtration aids other than salts were sought. Overbeek suggested starch pastes. (La Mer and Smellie 1956a, La Mer 1967).

Cauticised corn starch had been used for years in the Bayer process for the flocculation of bauxite alumina, although the reason for its success was unknown. Henry (1928) brought out a patent for the use of starch in precipitating the fines from coal washery effluents, and boiled starch pastes had since been employed in this way in Belgium and Holland (van Iterson 1938). It was found that dropwise addition of a 70 ppm solution of a Dutch starch product 'Flocgel' to the phosphate slime first curdled it, and then led to the formation of flocs which subsided in a manner called 'hindered settling', leaving a clear supernatant. The flocculated material filtered rapidly, sometimes 200 times faster than the coagulated slime, and the filter cake was a loosely packed structure with large pores.

Other polyelectrolytes were tried and studies made of the flocculating efficiency of various substrate-polymer combinations. The extent of flocculation was followed by three methods (a) supernatant turbidity (b) rate of subsidence (c) refiltration of the polyelectrolyte through the previously formed filter cake. This last method proved the most informative. When refiltration curves were drawn it was found that as the concentration of added polyelectrolyte was increased, the rate of filtration achieved a reproducible maximum which was characteristic for each pair of substrate and flocculant, and was followed by a decrease which culminated in redispersion. The specificity of these curves suggested that chemical interactions rather than electrostatic ones were operating.

In searching for an explanation of the flocculation mechanism, it was noticed that not all starches behaved like the Dutch potato starch. Untreated corn starch was ineffective, as judged by filtration rates, and tapioca starch was poor. Potato starch contains 0·13% phosphorous as terminal groups of monophosphoryl ester on the glucose chain of the amylose component. Corn starch has no phosphorous and tapioca starch only a small amount. When corn starch was phosphorylated or cauticised with alkali to form carboxyl groups it became effective. (La Mer 1967).

NOTE: La Mer (1967) stated that it was the $\beta$-amylose (ie. amylose) or long chain fraction of potato starch which carried the phosphate and was negatively charged. This is incorrect. It is the amylopection (once called $\alpha$-amylose) or branched chain fraction which is negatively charged. Whistler (1965) for example says "potato amylopectin bears a formal charge in the nature of 0.08% esterified phosphate groups. Thus in solution, potato amylopectin will migrate towards the anode and can be separated from the amylose which is free of phosphate ester."

Potato starch, or phosphorylated or cauticised starch is negatively charged. Indeed it was found that the amylose could be separated from the amylopectin by differential electrophoresis. All the active polyelectrolytes tested proved to be electronegative. These included polymethyl celluloses, polyacrylamides and krilium, the soil conditioner. Introduction of pyridinium groups to starch to give it cationic properties had a slightly deleterious effect. The discovery that a negatively charged polymer could precipitate a negatively charged sol proved to the authors that the electrostatic forces were being over-ridden by chemical forces. The polyacrylamides' behaviour which showed that the more hydrolysed ie. negative they were the greater their flocculating powers, suggested that the electrostatic barrier was of minimum importance compared to the increased number of hydroxy groups available for adsorption to the clay. La Mer and others postulated a Langmuir type adsorption of polymer to clay via their interacting hydroxy groups. Such bonding would be strong, because although the individual energies of van der Waals or hydrogen bonds are low, of the order 5 kcal/mole, they are additive for each pair of atoms.

One other finding made the case more complex but suggested a role for the phosphate groups. Good flocculation would only take place in the presence of certain cations. In a flocgel experiment, no flocculation took place if only either $Na^+$, $K^+$ or $NH_4^+$ was present. All other ions tested, including the univalent $Ag^+$, promoted flocculation (La Mer and Smellie 1956 b). The authors postulated that the common property of these ions was that they formed insoluble phosphates, and suggested that carbohydrate was adsorbed on to the clay by hydroxyl interaction, while crosslinking into a three dimensional network through the phosphate by a cation bridge was the mechanism that produced the flocs.

The writer is sceptical of this interpretation: (a) if the ability of the cations to form bridges depended on their ability to form insoluble phosphates, why was cauticised starch as efficient as phosphorylated starch? (b) silver would not necessarily be expected to behave as a univalent ion; (c) what was the pH? A possible model would have adsorption of the phosphate or carboxyl group on the clay positive edges with carbohydrate bridging between particles. Counter ion adsorption might control the double layer thickness and determine whether the carbohydrate could approach close enough for hydroxyl interaction with the face. This model allows an explanation for the specificity of the adsorption and also of La Mer's discovery that among his substrates silica flocculated with only a very few of his polyelectrolytes; and by later reports that various divalent cations act as promoters and depressants in the flocculation of single mineral suspensions by polyacrylamide and polyacrylate flocculants (Kitchener et al. 1968).

Excess polyelectrolyte, as with the surfactants, leads to redispersion of the flocs. It was found that 10- 100 ppm starch flocculated the slimes but $> 300$ ppm sometimes peptised them (La Mer and Smellie 1956 b). This was attributed to the coating of the lyophobic colloid by the lyophilic polymer. Similar effects have been observed by Rees (1963) and Fullerton (1964) in the solubilisation of metal cations by 1:1 concentrations of monosaccharides over the pH range when the hydroxides would normally precipitate.

La Mer proposed that the action of the inorganic polymolecular complexes such as that of aluminium in water clarification was also by a bridging mechanism through clay and polymer hydroxy groups. Filtration curves similar to those of the anionic polyelectrolytes had been obtained with $Al(ClO_4)_3$ . Electrostatic forces were involved, he suggested only as a correction factor to the primary bridging mechanism (La Mer 1967).

Workers in mining research have developed these discoveries into methods of high selectivity. A few examples drawn from a recent review of the treatment of slimes must suffice (Collins and Read 1971). These include:- Concentration of iron by selective flocculation of hematite with tapioca flour, and cationic flotation of the residual silica (Frommer 1964); separation of a dilatant fraction from the thixotropic fraction of a clay mixture by a combination of peptiser and flocculant (Rowland 1961); separation of hematite from felspar by flocculating the hematite with a strongly hydrolysing polyacrylamide and the felspar with a weakly hydrolysing polyacrylamide, with additions of 1:1 electrolyte to promote selectivity (Read 1969).

Nowhere but in the field of mineral processing is there such a range of examples to illustrate the complexities of the adsorption process and the interaction of electrostatic, specific and non-specific chemical forces between substrate, flocculant, dispersant and ions in solution. Numerous studies of adsorption isotherms, electrokinetic measurements and zeta potential calculations now seek to interpret the empirical observations (Mackenzie 1971). One factor stands out, however, and that is the lack of understanding of hydroxyl-hydroxyl interactions. Two further examples can emphasise this point. The first is of the well known ability of aluminium sulphate (pH 5 - 6) to separate the components of starch : amylose and amylopectin by selectively flocculating the branched amylopectin and leaving the long chained amylose in the supernatant. The second is in the flocculating behaviour of allophane.

# CHAPTER IV A : SOIL DISPERSION.

## 1. Classical methods of mechanical analysis.

The aim of mechanical analysis is to give a quantitative measurement of soil texture ie. the percent size fraction distribution when aggregates are broken down into their primary particles of sand, silt and clay. This may be followed by separation of the fractions for mineralogical analysis and an investigation of the properties of the clay. To this end, complete dispersion of the soil is necessary and a treatment is sought which will (a) disrupt the aggregates (b) prevent flocculation (c) avoid the abrasion of fragile minerals such as biotite and hematite (d) be of routine application. In addition, for clay studies, the method will require to (e) avoid dissolution of the amorphous constituents and perhaps also of the organic matter (f) avoid addition of constituents which might affect the properties of the clay.

Classical techniques have been concerned with disrupting aggregates and preventing flocculation. Their treatments both destroyed organic matter and dissolved some part of the soil colloids. This was indeed their object, since the organic matter and the amorphous material are largely responsible for the aggregation. The following summarises the various methods used.

Carbonates if present may be removed with dilute HCl. The step is omitted where possible, for fear of acid attack on the clay minerals. Organic matter is destroyed with hydrogen peroxide and the clay is dispersed by shaking in alkali or in alkaline sodium hexametaphosphate ('calgon'). Peroxidisation does not remove all the organic matter in combination with the clay, and a more efficient dispersion may be obtained by alkali oxidation with hypobromite (Troell 1931), which peptises the colloids at the same time and can disperse calcareous soils without prior removal of lime. Mechanical energy supplied by shaking for some specified period disrupts the aggregates, but the time and method of shaking may influence the results. Sodium hexametaphosphate in alkali is often preferred to alkali alone, since it removes polyvalent cations such as calcium, iron or aluminium as soluble complexes and is useful for calcareous soils and soils where iron or aluminium oxides may be cementing the aggregates. The pH of the suspension should be more than 8, below which sodium hexametaphosphate is unstable[✗] (Tyner 1939). Classical

[✗] This cannot be true. See p.671.

pre-treatment may be undesirable however, for subsequent examination of the clay.

In Britain, most laboratories appear to have used peroxidisation, followed by shaking in alkali (Mackenzie 1956) or by shaking in calgon (British Standards Institution 1957). Troell's method does not seem to be favoured, although a comparative study of various peroxide/calgon treatments with the alkaline hypobromite method found that the latter gave the highest clay percentages and would thus be considered the most efficient. It was not recommended for routine analysis however, because of the need to filter excess hypobromite (Protz and Arnaud 1964).

In passing, one should note that since complete disruption of the aggregates may require a large amount of energy, some central European scientists (Switzerland, Czeckoslovakia) prefer to record measurement of 'stable aggregates' as a practical assessment of texture in the field (Keen 1931). There is much to be said for this criterion in advisory work, and evidence will be produced from observations on the Darleith soils which support it. It is possible that not enough attention has been paid to the importance of a classification of aggregates in soils (Emerson 1967).

## 2. New techniques.

### (i) Ion exchange resins.

In recent years, loss of the inorganic amorphous colloids from the soil has been regarded as a serious drawback. Edwards and Bremner (1965) undertook a search for methods which would leave the soils chemically unchanged even with regard to the organic matter. The first discovery was the resin technique. They shook a wide range of surface and subsoil materials from United States, Canada and Australia with sodium-saturated cation exchange resins and obtained clay percentages which compared favourably with those achieved on the same soils by the hypobromite method. Peroxide pre-treatment was not necessary. The method was to shake 10g soil in 60 ml. deionised water with sufficient 16 - 50 mesh resin to supply 15 me. of monovalent cation. Soils high in montmorillonite and organic matter were found most difficult to disperse and the recommended shaking times required for these to reach a clay percentage plateau with a variety of resins were given as shown in Table 8 . They stated that: "The soils effectively dispersed using the cation exchange resin technique have been grassland and forest soils with a high base status in which aggregation is largely due to

Table 8 Shaking times required to reach a clay percentage plateau with various resins.

(Edwards and Bremner 1965).

| Resin | Dowex A-1 | Amberlite IRC-50 | Amberlite IR-120 | Amberlite 200 |
|---|---|---|---|---|
| Hours | 2 | 10 | 20 | 10 |

the presence of a clay-organic matter complex. The maximum dispersion of mineral colloids in such soils has been achieved co-incident with a high degree of dissolution of organic materials." These, although clay contaminated, were essentially unaltered.

In a further paper (1967), the authors report that $Na^+$ and $Li^+$ resins were more efficient than those saturated with $K^+$ or $NH_4^+$, and that $H^+$ or polyvalent cation resins dispersed soil less effectively than if it was shaken in water alone. Among the sodium resins the rate of dispersion increased with an increase in the selectivity of the resin for polyvalent cations.

They put forward their 'micro-aggregate' theory, in which the basic unit of the aggregate consisted in a clay-polyvalent metal-organic matter complex. Since organic matter was well known to complex polyvalent metals and to be bound in some form with clay, dispersion was essentially a process of bond rupture, achieved in this case by contact exchange of the highly hydrated, weakly bonding sodium ion for the polyvalent metal. They pointed out that other anions, such as hexametaphosphate and oxalate also complexed polyvalent metals and had the same dispersing effect as the resin. It was this, they proposed, rather than any peptising effect due to sodium which was important. Unfortunately they did not produce any figures for the polyvalent cations taken up by the resin and these would have been of interest.

(ii) Ultrasonic dispersion.

Edwards and Bremner followed up the resin experiments by a new technique which dispensed with all chemical pretreatment and relied only on mechanical energy to disrupt the aggregates: sonic and ultrasonic vibration. Olmstead (1931) had been the first to try sonic treatment but there were difficulties, before the development and commercial availability of modern instruments, that made the method unattractive. Vasileva (1958) reported it as more efficient than conventional ones. Barkoff (1960) found that soils could be dispersed by calgon more effectively with 15-60 minutes sonic vibration than in five hours shaking. Edwards and Bremner (1967) made a detailed comparison of the new technique with other methods, using a range of soils and minerals, with a view to establishing the efficiency of sonic dispersion, alone or with chemical treatment.

They also compared the performance of a sonic (9 kc) instrument with an ultrasonic (18 -20 kc) instrument and found little difference in the results. In future the term 'ultrasonic' in this text will be contracted to 'sonic' for convenience.

A selection of the authors' results have been compiled from their two 1967 papers and are shown in Table 9 . They drew the following conclusions from the results.

(a) 'Mechanical energy only' was capable of giving the highest clay percentages. The longer the sonic treatment, the more clay was produced. For routine work, 30 - 60 minutes was thought sufficient to reach a clay percentage plateau without risking serious abrasion of particles.

(b) Prolonged shaking with water had a similar effect, and was enhanced by a high soil: water ratio, or if the soil was high in sand.

(c) Peroxide treatment much improved the efficiency of the calgon method, and indeed if calgon followed peroxidisation it had little further effect. Peroxide pre-treatment had only a small effect on the resin and sonic methods. Organic matter was more effectively removed by sonicing first and then peroxidising, than the other way round.

Table 9 % Clay values obtained using various dispersion methods on 10g. soil. (Edwards and Bremner 1967).

| SOIL | Organic carbon % | pH | CEC | Methods of Dispersion | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | CEC | water shake 180ml/ 10 hr. | water shake 25 ml/ 240 hr. | $H_2O_2$ 180ml/ 10 hr. | Calgon 180ml/ 10 hr. | $H_2O_2$/Calgon 180ml/ 10 hr. | Na OBr | Na-resin 60ml/ 10 hr. | $H_2O_2$/Na-resin 180ml/10 hr. | Sonic 30 mins. | Sonic 60 mins. | $H_2O_2$/Sonic 60 mins. |
| Sceptre (Chestnut Ap) | 1•90 | 7•1 | 50•3 | 53•3 | n.d. | n.d. | n.d. | 74•6 | 78•4 | 77•1 | n.d. | 75•8 | n.d. | n.d. |
| Meota (Chernozem Ap) | 3•10 | 6•8 | 22•3 | 8•4 | n.d. | n.d. | n.d. | 16•7 | 16•3 | 17•6 | n.d. | 15•2 | n.d. | n.d. |
| Waitville (Graywood B) | 1•13 | 5•9 | 19•1 | 22•6 | n.d. | n.d. | n.d. | 32•4 | 34•7 | 33•5 | n.d. | 32•6 | n.d. | n.d. |
| Glencoe (Humic gley Ap) | 9•60 | 6•7 | 58•5 | 15•5 | n.d. | n.d. | n.d. | 37•6 | n.d. | 36•1 | n.d. | 36•1 | n.d. | n.d. |
| Marshall (Brunizem Ap) | 2•11 | 5•3 | 22•9 | 14•5 | 34•0 | 35•7 | 35•3 | 38•8 | n.d. | 40•9 | 40•9 | 36•8 | 40•3 | 40•4 |
| Regina (Chestnut Ap) | 2•55 | 7•9 | 49•4 | 42•6 | 61•9 | n.d. | 58•4 | 66•7 | n.d. | 72•9 | 71•9 | 70•2 | 73•2 | n.d. |
| Webster (Brunizem Ap) | 3•19 | 6•8 | 33•8 | 10•2 | 30•7 | 23•4 | 23•1 | 29•8 | n.d. | 32•2 | 31•6 | 29•9 | 32 | n.d. |
| Oxbow (Type ? C) | 0•35 | 7•8 | 8•6 | 17•8 | n.d. | 23 | n.d. | 24•3 | 22•7 | 26•4 | n.d. | 25•0 | n.d. | n.d. |

(d) The pH of the soils varied between 5·3 and 7·3 so that the success of the dispersions in 'water only' disposed of the belief that it was necessary to disperse soils at high pH.

(e) Chemical disruption was best achieved by peroxidising the organic matter, or by supplying a strong complexing agent such as a resin to remove the polyvalent metals. Most of the soils were of high base status, but the success of the resin with the acidic Marshall brunizem suggested to them that aluminium and hydrogen bonding contributed to microaggregate stability in acid soils.

(f) They stated that: "The validity of the zeta-potential concept when used to explain dispersion and flocculation of soil colloids seems questionable, because soils saturated with polyvalent cations are easily dispersed by sonic or ultrasonic vibration without previous saturation with $Na^+$ or $Li^+$, and soil-water suspensions show no tendency to flocculate on standing after vibration even when concentrated suspensions (10 g in 25 ml. water) are not diluted before standing."

In the writer's view there were three discoveries in this work of great significance. The first was of the ability of sonic mechanical energy to disrupt the aggregates without chemical help. The second was that the same result could be achieved by merely shaking the soil in water, and that this need not be too prolonged provided the soil : water ratio was high. The third was the efficiency of the resin. Unfortunately they only assumed that iron and aluminium were taken up by the resin. They produced no experimental evidence for it. But if their surmise was correct, it would seem as if the resin had acted like a mild Tamm-oxalate reagent, or citrate at near neutral pH. On a pessimistic view, the resin might have attacked those amorphous materials which one wishes to preserve in the manner of acid oxalate. On the other hand, at neutral pH, the effect might have been mild enough to create dispersion but negligible dissolution.

Some of the interpretations that the authors put on their results are controversial. In their claim, for instance, that they had 'disposed of the belief that attainment of a high suspension pH is a prerequisite for complete dispersion', they seem to have missed the point. Alkali increases the rate of dispersion by bringing into solution a second peptising agent, the organic matter; and it also normally prevents flocculation if any such tendency exists. None of the soils used had this tendency and the possibility was not discussed, although they did mention that Olmstead (1931) had found it necessary to add ammonia to prevent his sonic dispersions from flocculating. It would seem essential in a discussion of this kind to separate the process of disruption from that of dispersion, and of coagulation from flocculation.

Edwards and Bremner's attack on 'the validity of the zeta potential concept' also seems misplaced. There is no contradiction between its use to explain soil flocculation and dispersion and their results. In most soil suspensions, the electrolyte concentration would be expected to be dilute enough to promote dispersion, in accordance with double layer theory, once disruption had been achieved. When chemical disrupting agents are used, such as hexametaphosphate or alkali, it is obviously necessary to choose the salt of a peptising cation such as sodium for the purpose.

It might however, be expected that calcareous or gypseous soils would dissolve sufficient $Ca^{2+}$ to exceed the threshold limit for divalent ions, and thus call into question the zeta potential concept. Two examples are available from their paper (a) the C horizon of the Oxbow chernozem (b) the Regina soil which was given sonic treatment in $CaSO_4.2H_2O$. Assuming the chernozem contained $CaCO_3$, whose solubility product is $4.7 \times 10^{-9}$, the calcium concentration would be $6.9 \times 10^{-5}$ M; or $5.6 \times 10^{-4}$ M when the partial pressure of atmospheric $CO_2$ is taken into account. Hence the dissolved $Ca^{2+}$ would be 0.56 mmole/l and on the very edge of the threshold limit 0.5 - 2.0 mmole/l for a divalent ion. This might not be inconsistent with the dispersion of the Oxbow soil. The only piece of evidence that questions the validity of the zeta potential concept in its application here (and the authors do not suggest it), is an experiment in which they soniced the Regina soil in saturated $CaSO_4.2H_2O$ solution and obtained a dispersion of 73.1% clay in 60 minutes (compare Table 9). Since gypsum dissolves 15.3 mmole $Ca^{2+}$/l (Seidell and Linke 1958) this is indeed incompatible with double layer theory prediction. There may be some explanation for it, perhaps in terms of depressed $Ca^{2+}$ activity or the influence of organic matter.

However, Emerson (1971) in a recent paper has provided a practical answer to these questions. He made a detailed comparison of the clay percentage yielded by the methods of sonic vibration in water, sonic vibration in the presence of a dispersant, and the conventional I.S.S.S. method (1927) of peroxidisation

Table 10 Description of soils used in dispersions of Table 11.

(compiled from Emerson 1971)

| Soil | Depth cm | Carbonate content % weight | Organic C content % weight | Soluble salts % |
|---|---|---|---|---|
| Krasnozem | 0 - 15 | - | 4.6 | 0.01 |
|  | 60 - 90 | - | 0.7 | 0.01 |
| Solonized brown soil | 48 - 54 | 18 | 0.6 | 0.05 |
| Chernozem | 60 - 75 | 21 | 1.4 | 0.05 |
| Red calcareous soil | 70 - 80 | 17 | 0.5 | 4.0 |
|  | 80 - 97 | 17 | 0.4 | gypsum |

Table 11 <u>% of $<2\mu$ particles released by sonic treatment for 20 minutes and by ISSS method for 4 Australian soils.</u>

| sample | % $<2\mu$ particles after sonic treatment | | | after ISSS method |
|---|---|---|---|---|
| | in water | in water<br>Calgon added later | in calgon | |
| Krasnozem<br>0 - 15 cm | 23 | 27 | 62 | 57 |
| Krasnozem<br>60 - 90 cm | 0 | 87 | 87 | 87 |
| Solonized<br>brown | 31 | 38 | 38 | 32 |
| Chernozem | 12 | 12 | 14 | 11 |
| Red calcareous<br>70 - 80 cm | | | | |
| Salts present | 1 | 48 | 48 | - |
| Salts removed | 34 | 47 | 47 | 38 |
| Red calcareous<br>80 - 97 cm | | | | |
| Salts present | 0 | 0 | 0 | - |
| Salts removed | 31 | 47 | 47 | 38 |

followed first by acid leaching and then by shaking in alkaline sodium hexametaphosphate. His purpose was to determine the range of soils over which satisfactory analysis could be made without the addition of dispersant and this range was carefully chosen to cover the spectrum of his own classification of soils based on the relative ease of dispersion of the soil aggregates in water (Emerson 1967). A number of them were high in calcium carbonate or gypsum. He was also concerned to ensure that soils which were efficiently disrupted remained stable to flocculation during mechanical analysis. Tables 10 and 11 are compiled from his results, and his findings are summarised as follows:-

(a) Of the four carbonate soils, only the chernozem, with 1•4% organic carbon, was dispersed in the absence of dispersant.

(b) In an experiment in which step-wise additions of divalent ion ($Ca^{2+} + Mg^{2+}$) solutions were made to the chernozem and the solonized brown soils which contained 1•4 and 0•6% organic carbon respectively, coagulation of the solonised brown increased steadily as the molarity increased from 0•16 to 0•3 mmole/l, while it did not begin with the chernozem until a concentration 0•38 mmole/l was reached. One notes that the threshold limit was lower than that quoted for divalent ions by van Olphen (1963). This is further discussed in Chapter V, 1, p.207.

(c) The gypseous soil coagulated completely with all three methods, until the soluble salts were removed.

(d) The subsoil of the krasnozem (a soil developed on basic rock) flocculated completely during sonic treatment in the absence of dispersant, but dispersed satisfactorily when this was added subsequently.

(e) The topsoil of the krasnozem was only about half dispersed by sonicing in water only, and subsequent addition of dispersant had little further effect. This showed that the dispersed clay was not subject to flocculation, for it was peptised by the organic matter, and that chemical treatment (ie. peroxidisation)was necessary to disrupt the organic bound aggregates and release the rest of the clay.

(f) Emerson also tested other soils, including brown clay, red brown earth, yellow podzolic and lateritic podzolic soils, and concluded that "Sonic vibration in 'water only' will be satisfactory for a wide range of soils. The exceptions will be acid soils which contain a suite of minerals which normally form flocculated suspensions in water (class 6 soils), gypseous soils and carbonate soils with a clay fraction of low organic matter content."

Emmerson had used Australian soils, in which gypsum and carbonate are widespread, and whose typical soils are very different to the leached soils of temperate climates. Edwards and Bremner (1967) stated that they had used the method since 1960 and had failed to find a soil which was not obviously dispersed by it, although they allowed such soils would almost certainly exist. It might be thought that after such extensive trials only rather rare soils, other than those from arid places would present difficulties, and hence it came somewhat as a surprise when the C horizon of the Dunlop soil flocculated on sonic vibration and when all the other soils tested produced a massive and irreversible flocculation after peroxide pretreatment. This was believed to follow from its allophane content.

## 3. Mechanical analysis of allophane soils.

Davies (1933) seems to have been the first to note the resistance of certain New Zealand soils to dispersion by conventional techniques, although at that time they were not identified as allophane soils. They were normally subsoils, occasionally the associated topsoils, developed on volcanic material and sometimes underlain by a waxy pan of hydrated aluminium silicate. They were both difficult to disperse and very susceptible to flocculation, as the following observations indicate:-

(a) Hydrogen peroxide or alternatively sodium hypobromite failed to disperse the soils effectively.

(b) Alkali reagents including ammonia, sodium hydroxide, sodium oxalate and sodium carbonate coagulated aqueous suspensions previously quite stable.

(c) Motor dispersion assisted flocculation.

(d) Filtering and sieving of dispersions made the soils sticky and impervious, but they could be deflocculated again by shaking in distilled water or N/500 HCl.

(e) Peroxidisation, and gentle boiling in N/2 HCl, followed by addition of ammonia gave complete dispersion. This method was unacceptable because 14·2% soil was dissolved and recovered from the washings mainly as alumina.

Davies recommended removal of the organic matter with alkaline peroxide and dispersion of the soils in N/500 HCl with a motor stirrer. He suggested that the disturbing factor was probably an aluminium compound and that field evidence pointed to its being leached from the topsoil and accumulated lower down.

The soils were later identified as allophane soils and Birrell and Fieldes (1952) continued the investigation. Table 12 sets out various procedures which were tried for a range of allophane soils and the comparative figures for clay percentage. The following is a summary of what they found:-

(a) The usual method for obtaining clay fractions of allophane soils was dispersion in alkali after a deferration treatment (Dion 1944 or Jeffreys 1946). It might be expected that this would also dissolve aluminium, and the water-sorted ash results illustrate the point. Sodium carbonate dispersion (pH 8·0) without deferration yielded 64% clay, one deferration 22·6% and three deferrations $< 5\%$. The Tirau sample dropped from 11·3% to 7·9% clay on deferration. This might appear

Table 12 **Soil pretreatments and dispersants for mechanical analysis of New Zealand allophane soils (peroxidation presumed)**

(Compiled from Birrell and Fieldes 1952)

| Soil | Pretreatment | Dispersant | clay % | $SiO_2 : Al_2O_3$ clay |
|---|---|---|---|---|
| Egmont | Dion deferration | $Na_2CO_3$ pH 8 | 13·8 | 1·85 |
| Egmont | Dion deferration | N/500 HCl | 14·0 | .. |
| Tirau | Dion deferration | $Na_2CO_3$ pH 8 | 7·9 | 2·17 |
| Tirau | --- | N/100 $NH_4OH$ | 11·3 | 1·78 |
| Mairoa | Dion deferration | $Na_2CO_3$ pH 8 | 27·0 | 1·61 |
| Mairoa | Dion deferration | N/500 HCl | 21·2 | 1·73 |
| Mairoa | --- | N/500 HCl | 30·0 | 1·01 |
| pre-Hamilton ash | N/5 HCl leaching, Jeffries deferr. | $Na_2CO_3$ pH 8 | ~0·5 | 0·55 |
| water-sorted ash | Jeffries deferr. | $Na_2CO_3$ | 22·6 | 1·64 |
| water-sorted ash | Jeffries deferr. thrice | $Na_2CO_3$ | < 5·0 | 30·6 |
| water-sorted ash | --- | N/100 $NH_4OH$ | 64·0 | 1·21 |

Table 13 Differential thermal analysis of mineralogy of clays in table 12.

(Compiled from Birrell and Fieldes 1952)

| Soil | DTA conclusions |
|---|---|
| Egmont | allophane with 3% kaolinite |
| Tirau | allophane with 3% kaolinite and 2 -5% quartz |
| Mairoa | allophane with 5% kaolinite and some limonite |
| pre-Hamilton | allophane with much gibbsite and 5% quartz |
| water-sorted ash | allophane with 3% kaolinite and 2 - 5% quartz |

to be less but it represents a similar reduction of about 30%.

(b) Of the seven soils, only the water-sorted ash was easily dispersible in alkali without pretreatment. Dispersion in N/500 HCl reduced the clay from 64 to 34·6%. It is not clear whether this was due to acid attack on the clay or to flocculation.

(c) The most difficult soil to disperse was the pre-Hamilton ash, which contained 10 - 20% gibbsite.

(d) When a 10g suspension of pre-Hamilton ash was shaken daily with the stable ammonia dispersion of the water-sorted ash, flocculation occurred after about a week. Only negligible alumina was dissolved in the solution (pH 10·4). The authors took this result as strong evidence for the theory that when gibbsite and allophane were present together, the soil flocculated. One notes however, that they did not add gibbsite on its own to the stable dispersion.

(e) The Mairoa ash soil contained no gibbsite but some limonite, and this was thought to have the same effect. A dispersion in N/200 HCl (pH 4·1) was strongly flocculated by the addition of N/10 $NH_4OH$ to pH 6·6.

Flocculation began at pH 5•9 and still persisted at 11•4. Redispersion was effected by boiling in N/10 NaOH, centrifuging off and shaking with water. Addition of N/5 HCl to this dispersion brought on flocculation at pH 9•6 and redispersion did not occur at any stage of the acid addition although this was taken down to pH 2•5. On centrifuging off and shaking with N/200 HCl a dispersion was again obtained.

Birrell and Fieldes concluded that they were probably dealing "with two colloidal systems of different iso-electric points capable of mutual coagulation under the appropriate pH conditions, these being allophane on the one hand and aluminium or ferric hydroxide on the other." The isoelectric point of an allophane floc with a composition $SiO_2:Al_2O_3$ of 1•09 had been found by Mattson (1930a)to be pH 6•6. The isoelectric points of $Al(OH)_3$ and $Fe(OH)_3$ were usually taken to be pH 7 - 8. "Consequently," they continued, "dispersion of a soil containing both allophane and free sesquioxides should be possible in a weakly acid medium (provided the anion concentration is sufficiently low) or in a strongly alkaline medium (provided the cation concentration is low enough). There seems to be also some critical concentration of iron or aluminium oxide in the soil above which neither acid nor alkaline dispersing media is effective. There is no practical method in sight for completely dispersing soils containing all but traces of iron and aluminium oxide as well as allophane."

The authors do not comment on whether dispersion in very low electrolyte concentration was a double layer or some other effect. They seem to have assumed however, that the centrifuging off of the Mairoa soil at high and low pH which then allowed redispersion, had removed electrolyte. Campbell et al. (1968) and Bracewell et al. (1970) in studies of allophane soils do not mention flocculation difficulties, but state that the 'soils were dispersed by end-over-end shaking until no further dispersion occurred, using distilled water alone'. However, they only separated very small amounts, such as 1.1% of Tirau soil, as this was sufficient for their requirements.

The Soils Bureau produced a three volume bulletin "Soils of New Zealand" (1968) in which the problem of the mechanical analysis of allophane soils is again discussed. Estimates of the clay content and allophane content were made by a variety of methods. Mechanical analysis for the soil physics data was done by dispersing 50 g soil in calgon (3.5 g/l), determining clay and silt + clay by the hydrometer method, and the sands by difference. The results for the allophane soils were low or very low (tables 14,15,16). The pedologists, when they came to use these results in assigning textural class, rejected them with the explanation that: "for some soils, mainly those derived from volcanic ash, basic rocks and peat, the mechanical analysis was unsatisfactory and textures as assessed in the field were recorded in the soil name."

In the mineralogical work, clay percentages of normal soils were determined after pretreatments in which the soil was adjusted to pH 4 with HCl to remove free lime, heated with $H_2O_2$ to destroy organic matter, treated with citrate-dithionite at pH 7 to remove free $Fe_2O_3$, and dispersed in 0•02% $Na_2CO_3$. If allophane was present this was removed prior to dispersal by boiling the soil for 2½ minutes in 0•5 N NaOH (Hashimoto and Jackson 1958). The allophane content was then calculated as equivalent to twice the sum of the $Al_2O_3 + SiO_2$ determined in the extract. The sum of the oxides was doubled on the assumption that allophane loses 50% water on ignition. Fieldes et al. stated that this method gave reasonably satisfactory results for soils whose principal clay was allophane, although it was not

Table 14 Egmont Black Loam, selected data
(from "Soils of New Zealand" 3, p.80).

| Depth ins | 0 | 3 | 8 | 18 | 29 |
|---|---|---|---|---|---|
| Clay % of soil ($<2\mu$) | | | | | |
| by calgon | 22 | 18 | 9 | 12 | |
| by dissolution | 50 | 48 | 42 | 41 | 49 |
| Free $Fe_2O_3$ % of soil | | | | | |
| Clay constituents as % $<2\mu$ | | | | | |
| allophane | 36 | $^{\phi}$46 | 66 | 75 | 70 |
| clay minerals | | | | | |
| gibbsite | | | | | |
| hydrous felspar | 64 | 54 | 34 | 25 | 30 |
| pH (moist soil) | 6·0 | 6·0 | 6·4 | 6·4 | 6·4 |
| CEC me% | 36·9 | 31·2 | 19·1 | 13·2 | 14·2 |
| Organic C % | 12·3 | 8·7 | 3·6 | 1·7 | 1·1 |
| Phosphate | | | | | |
| total P mg% | 256 | 238 | 248 | 167 | 127 |
| citric sol. P mg% | 12 | 10 | 8 | 4 | 2 |
| P - retention % | 89 | 92 | 96 | 98 | 97 |
| Tamm oxalate | | | | | |
| Al % | 3·74 | 3·34 | 4·06 | 4·51 | 4·72 |
| Fe % | 1·41 | 1·85 | 3·14 | 3·7 | 2·94 |
| $^{\phi}$ $SiO_2 : Al_2O_3 = 2·9$ | | | | | |

Table 15 Taupo Sandy Silt, selected data.
(from "Soils of New Zealand" 3, p.74).

| Depth ins. | 0 | 7½ | 14 | 17 | 20 |
|---|---|---|---|---|---|
| Clay % of soil ($<2\mu$) | | | | | |
| by calgon | 9 | | 3 | | 1 |
| by dissolution | 17 | | 11 | | 12 |
| Free $Fe_2O_3$ % of soil | | | | | |
| Clay constituents as % $<2\mu$ | | | | | |
| allophane | 100 | | $^{\phi}$100 | 100 | 100 |
| clay minerals | | | | | |
| gibbsite | | | | | |
| pH (moist soil) | 5·5 | 6·2 | 6·3 | 6·6 | 6·5 |
| CEC me% | 31·3 | 6·9 | 4·2 | 3·4 | 2·6 |
| Organic C % | 10·1 | 1·4 | 0·6 | 0·2 | 0·3 |
| Phosphate | | | | | |
| total P mg% | 92 | | 31 | | 32 |
| citric sol. P mg% | 15 | | 3 | | 5 |
| P - retention % | 63 | | 43 | | 7 |
| Tamm Oxalate | | | | | |
| Al % | 0·60 | | 0·78 | | 0·24 |
| Fe % | 0·30 | | 0·22 | | 0·36 |
| $^{\phi}$ $SiO_2 : Al_2O_3 = 2{\cdot}2$ | | | | | |

Table 16 Tirau Silt Loam, selected data.
(from "Soils of New Zealand"[3],p.80).

| Depth ins. | 0 | 3 | 8 | 13 | 24 |
|---|---|---|---|---|---|
| Clay % of soil (<2µ) | | | | | |
| by calgon | 17 | | 5 | 7 | |
| by dissolution | 20 | | 24 | 33 | 20 |
| Free $Fe_2O_3$ % of soil | | | | | |
| Clay constituents as % <2µ | | | | | |
| allophane | 100 | | φ100 | 100 | 100 |
| clay minerals | | | | | |
| gibbsite | | | | | |
| pH (moist soil) | 5·6 | 5·4 | 5·9 | 6·3 | 6·8 |
| CEC me% | 36·8 | 28·1 | 15·6 | 15·1 | 14·1 |
| Organic C % | 10·6 | 7·2 | 2·3 | 1·1 | 0·5 |
| Phosphate | | | | | |
| total P mg% | 143 | | 98 | 60 | 34 |
| citric sol. P mg% | 10 | | 3 | 1 | 0·5 |
| P - retention % | 95 | | 98 | 95 | 92 |
| Tamm oxalate | | | | | |
| Al % | 3·23 | | 4·26 | 4·24 | 2·75 |
| Fe % | 0·64 | | 0·85 | 1·10 | 1·08 |
| φ $SiO_2 : Al_2O_3 = 2·2$ | | | | | |

suitable where finely divided gibbsite was present. For soils high in clay minerals, slightly high results might be obtained due to dissolution of finely divided crystals, but not usually by more than 2%. The main effect of the hydroxide was to disperse the silt sized aggregates bound by allophane and yield more clay. The writer suggests however, that the effect is due to the removal of a flocculating mechanism, rather than to aggregate dispersion.

Other indirect methods used to measure clay % include:

(i) Ignition of the soil at 300°C and measurement of the water regained by it at 56.6% relative humidity. Under these conditions allophane regains 20% water. Hence, water-regain percentage x 5 is an estimate of allophane. In the presence of appreciable clay minerals or gibbsite the method is unreliable.

(ii) Clay percent can be calculated from surface area measurements given by the BET method. Thus:-

$$\text{clay \%} = \frac{\text{surface area of whole soil}}{\text{surface area of clay fraction}} \times 100 \, ;$$

for example Tirau ash, sampled at 50 inches depth, gave the results shown in Table 17.

Table 17 Surface areas (BET) and Clay contents of Volcanic Ash Soils.

(From "Soils of New Zealand", table 6 - 4 - 1).

| Soil and depth | Clay constituents | Fraction | Surface area $m^2/g$ | Dispersing agent | Clay % | |
|---|---|---|---|---|---|---|
| | | | | | fractionated | calculated |
| Taupo brown sand 8 - 11" | Allophane B | whole soil | 19 | | | |
| | | $<2\mu$ | 163 | $(NaPO_3)_6$ | 2 | 11 |
| Tirau ash 50" | Allophane A | whole material | 130 | | | |
| | | $<2\mu$ | 330 | NaOH, pH 12 | 13 | 39 |
| | | $<2\mu$ | 350 | HCl, pH 3·8 | 13 | 37 |
| Egmont Ash 23 ft. | Halloysite and Allophane | whole material | 111 | | | |
| | | $<2\mu$ | 133 | $(NaPO_3)_6$ | 40 | 83 |

(iii) A method due to Aomine and Jackson (1959) proposes that allophane be estimated by the difference in CEC values resulting from treatment with, on the one hand 2% $Na_2CO_3$ and on the other sodium acetate solution at pH 3·5.

Volume 3 of "Soils of New Zealand" is comprised of the complete analytical data for a wide range of the soils. A selection of this data is given in tables 14, 15 and 16 for three allophane soils. It will be seen that none of the clay percentages as determined by the calgon method correlated with those determined by the alkali dissolution method. Tirau silt loam usually has a kaolinite component (Fieldes 1957, Follett et al. 1965) and this was possibly missed in the routine analysis. Tamm acid oxalate extractions are included because these showed abnormally high amounts and also very high Al: Fe ratios. Gibbsite and $Fe_2O_3$ were absent from all three samples, and if the volume 3 profiles are representative, it would seem that the presence of allophane and sesquioxides together is a rarity, and that dispersion is usually inhibited by allophane alone.

Little more was added to the discussion than had already been said by Birrell and Fieldes in 1952. On p.34 2 Fieldes et al. commented "The size of particles of allophane in yellow brown loams is truly colloidal and as allophane comprises 25 - 50% of the total of some soils, active gel formation would be expected at pH values remote from its isoelectric point. However, as shown by Birrell and Fieldes (1952) allophane remains flocculated over a wide range of pH values. It remains flocculated in the pH range of soils. The reason for this is related to its structure. Hydrous silica (isoelectric pH value about 3) is weakly linked with hydrous alumina (isoelectric pH value about 7) so that at soil pH values between 5 and 7 each particle has both positive and negative sites and particles cohere together."

Birrell and Fieldes in another passage (p. 40) reiterated their conclusions of 1952 and added:- "Allophane will disperse partially in both weakly acid and fairly strong alkaline media provided the total electrolyte concentration is sufficiently low. By careful neutralisation of either acid or alkaline suspensions it is found that maximum flocculation occurs around pH 5•5 to 6•0. If electrolyte is then removed, redispersion is possible in the weakly acid or strongly alkaline range. The addition of gibbsite will also cause gradual flocculation of an apparently stable suspension. It is concluded therefore, that difficulties in dispersing allophane soils are due to two factors:

1. Isoelectric point higher than for the usual crystalline clay minerals.
2. Mutual co-precipitation in the presence of hydrous oxides."

## 4. Dispersion of allophane soils by charge reversal.

A comment on the failure of the sonic dispersion method appeared in a paper by Ahmad and Prashad (1970) who had found difficulty with some Caribbean soils. These soils, formed from volcanic materials, were described as having a stable granular structure and free drainage that together permitted agriculture on steep slopes. Their fertility was hard to assess because crops seemed able to obtain more nutrients than would be indicated by soil analysis, and their low base saturation was inconsistent with their pH values 5 - 5.6. But attempts to study the properties of the colloidal fraction were frustrated by the resistance of the soils to dispersion by conventional methods including sonic vibration. It was only achieved after pretreatment with dithionite to remove $Fe_2O_3$, but the abnormal amounts of Si and Al dissolved from the allophanoid minerals made the method unacceptable. In all these respects they resembled the New Zealand and Japanese allophane soils.

The authors compared the effectiveness of three methods (a) sodium hexametaphosphate (b) adjustment of pH (c) zirconium nitrate solution, on the dispersion of two loam soils.

(a) Sodium hexametaphosphate: there was no dispersion of either soil. This was thought to be due to isoelectric precipitation.

(b) Adjustment of pH: in the expectation that there might be some pH at which no isoelectric precipitation would take place, 0.2 g peroxidised silt + clay was shaken overnight in 50 ml solutions of graded pH. The turbidity was measured against a standard. Table 18 gives the results expressed as percent dispersion of total clay (found by the zirconium nitrate method). It is seen that dispersion was negligible for both soils except in the acid range when the Montreal loam yielded a maximum of 58% of its total clay at pH 2.5 and the

Table 18 The effect of pH on the percent dispersion of total clay of two Caribbean Andepts.

(Ahmad and Prashad 1970).

| Soil | pH values | | | | | | | | | Clay content % soil (Zr method) |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1·0 | 2·1 | 2.5 | 3.0 | 4·0 | 6·0 | 7·0 | 10·0 | 11·1 | |
| Montreal loam | 1·2 | 56·0 | 58·0 | 24.0 | 20.0 | 2·4 | 1·8 | 0·6 | 1·8 | 16.0 |
| Boetica loam | 1·1 | 7·2 | 9·5 | 10 | 8·8 | 0·8 | 0·8 | 0·8 | 1·1 | 36.0 |

Boetica loam 10% at pH 3.0. There was thus no pH between 1 and 11 at which the soils could be properly dispersed. Moreover, the acidity for partial dispersion was too great to be acceptable: 1800 and 5750 ppm $Al^{3+}$ was found in solution at pH 3 and 2.5 respectively.

(c) <u>Zirconium nitrate</u>: This method achieved dispersion. The authors took 10 g samples of aqueous suspensions of peroxidised silt + clay and shook them overnight in various volumes and concentrations of zirconium nitrate solution. Table 19 gives the results, together with the best percentage obtained with HCl. A suspension containing 0.2 mmole/l $Zr(NO_3)_4.5H_2O$yielded 12% clay at pH 3.4 and further additions increased the yield until a maximum of 36% was reached with 3 mmole/l Zr at pH 2.9. Since higher concentrations dispersed no more clay and decreased the pH too much, 3 mmole/l was selected for use, although no comment was made on the effect of the acidity. Five Caribbean Andepts were successfully analysed for their percent size fractions.

Ahmad and Prashad did not say how they came to use zirconium nitrate as a dispersing agent. They discussed the mechanism and assumed it was charge reversal, but did not know whether the reversal was positive or negative. They measured the ion exchange capacities of

Table 19 The effect of varying concentrations of zirconium nitrate on the dispersion and pH of soil suspensions of two Caribbean Andepts

(per cent clay, oven-dry soil)

(compiled from Ahmad and Prashad 1970)

| Conc. Zr mmole/l | Boetica loam |  | Montreal loam |  |
|---|---|---|---|---|
|  | % clay | pH suspension | % clay | pH suspension |
| 0•2 | 12 | 3•4 | 9 | 4•7 |
| 0•4 | 14 | 3•2 | nd | nd |
| 0•8 | 28 | 3•0 | nd | nd |
| 1•0 | 34 | 3•0 | nd | nd |
| 3•0 | 36 | 2•9 | 15 | 3•0 |
| maximum, pH adj. method | 3•6 | 2•5 | 8•7 | 3•0 |

the Boetica soil and analysed for extractable aluminium, before and after treatment and the increase in anion exchange capacity and in extractable aluminium suggested to them that $Zr^{4+}$ was replacing both exchangeable and structural $Al^{3+}$, and thus brought about positive charge reversal.

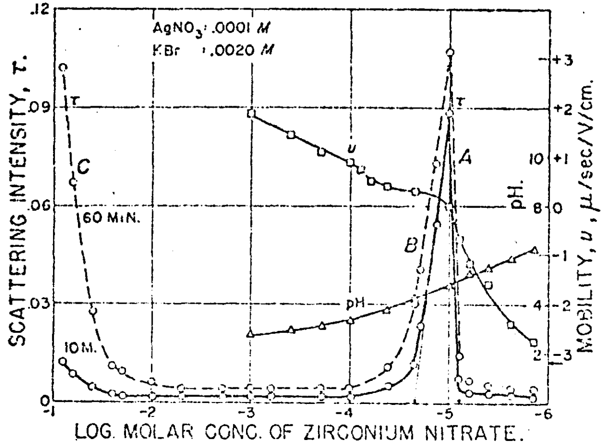
The discussions in Chapter III indicate that these conclusions are incorrect and that it was the hydrolysis products of the zirconium ion which had reversed the charge on electronegative clay. This is confirmed by numerous investigations on aqueous zirconium polymers. Matijević et al. (1962) investigated the composition of the species in zirconium nitrate-dispersed silver iodide sols. Their critical coagulation plot (fig. 20b) shows that $Zr^{4+}$ would only be expected to exist below pH 2.5 and solutions $< 8 \times 10^{-7}$M. Ahmad and Prashad used $3 \times 10^{-3}$M at pH 2.5 - 2.3. On the same plot, the gradual increase in coagulation concentration between pH 2.5 and 5.5 indicates the presence of two polymers in the equilibrium solution of lower charge than 4 , and the plateau from pH 5.5 to 7.0 suggests one predominant species triply charged. Other workers, investigating the hydrolysis of zirconyl chloride at stronger acidities and high concentrations have detected more extensive polymerisation. For example, Hutcheson (1970) found evidence for the cyclic tetramer $\left[Zr\ (OH)_2.4H_2O\right]_4^{8+}$, using electronoptical techniques. Unaccountably, Ahmad and Prashad found zirconyl chloride relatively ineffective.

In fig.20a Matijević's coagulation curve for zirconium nitrate with a silver bromide sol is shown, together with the pH and electrophoretic data. The information in the diagram can be summarised as follows:-

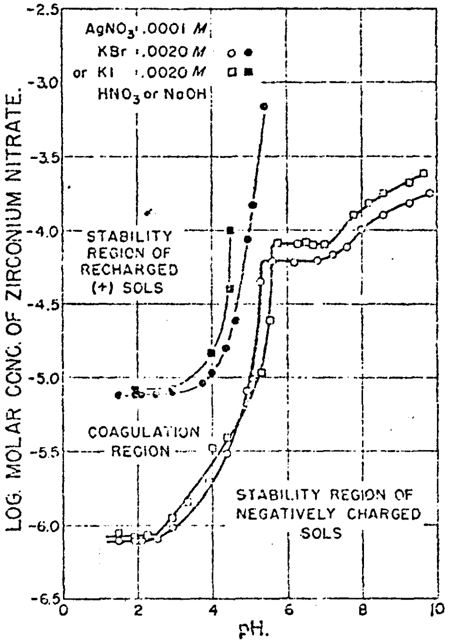
At very low concentrations of added Zr salt there is too little electrolyte to coagulate the sol, which is stabilised by halide ions. At limit A the sol is coagulated in the region of the isoelectric point. Extrapolation of A to zero scattering intensity gives the critical coagulation concentration for the given pH. Reversal of charge takes place as the concentration is increased to limit B. Extrapolation of B gives the critical stability concentration. At limit C the positive sol is coagulated by $NO_3^-$ ions. Limits A and B are sensitive to shifts in the concentration of the hydrolysed species. The curve shows the case when pH is determined primarily by the zirconium concentration, but if the pH is adjusted with $HNO_3$ or NaOH, the limits A and B are shifted to lower and higher Zr concentrations

Fig. 20 <u>Charge reversal of silver bromide sols by zirconium ion species (a) coagulation curve (b) critical coagulation and stability limit curves.</u>

(Matijević et al. 1962b)



(a)—Coagulation (τ, ○; full line, 10 min., dashed line, 60 min.), mobility (u, □), and pH (△) curves of a negative silver bromide sol *in statu nascendi* in the presence of various concentrations of zirconium nitrate. Concentrations: AgNO$_3$, 1 × 10$^{-4}$ *M*; KBr, 2 × 10$^{-3}$ *M*. *A*, the coagulation limit of zirconium species for negative AgBr sol; *B*, stability limit due to the reversal of charge effect; *C*, coagulation limit of nitrate ion for the AgBr sol of reversed (positive) charge.



(b)—Plot of the critical coagulation concentration (lower curves, open signs) and stability limit due to the reversal of charge (upper curve, blackened signs) against pH for zirconium nitrate for a silver bromide sol (○, ●) and a silver iodide sol (□, ■) *in statu nascendi*. Concentrations: AgNO$_3$, 1 × 10$^{-4}$ *M*; KBr or KI, 2 × 10$^{-3}$ *M*; HNO$_3$ or NaOH, varied.

respectively. In other words at lowered pH, less Zr is required to stabilise the sol, and at raised pH, more Zr is required to stabilise it. The arrows indicate the extrapolated stabilisation limits when the suspensions were made $2 \times 10^{-3}$M in $HNO_3$ and $1.5 \times 10^{-4}$M in NaOH.

NOTE: Similar curves were given for thorium (Matijević et al. 1960) and aluminium (1961). These would appear to contradict the finding (1964) that higher concentrations of the hydrolysed species existed per mole of dissolved salt as the pH was raised, which was illustrated in fig. 17 (Matijević 1967). The writer has not been able to solve this anomaly.

The use of positive charge reversal as a method for dispersing a hitherto intractable colloid system represents a major breakthrough for the mechanical analysis of allophane soils. The fact that this technique had been known to water purification chemists for some time and seems to have been stumbled upon by soil scientists unaware of its chemistry, illustrates the slowness of the transfer of basic knowledge.

## CHAPTER IV B: THE FLOCCULATION OF SOIL DISPERSIONS.

### 1. Flocculation by hydroxyl ions (Mattson 1922).

Towards the end of the experimental work described in Part 2, the writer became convinced that a clue to the mechanism of the flocculation of allophane might be contained in an early paper by Mattson (1922) "The relationship between flocculation, adsorption and particle charge with special reference to hydroxyl ions." This was a long paper in German, and having acquired a translation the writer found both there and in "The laws of colloidal behaviour" (1929 a,b,) observations on flocculation and a developed theory which were at variance with those presented in the commonly accepted texts on colloid chemistry. To the writer they appeared of great importance and thus have been interpolated here.

When in 1922 Mattson undertook a study of the flocculation of soil colloids, there was a generally accepted view that (a) alkali hydroxides were dispersing agents (b) flocculation occurred at or near the isoelectric point, (c) dispersions owed their stability to an excess elect~~o~~ric charge on the particles, flocculation being brought about by neutralisation of the charge through adsorption of oppositely charged ions. This is the view still most widely accepted although the theory has become considerably more sophisticated. At that time however, there was much conflicting evidence and disagreement.

Mattson's concern was to resolve the anomalies and bring forward new facts by studying the flocculation of soil colloids accurately. He was also interested in assessing the strength of the aggregates so formed and in applying his findings to agriculture. His materials were finely ground quartz, a clay (Great-Hessian) and humified sphagnum. The quartz and clay were of known esd values. The clay and humus were cleaned with HCl and washed, distilled water being used at all times. The suspensions containing 10 mg quartz or clay or 1 mg humus were shaken in 5 ml electrolyte solution, the electrolyte being comprised of salts or alkalis, alone or in combination. Observations were made on the time taken to flocculate. The degree of adsorption of ions was determined by analysis of the supernatant liquid. pH values were assessed with litmus or phenolphthalein. The electrophoretic mobility of the flocs was measured in a microcataphoretic cell specially designed for the purpose.

Preliminary experiments with quartz suspensions gave results which did not fit the theory that hydroxyl ions disperse negatively charged colloids. The quartz flocculated in 1.8 me $Ca(OH)_2$ but remained dispersed in the same concentration of calcium salts. Addition of 0.02 me NaOH to these salt solutions brought on immediate flocculation. Addition of HCl or $H_2SO_4$ redispersed the suspension. The questions were: whether the $OH^-$ ions favoured flocculation or the salt anions prevented it, and whether acids were themselves dispersing agents or destroyed the flocculating agent. It was argued that if hydroxyl ion was the flocculating agent and destroyed hydrogen ions, then a similar effect might be observed with $NH_4Cl$ which reduces $OH^-$ concentration by the reaction:

$$OH^- + NH_4^+ \rightleftharpoons H_2O + NH_3.$$

A quartz suspension containing $Ca(OH)_2$ was shaken with $NH_4Cl$ and its flocs dispersed. NaCl had no effect. Addition of $NH_3$ solution to a $CaCl_2$ suspension whose salt concentration was below the threshold limit flocculated it. The results, maintaining the $Ca^{2+}$ concentration constant, are summarised as follows:

$Ca(OH)_2 \longrightarrow$ flocculation
$Ca(OH)_2 + H^+ \longrightarrow$ dispersion
$Ca(OH)_2 + NH_4Cl \longrightarrow$ dispersion
$Ca(OH)_2 + NaCl \longrightarrow$ flocculation
$CaCl_2 \longrightarrow$ dispersion
$CaCl_2 + NaOH \longrightarrow$ flocculation
$CaCl_2 + NH_3 \longrightarrow$ flocculation

From these experiments it was concluded that the $H^+$ and $NH_4^+$ ions peptised the quartz by displacing the $OH^-$ ions. This did not imply that the hydroxyl ions themselves initiated flocculation, for neither NaOH nor $NH_3$ could alone flocculate quartz except when in very high concentrations. It was the combined effect of calcium and hydroxyl which flocculated the suspension. The behaviour is illustrated in Tables 20 and 21 . Table 20 shows that 100 me $CaCl_2$ was required to flocculate the quartz in 17 minutes, while in the presence of 2 me NaOH as little as 0.9 me $CaCl_2$ flocculated it in 7 minutes, or 90 times less $Ca^{2+}$ concentration. Table 21 shows how the calcium and hydroxide reacted upon each other: $Ca(OH)_2$ flocculated slightly faster in the presence of NaOH; more impressive was the finding that 2 me $CaCl_2$ reduced the threshold value of $Ca(OH)_2$ by about 5 times. The inhibiting

Table 20 Flocculation of a quartz suspension by $CaCl_2$ and $CaCl_2$ + NaOH.

(Compiled from Mattson 1922).

| $CaCl_2$ me/l | time taken | degree of flocc. 24 hrs. | 2 me NaOH $CaCl_2$ me/l | time taken | degree of flocc. 24 hrs. |
|---|---|---|---|---|---|
| 20 | - | 0 | 0.5 | - | 0 |
| 40 | - | + | 0.6 | - | + |
| 60 | - | +++ | 0.8 | - | +++ |
| 80 | - | ++++ | 0.9 | 7' | ++++ |
| 100 | 17' | ++++ | 1.2 | 2' | ++++ |
| 200 | 3' | ++++ | 1.4 | 45" | ++++ |
| 300 | 25" | ++++ | 1.6 | 20" | ++++ |

crosses + = degree of flocculation after 24 hours.

Table 21 <u>Flocculation of a quartz suspension by $Ca(OH)_2$ alone and in the presence of other electrolytes</u>.

(Compiled from Mattson 1922).

| $Ca(OH)_2$ me/1 | time taken | 2 me/1 $CaCl_2$ $Ca(OH)_2$ me/1 | time taken | 2 me/1 NaOH $Ca(OH)_2$ me/1 | time taken | 20 me/1 $NH_4Cl$ $Ca(OH)_2$ me/1 | time taken |
|---|---|---|---|---|---|---|---|
| 0.9 | - | 0.09 | - | 0.4 | - | 8.0 | 6' |
| 1.0 | 6' | 0.18 | 21' | 0.6 | 1' 30" | 9.9 | 1' |
| 1.8 | 2" | 0.36 | 2" | 1.0 | 10" | 11.2 | 10" |

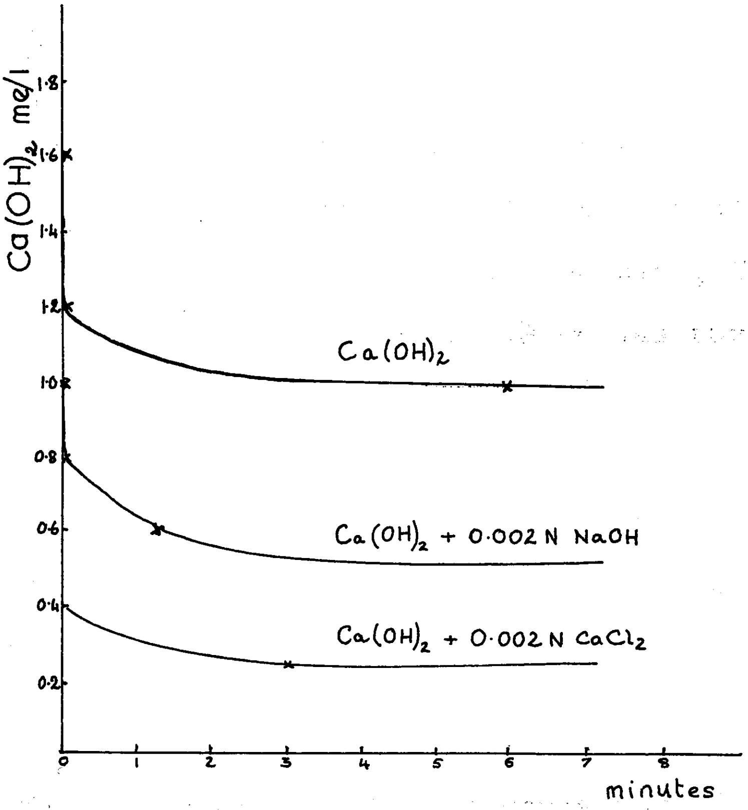
effect of $NH_4^+$ is also demonstrated: 20 me $NH_4Cl$ made it necessary to add 20 me $Ca(OH)_2$ before the quartz flocculated. Fig. 21 summarises the results.

The next step was to see whether this behaviour occurred with other suspensions of negative colloids. When humus was tried it was found that 8 me $CaCl_2$ flocculated it in 40 minutes, but in the presence of 2 me NaOH, 6 me $CaCl_2$ flocculated it in 20 seconds. Humus differed from quartz however, in its greater sensitivity to neutral salts: the threshold values of $Ca(OH)_2$ and $CaCl_2$ were both of the order 7 me/l.

The clay, which was unsaturated, appeared at first to show the dispersive effect of hydroxide. It was very sensitive to salt addition, flocculating with only 0.225 me/l $CaCl_2$ or $CaSO_4$ while requiring 0.9 me/l $Ca(OH)_2$ to flocculate it. 0.3 me NaOH was able to disperse clay saturated with up to 0.675 me $CaSO_4$. A paradox was seen however in that if the NaOH concentration was raised to 1.0 me, the 0.675 me suspension flocculated, and at higher NaOH concentrations the clay flocculated when even smaller amounts of $CaSO_4$ were present. Table 22 shows the hydroxyl behaviour in the $CaSO_4$ and $Ca(OH)_2$ systems. Later it became clear that the condition of the clay itself partly controlled the

Fig.21 The speed of flocculation of a quartz suspension in the presence of various concentrations of $Ca(OH)_2$ alone, and with NaOH or $CaCl_2$.

(Mattson 1922)



flocculation, for when it was prepared as a Ca - clay, the order of sensitivity was reversed and the clay behaved like quartz. Some years later Mattson (1929b) resolved the anomaly showing that 'cleaned' or dialysed clays were extremely sensitive to salt additions. He interpreted this as due to the 'exchange acidity' produced by dissociation of $Al^{3+}$ and $Fe^{3+}$ from the colloid surface.

One other interesting discovery was that although larger amounts of hydroxide than salt were required to initiate flocculation in the unsaturated clay, flocculation at an equivalent concentration of 1.8 me was three times faster for the hydroxide than for the salt. This could have practical significance in that $Ca(OH)_2$ formed the largest and strongest flocs; and theoretical significance in that the breakdown in stability appeared more suddenly than with the salts.

The observations described above seemed to have been the first to show that the flocculating effect of divalent ions could be raised significantly in the presence of hydroxyl. Owing to their dispersive properties the hydroxyl ions were then widely believed damaging to soil structure, despite the fact lime was known to have a more favourable effect on soils than

Table 22 <u>Flocculation of a clay suspension in the presence of various electrolytes.</u>

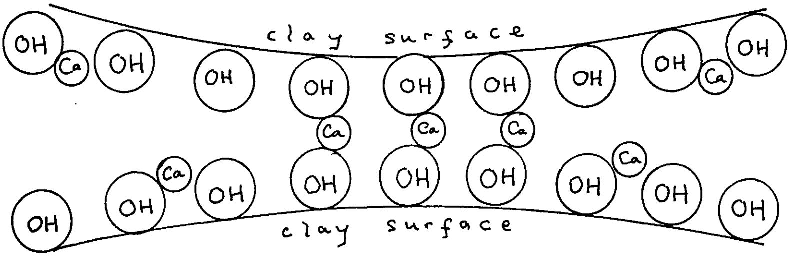
(Compiled from Mattson 1922).

| $CaSO_4$ | NaOH | | | | | $Ca(OH)_2$ | | | $Ca(OH)_2$ | NaOH | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| me/l | 0.00 | 0.20 | 0.30 | 1.0 | 2.0 | 0.00 | 0.225 | 0.450 | | 0.00 | 0.30 | 1.00 |
| 0.225 | 1' | 0 | 0 | 0 | 0 | 1' | 0 | + | 0.45 | 0 | 0 | + |
| 0.450 | 50" | + + | 0 | 0 | ++ | 45" | 0 | 19' | 0.675 | + | 11' | 1' |
| 0.675 | 45" | ++++ | + | ++++ | 50" | 45" | ++++ | 9' | 0.90 | 2' | 50" | 20" |
| 0.900 | 40" | ++++ | ++++ | 5' | 50" | 40" | ++++ | 4'20" | | | | |

cresses + = degree of flocculation after 24 hours.

gypsum. None of the theories then in circulation could be used to explain the observations and as a working hypothesis Mattson adopted the following argument.

If it were only necessary to bring about a partial neutralisation of the negative charge on the particles, why then was it necessary to add 90 times as many $Ca^{2+}$ ions in the form of chloride alone as in the presence of hydroxide to flocculate a quartz suspension? Since chloride ions were known not to be adsorbed, it must be that the hydroxyl ions were strongly adsorbed and the calcium ions were adsorbed in consequence. It was not possible to say why the $OH^-$ ions were adsorbed so strongly. The cause might lie in the constitution of water, for it was a fact that nearly all colloids charged themselves negatively in water. The mechanism of the flocculation however could be imagined analagous to the mutual flocculation of positive and negative sols in the same suspension. The calcium ions were to be considered positive particles. Although too small themselves to cause flocculation, when adsorbed in sufficient numbers, they could link the hydroxylated surfaces of the colloids together into chains. When the number of connecting links or $Ca^{2+}$ ions was small, the chains were immediately torn again by the repulsion between the colloids and by the Brownian movement; but as the Ca$^{2+}$ concentration increased and the negative charge decreased, so the chains persisted and the particles were held together as flocs. This could be shown very primitively in a picture:



Flocculation by electrostatic attraction was to be distinguished from the coagulation of particles in a sediment. There the particles were packed spherically or touched at the maximum number of points, and were bonded together by the postulated 'adhesion forces'. Flocs were only bonded at their points of attachment and thus were loosely packed and voluminous.

The adsorption of the hydroxyl ions and the accompanying uptake of calcium ions was confirmed for both quartz and clay by analysis of the supernatants. This is shown in Tables 23 and 24 . In the absence of hydroxyl, uptake of calcium by quartz from a 0.808 me Ca$^{+}$/1 solution was negligible, but hydroxyl ions were

Table 23 Analysis of the uptake of calcium and hydroxyl ions by a 100 mg quartz suspension.

(Mattson 1922).

| me/l added | | me/l in supernatant | | me/l adsorbed | |
|---|---|---|---|---|---|
| $CaCl_2$ | NaOH | $Ca^{2+}$ | $OH^-$ | $Ca^{2+}$ | $OH^-$ |
| 0.808 | - | 0.804 | - | 0.004 | - |
| 0.808 | 0.090 | 0.737 | - | 0.071 | 0.090 |
| 0.808 | 0.300 | 0.597 | - | 0.211 | 0.300 |
| 0.808 | 0.600 | 0.459 | 0.108 | 0.349 | 0.492 |
| 0.808 | 1.200 | 0.293 | 0.464 | 0.515 | 0.736 |
| 0.808 | 1.800 | 0.146 | 0.852 | 0.662 | 0.948 |
| 0.0 | 1.0 | - | 0.646 | - | 0.354 |
| 1.0 | 1.0 | n.d. | 0.353 | n.d. | 0.647 |
| 6.0 | 1.0 | n.d. | 0.320 | n.d. | 0.680 |

Table 24 Analysis of the uptake of calcium by an unsaturated clay in the presence of increasing hydroxyl concentration.

(Mattson 1922)

| me/1 added | | me/1 in supernatant | me/1 adsorbed |
|---|---|---|---|
| $Ca(OH)_2$ | NaOH | $Ca^{2+}$ | $Ca^{2+}$ |
| 2.26 | 0.0 | 1.127 | 1.133 |
| | | 1.148 | 1.112 |
| 2.26 | 0.5 | 1.106 | 1.154 |
| | | 1.074 | 1.186 |
| 2.26 | 2.5 | 1.008 | 1.252 |
| | | 1.015 | 1.245 |

taken up avidly even in absence of calcium. There was no question in the quartz case of hydroxyl neutralising 'exchange acidity.' Calcium uptake followed hydroxyl adsorption. In the presence of 1.8 me NaOH, 83% of the 0.808 me $Ca^{2+}$ were adsorbed.

The adsorption experiments were followed by measurements of the electrophoretic mobility of the suspensions. These dispelled the belief that dispersions lost stability as a result of acquiring some low critical charge. Table 25 shows that in the quartz system, although all electrolytes except NaOH lowered the charge on the particles, flocculation occurred when the quartz was still strongly negative. For $Ca(OH)_2$ the threshold velocity was $-4.8\ \mu$/sec, for $CaCl_2$ $-3.6\ \mu$/sec. In d the $Ca(OH)_2 | NaOH$ system, flocs precipitated when the mobility was as high as $6.8\ \mu$/sec. One also notes that in a, no matter how high the $Ca(OH)_2$ concentration, the flocs acquired a limiting value of $-2.6\ \mu$/sec and could not be made isoelectric in the presence of the hydroxyl.

It was concluded from these and further experiments that the adsorption of $Ca(OH)_2$ in a quartz system could be increased either by an increase in the osmotic pressure of the $Ca^{2+}$ ions on addition of a calcium salt

Table 25 Migration velocities (μ/sec/volt/cm) of quartz suspensions in various electrolyte solutions.

(Compiled from Mattson 1922).

| ⓐ Ca(OH)$_2$ me/l | μ/sec | ⓑ 2me CaCl$_2$ Ca(OH)$_2$ me/l | μ/sec | ⓒ 1.35me Ca(OH)$_2$ NH$_4$Cl me/l | μ/sec | ⓓ 1.35me Ca(OH)$_2$ NaOH me/l | μ/sec | ⓔ NaOH me/l | μ/sec |
|---|---|---|---|---|---|---|---|---|---|
| 0.00 | -11.2 | 0.00 | -6.8 | 0.00 * | -4.7 | 0.00 * | -4.8 | 0.00 | -11.2 |
| 0.18 | -10.5 | | | 2.00 | -5.4 | 0.20 * | -6.0 | 0.2 | -19.0 |
| 0.45 | -8.6 | 0.45 * | -4.8 | 10.0 | -8.6 | 0.50 * | -6.3 | 0.3 | -20.0 |
| o.90 | -6.1 | 0.90 * | -3.4 | | | 1.00 * | -6.8 | 1.0 | -19.0 |
| 1.35 * | -4.8 | | | | | 2.00 * | -6.3 | 2.0 | -19.0 |
| 1.80 * | -4.0 | | | | | | | | |
| 3.60 * | -2.9 | | | | | | | | |
| 7.20 * | -2.6 | | | | | | | | |
| 14.40 * | -2.6 | | | | | | | | |

| ⓕ CaCl$_2$ me/l | μ/sec | ⓖ 0.9me Ca(OH)$_2$ CaCl$_2$ me/l | μ/sec | ⓗ 2 me CaCl$_2$ NaOH me/l | μ/sec |
|---|---|---|---|---|---|
| 0.00 | -11.2 | 0.0 | -6.3 | 0.00 | -6.8 |
| 0.45 | -9.5 | 0.5 * | -4.6 | 0.20 | -6.0 |
| 2.00 | -6.8 | 2.0 * | -3.5 | 0.50 | -4.8 |
| 5.00 | -5.6 | | | 1.00 * | -3.8 |
| 10.00 | -4.3 | | | 2.00 * | -3.6 |
| 22.50 * | -3.6 | | | | |

* = flocculation

(compare b and g with a), or by an increase in the $OH^-$ concentration whereby the negative charge was raised and further $Ca^{2+}$ ions were adsorbed from solution. Thus in d the presence of NaOH allowed the number of linking $Ca^{2+}$ ions to increase so that flocculation was possible despite the increased charge. The reaction could proceed further, for as the $Ca^{2+}$ ions were adsorbed, the solution pressure of the $OH^-$ ions was lowered and more hydroxyl was taken up. This was made visual in an experiment with phenolphthalein: $Ca(OH)_2$ was added until the liquid turned pink. Addition of $CaCl_2$ then destroyed the colour. If, on the other hand one or other of the ions were removed from solution, desorption followed. c shows the result when ammonium ions were added to a quartz/$Ca(OH)_2$ system. The $OH^-$ concentration was reduced by elimination as water. The $Ca^{2+}$ ions were desorbed and replaced by $NH_4^+$. The charge on the particle increased and the flocs dispersed. All these reactions suggested that in the quartz system, where hydroxyl was strongly adsorbed, $Ca(OH)_2$ played the part of a weak base.

The migration velocities for the unsaturated clay suspension are shown in Table 26 . Once again it is seen that addition of $OH^-$ ion, except in low concentrations,

Table 26 Migration velocities (μ/sec/volt/cm) of a clay suspension in various electrolyte solutions.

(Compiled from Mattson 1922).

| $Ca(OH)_2$ | | 0.672 me $Ca(OH)_2$ NaOH | | $CaSO_4$ | NaOH | | | NaOH | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | 0.0 | 0.2 | 5.0 | | |
| me/1 | μ/sec | me/1 | μ/sec | me/1 | μ/sec | μ/sec | μ/sec | me/ml | μ/sec |
| 0.00 | -7.9 | 0.00 | -4.3 | 0.00 | -7.9 | -15.8 | n.d. | 0.00 | -7.9 |
| 0.09 | -7.2 | 0.5 * | -5.0 | 0.09 | -6.0 | n.d. | n.d. | 0.20 | -15.8 |
| 0.18 | -6.3 | 2.0 * | -6.1 | 0.13 | -5.6 | n.d. | n.d. | 1.00 | -13.6 |
| 0.45 | -5.3 | | | 0.225 * | -5.3 | -6.8 | -8.6 | 5.00 | -11.2 |
| 0.90 * | -4.1 | | | 0.45 * | -5.0 | -6.0 | *-7.9 | 10.00 | -10.5 |
| 1.80 * | -3.4 | | | 0.90 * | -4.8 | *-5.3 | *-6.3 | 20.00 * | -10.5 |
| 9.00 * | -2.0 | | | 4.50 * | -4.8 | -4.0 | n.d. | | |
| 18.00 * | -1.9 | | | | | | | | |

* = flocculation

promoted flocculation while at the same time it raised the charge on the particle. NaOH eventually flocculated the clay at 15 me/l when the mobility was -10.5 μ/sec. The dispersing effect of $NH_4Cl$ was not seen in the clay system because of its sensitivity to flocculation by the salt (2.3 me $NH_4Cl$ was the reported threshold value for a kaolin suspension). However a delay in flocculation by $Ca(OH)_2$ was noted, and the destruction of $OH^-$ ions and desorption of $Ca^{2+}$ is illustrated in Table 27 p. 183

In conclusion, the onset of flocculation for the quartz, humus and clay systems was interpreted as determined by the balance between the adsorption of hydroxyl ions which increased the charge and repulsion, and the adsorbtion of calcium ions which increased the number of connecting links.

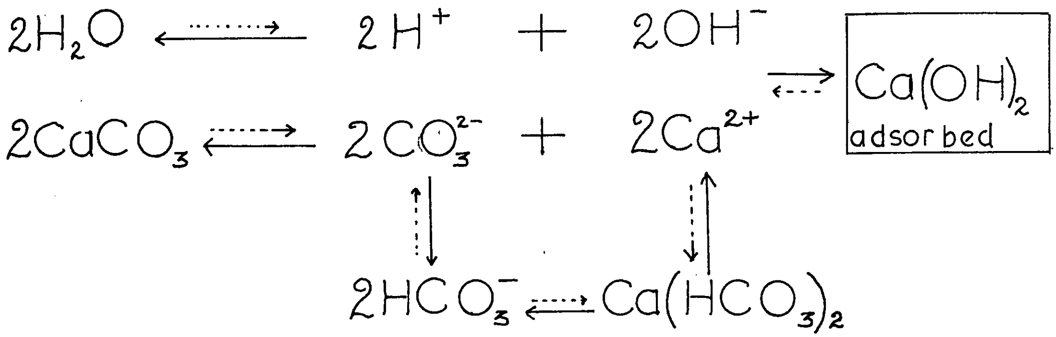
Many practical applications are foreshadowed by the observations made in this great paper. The charge reversal of colloids brought about by adsorption of the hydrolysis products of iron and aluminium was described, to be developed later into a theory for water treatment (1928 a). It was shown that the capacity of the soil to adsorb hydroxyl ions had far reaching consequences in creating soil structure, in regulating and buffering the soil reaction and in the dissolution

Table 27 The removal of hydroxyl and desorption of calcium ions from a clay suspension on addition of $NH_4Cl$.

(Mattson 1922).

| me/l added | | me/l in supernatant | me/l adsorbed | alkalinity or phenolphthalein colour |
|---|---|---|---|---|
| $Ca(OH)_2$ | $NH_4Cl$ | $Ca^{2+}$ | $Ca^{2+}$ | |
| 1.130 | 0.0 | 0.160 | 0.970 | strongly alkaline |
| 1.130 | 5.0 | 0.626 | 0.504 | pink |
| 1.130 | 25.0 | 1.143 | -0.013 | colourless |
| 0.0 | 25.0 | 0.058 | -0.058 | colourless |

of soil minerals. Of the many examples given, one will suffice, in which the powerful effect of soil colloids, particularly organic matter, in making nutrients available by dissolution of 'insoluble' minerals was demonstrated. This is shown in Table 28 where for example, a suspension of sphagnum humus was found to dissolve 1.86 g CaO and 3.13 g $P_2O_5$ from 100 g $CaCO_3$ and $Ca_3(PO_4)_2$ respectively. The very simple mechanism suggested was as follows:



Thus Mattson's recognition of the importance of the hydroxyl ion allows one to understand how even a most inert form of organic matter is able by simple adsorption and displacement of equilibria, to dissolve soil nutrients quantitatively. This is relevant to the discussion on the role of organic matter in soil fertility. Other phenomena not explained by the conventional theory, such as the poor structure of hydrogen soils, the rise in pH when saline soils are irrigated,

Table 28 The dissolution of $CaCO_3$ and $Ca_3(P_2O_5)_2$ in the presence of humus, clay and quartz suspensions (as CaO and $P_2O_5$ per 100 g solid, water soluble material subtracted).

(Mattson 1922).

| Suspension | CaO g | $P_2O_5$ g |
|---|---|---|
| sphagnum-humus | 1.8601 | 3.1270 |
| clay (unsaturated) | 0.3834 | 0.1136 |
| quartz | 0.0138 | 0.0019 |

polyelectrolyte flocculation and the behaviour of allophane, may all perhaps be interpreted in terms of the adsorption properties of the hydroxyl ion.

## 2. Interpretation of clay colloid stability (Mattson 1929).

### (i) Suppositions questioned.

In 1929, Mattson's first two papers in the series The Laws of Colloidal Behaviour were published. Their study was the origin of stability and instability in clay suspensions. Since his conclusions were the very opposite of those put forward in the accepted version of double layer theory, and based on evidence which, to the writer's knowledge has never been considered, a brief summary is given here with the object of drawing attention to Mattson's work.

It was generally assumed that the stability of a clay suspension was directly connected with the potential difference within the double layer. The suppression of this potential was due to the adsorption of cations, and in the presence of threshold concentrations of these, specific for each ion, the attractive forces were able to dominate the repulsive forces and flocculation or coagulation ensued. The terms flocculation and coagulation were interchangeable. The potential was identified as the zeta potential and could be calculated from electrophoretic measurements by means of the Helmholtz - Smoluchowski formula (p. 61). The potential was a work unit but could be taken as a measure of the repulsive charge which prevented effective collisions between the particles until lowered to a critical value.

These suppositions were questioned by Mattson (1929 a,b) who posed the following points:

(a) Was the suppression of the stability caused by an adsorption of ions of opposite charge, or was it caused by the effect of the free uncombined ions in the solution?

(b) Was flocculation the result of a collision between particles or of linkage between micelles?

(c) Was the stability of a clay suspension maintained by the repulsion of negatively charged particles and did such repulsion exist?

Experiments were devised to determine the concentrations of adsorbed and free ions under conditions of varying electrolyte concentration and composition and varying water : colloid ratio. Calculations on the Donnan distribution were made to find the concentration of dissociated ions and the value of the Donnan potential (1929 a). Flocculation studies similar to those of 1922 were undertaken using combinations of calcium salts and calcium and sodium hydroxide, but this time the clays were prepared saturated with a specific cation or dialysed (1929 b).

## (ii) Dissociated ions and free electrolyte.

Two properties of a suspension were distinguished which together determined its stability. One was the degree of dissociation of the exchangeable cations, the other the nature of the free electrolyte. In the absence of a free electrolyte the potential difference and swelling of the hydrated particle was solely governed by the degree of dissociation of the exchangeable cations expressed in molar concentration as z. One notes that in conventional double layer theory it is the cations adsorbed rather than the cations dissociated which are considered, Mattson calculated (1926 a,b) that only a fraction of the exchangeable bases of the colloid could exist in dissociated condition and his experiments (1929 a) confirmed this prediction as shown in Table 29 and fig. 22 and discussed below. The role of z was crucial to an understanding of sol stability. Its value was controlled by (a) the CEC of the particle (b) the nature of the cation and (c) the ionic strength of the solution.

The CEC determined the number of potentially dissociable ions. The nature of the cation, as reflected in the Hofmeister series, determined the degree to which they were dissociated. Those most strongly hydrated such as $Li^+$ or $Na^+$ were most readily dissociated, since their hydration screened them from the particle's charge. The mean location of dissociated cations was governed by the opposing forces of the particle's electrostatic attraction and the osmotic pressure of the solution, and when these forces were equal equilibrium was established and a potential difference set up between the particle and the solution. Thus the potential difference and the amount of osmotically imbibed water depended on the number of dissociated cations and this was controlled by the cation species. It was important to distinguish the osmotically imbibed water from the molecularly adsorbed water of hydration directly associated with the cation, for it was the imbibed water which accounted for the swelling of the clay and increased the thickness of the double layer.

In the presence of a free electrolyte, the potential difference and swelling were suppressed in accordance with the laws of the Donnan distribution. The distribution of the electrolyte and dissociated ions between the micelle liquid and solution was solely governed by their number and valence, and both cations and anions influenced the effects, although the anions were negatively adsorbed. The influence of the anion on colloid stability was illustrated by calculation (1929 a) and by experiment (1929 b). The order of their flocculating power was univalent > divalent > trivalent, the reverse of that for the cations. The most significant influence of the free electrolyte however, was that the higher its concentration the greater the percent dissociation of the cations by the particle. This was predicted by the Donnan calculations and confirmed by experiment (1929 a), but runs counter to the accepted view that the higher the electrolyte concentration the more the cations are associated.

The results obtained for the chloride ion distribution in a bentonite clay (CEC = 80 me/100 g) suspended in sodium chloride solutions of varying strength, are given in Table 29. Comparing the 0.005 N and 0.2 N solutions, the value of Z increased nearly five times and the percent dissociation from 5.35 to 20.9%. In 0.4 N solution, Z increased nearly ten times. Such an apparently paradoxical situation is explained on the basis of the influence of a salt on ion activity (Brönsted 1921). In high salt concentrations weak acids become more dissociated and salts and minerals become more soluble. This is because the increased electrolyte concentration decreases the activity of the dissolved ions (Debye and Hückel 1923) so that further acid or salt is dissociated to maintain the equilibrium. For example, the solubility of $CaCO_3$ in water is raised from 13 mg/l to 28 mg/l in N NaCl. (Cameron and Seidell 1902). Mattson showed that the dissociation of the colloid was linearly related to the square root of the ionic strength of the solution, as chemical theory would predict. Fig. 22 is an illustration, the values being taken from Table 29 p.192. It is seen that in the absence of electrolyte, dissociation is very small

Fig. 22 The relationship between $\sqrt{\mu}$, the square root of the ionic strength and z, the molar concentration of $Na^+$ ions dissociated by the particle for a suspension of bentonite in NaCl solutions (values from Table 29 p.192).

(Mattson 1929b)

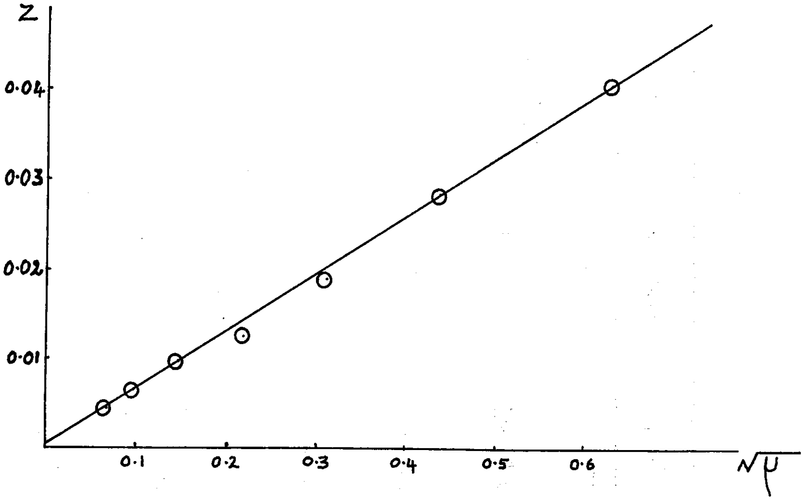


Table 29 <u>The Donnan distribution of Cl- ion in the NaCl - bentonite system (CEC = 80 me/100 g).</u> (Compiled from Mattson 1929a)

| Electrolyte normality | 0.005 | 0.02 | 0.05 | 0.10 | 0.20 |
|---|---|---|---|---|---|
| | — mmoles/1 — | | | | |
| ($Cl^-$, cation and anion conc. in outside solution) | 6.41 | 12.14 | 28.30 | 54.40 | 106.0 |
| Y ($Cl^-$, cation and anion conc. in micelle liquid) | 4.55 | 9.25 | 23.7 | 48.4 | 96.9 |
| z (conc. $Na^+$ dissociated by particle) | 4.48 | 6.68 | 10.01 | 12.74 | 19.05 |
| $e = 2y + \bar{z} - 2x$ (excess conc. in micelle liquid) | 0.76 | 0.90 | 0.89 | 0.74 | 0.85 |
| Water : colloid ratio | 9.51 | 9.45 | 9.41 | 9.57 | 8.77 |
| Donnan P.D. mv | 8.63 | 6.85 | 4.47 | 2.94 | 2.29 |
| me cations dissociated/100 g | 4.27 | 6.30 | 9.52 | 12.12 | 16.70 |
| % dissociation | 5.35 | 7.88 | 11.88 | 15.17 | 20.90 |
| P.D. X z | 0.0387 | 0.0458 | 0.0451 | 0.0374 | 0.0436 |

indeed. This is why exchangeable bases are not removed when a soil is leached with alcohol, and why an electrodialysed sol remains stable in alcohol, although very sensitive on addition of electrolyte, and equally so whether its exchange capacity is large or small.

The breakdown in stability was a logical consequence of the fact that as the value of $z$ increased, the difference in concentration between the micellar liquid and outside solution decreased and the osmotically imbibed water diffused out of the micelles until a new equilibrium was established. Thus, the reduction in osmotic hydration shrank the ionic atmospheres. The double layer was compressed to some point at which the flocculation mechanism came into play.

Mattson commented that in the case where the same cation saturated the colloid and composed the free electrolyte, neutralisation of the charge by adsorption would only be conceivable if the added electrolyte suppressed the dissociation of the colloidal complex. Since the very opposite had been established, the theory could not be accepted. He summarised his observations as follows:-

"The stability of the colloid depends upon the degree of dissociation of the complex, which in turn depends upon the nature of the ions of opposite sign of charge. The addition of an electrolyte results in (a) the formation, by exchange, of a new complex which may differ in stability from that of the original; (b) in a diminution in the activity, ie. in the self-potential of all ions resulting; (c) in a suppression in the P.D. between the micellar and intermicellar solution according to the Donnan equation; and (e) in a suppression of the excess osmotic pressure within the micellar solution, resulting in a diminution in the osmotic hydration of the micelles."

### (iii) Flocculation.

Mattson did not proceed from there to put forward a flocculation mechanism, maintaining that too little was known about interfacial structure and interfacial forces. He stressed the importance however, of distinguishing flocculation from aggregation. Aggregation was due to molecular cohesive forces between particles and came into play in sediments or when flocs aged and dried. But the solid particles in flocculated material were calculated in one case to occupy only a little over 2% of the 'gel'. It must therefore be the micelle surfaces which adhered and not their nuclei. This was in harmony with his theory of ionic linkage according to which micelles were linked electrostatically by ions of opposite charge. Where there was no ionic atmosphere, experiment showed there was no flocculation. But an ion atmosphere alone was not sufficient to link the micelles together. Some stability factor such as hydration and possibly also molecular orientation must be broken down. This was accomplished by the free electrolyte. Mattson was cautious, but very crudely one might redraw his picture (p.175) to show that as the ionic atmospheres were compressed, so the number of free ions or links per surface area would increase.

The original theory of ionic linkage had been modified because his calculations found (1926b) that only a small number of the cations taken up could be considered as existing free in the outer layer; for the potential difference between the micellar liquid and outside solution would otherwise be greater than any observed. Thus, the hydroxyl ions were adsorbed and thereby changed the nature of the complex, but they were rendered electrostatically neutral by their accompanying bases. Further hydroxide addition had the same effect in depressing the Donnan potential and the osmotic imbibition as any other electrolyte. The reason for the swifter reaction of hydroxyl in breaking down the suspension stability was unknown.

(iv) The effects of negative charge.

Examples were given earlier (1922) in which flocculation occurred when particles were still highly charged (Tables 25 and 26 pp. 179 - 181). Table 30 shows similar results, where flocculation in the presence of NaOH occurred at a higher cataphoretic (zeta) potential than that of the stable suspension; for example it was -40 mv in the original suspension and -56.3 mv when flocculated by NaOH. Mattson concluded it was unnecessary to postulate that the particles were kept in suspension by a repelling force. The osmotic hydration was sufficient to account for their stability. The connection between stability and high charge was an indirect effect, due to the dependence of hydration on the number of dissociated cations. These determined the initial charge. The free electrolyte controlled its suppression.

Table 30 Electrophoretic mobilities and cataphoretic potentials for threshold concentrations of flocculating electrolyte (Sharkey colloid 0.4g/1).

(Compiled from Mattson 1929 b).

| Electrolyte | me/1 | saturating cation | electrophoretic mobility $\mu$/sec/volt/cm | cataphoretic potential mv |
|---|---|---|---|---|
| $CaCl_2$ | 1.6 | $Ca^{2+}$ | -0.97 | -20.4 |
| $Ca(OH)_2$ | 1.0 | $Ca^{2+}$ | -1.02 | -21.4 |
| NaOH | 12.0 | $Ca^{2+}$ | -2.68 | -56.3 |
| $CaCl_2$<br>NaOH | 0.8<br>2.0 | $Na^+$ | -2.13 | -44.7 |
| $Ca(OH)_2$<br>NaOH | 0.6<br>2.0 | $Na^+$ | -2.49 | -52.3 |
| water suspension |  | $Na^+$ | -3.88 | -81.5 |
| water suspension |  | $Ca^{2+}$ | -1.91 | -40.0 |

## 3. Later developments in flocculation theory.

Mattson's views appear to be virtually unknown in modern colloid chemistry. To the writer's knowledge the experimental evidence put forward in the three papers outlined above has never been challenged. It has simply been ignored. His work on the charge reversing properties of hydrolysed metal salts was similarly neglected and even today he is seldom credited with their discovery. At the present time the double layer theory as it was developed by Verwey and Overbeek (1948) and Derjaguin and Landau (1941), and now known as the DLVO theory, dominates enquiry in colloid chemistry. This has proved of operational value in many practical applications, although it has been found inapplicable to polyelectrolyte flocculation, where bridging mechanisms are envisaged and also fails to explain fully the behaviour of hydrolysed metal cations (Mackenzie 1971). Others have gone further. La Mer and Smellie (1956 a) for example contested the importance of the repulsive charges in sols. They accepted the calculations of Derjaguin and Landau that these exist, but suggested that stability was primarily due to hydrophilic bonding between the clay and water. In support of this, they pointed out that clay colloids showed greater stability than was predicted for a lyophobic colloid stabilised by electrostatic repulsion. According to the Smoluchowski Law, the upper limit in particle number for a stable sol was $n = 10^6/cm^3$. The authors found that stable slimes in which the esd was 0.2 - 0.4$\mu$ contained particle numbers of the order $n = 10^{10}/cm^3$, and concluded that the clay colloids primarily owed their stability to chemical interactions with the medium, or hydrophilic bonding between the OH groups of the particle and the water; and only secondarily to the repulsions arising from the interaction of the electrical double layer surrounding each particle.

This would appear to be another version of the old hydration theory of colloid stability. It bears little resemblance of course to Mattson's theory of osmotic hydration. Van Olphen (1963) dismissed the 'hydration theory' as obsolete and did not mention Mattson. He interpreted colloid behaviour in terms of the DLVO theory, and distinguished 'aggregation' as due to face-face bonding and 'flocculation' as due to edge-face or edge-face bonding ie. floc formation could be interpreted in terms of particle juxtaposition. He used the terms 'coagulation' and 'flocculation' interchangeably. This point of view was again challenged by La Mer and his colleagues (1956, 1963, 1967), who ascribed the coagulation process to electrolytes such as $CaCl_2$ and $Ca(OH)_2$, and the flocculation process to polyelectrolytes such as starch, the polyacrylamides and perhaps also hydrolysed metal ions. These authors made a distinction which was (a) operational, in that it depended on precipitate behaviour and (b) theoretical, in that the bridging mechanism was applied to polyelectrolyte but not electrolyte precipitation. 'Water chemists' today have accepted this distinction, at least from the point of view that a different mechanism is involved. It is doubtful however, whether soil scientists would accept La Mer's operational criteria which identified aggregation and sedimentation to a compact coagulum with electrolyte behaviour, and subsidence of flocs to a voluminous sediment with polyelectrolyte behaviour. Russell (1961) for example, gave a graphic description of weak gel and floc formation that followed addition of electrolytes to clay sols and, while admitting that flocculation-deflocculation mechanism was little understood, suggested that "since the flocs are very loose the particles can presumably only join up in chains, thus enclosing a large volume of solution." Russell envisaged the cohesion of particle nuclei following double layer contraction, but only at certain points, so that fragile flocs rather than coherent aggregates were formed.

It is seen there is a wide measure of disagreement. The application of electrokinetic and adsorption studies to mineral recovery and waste separation is practised on a large scale today and has produced many empirical observations and working hypotheses (Mackenzie 1971). It may now be possible to develop a theory of more general scope in which the behaviour of the hydroxyl group will be recognised as playing the same key role in inorganic colloid chemistry as it plays in biochemistry, although the mechanism may be different. In the writer's view, reappraisal of Mattson's evidence and of his tentative suggestions is required, together with that of the mass of observations since collected. The special properties of the hydroxyl group should be examined, whether it exists adsorbed from free electrolyte or whether bonded to water, hydrolysed metal cation, silica, clay or to the carbon spine of a polyelectrolyte.

# CHAPTER V : SOIL AGGREGATION.

## 1. Techniques for investigating aggregate stability.

### (i) Field assessment.

Soil aggregation, or the binding of the soil primary particles into coherent units is fundamental to the development of a good soil structure. Water-stable aggregates favour the development of crumb structure, while unstable aggregates tend to form massive structures (if sandy), structures that set hard and crack vertically into large peds (if clay). Aggregates that slake or disperse in water may settle out as surface crusts or subsoil pans preventing shoot and root germination. Structural types are classified in the field from an examination of the peds in the soil profile, and an ability to recognise them and the properties they confer on the soil is an aid to husbandry, in so far as the structure may be improved, or may impose limitations on management, or may guide the lay-out of drainage systems. In addition, structural deterioration may be prevented by noting any adverse changes produced by intensifying land use : incipient pan development is signalled by resistance to a knife blade at some 12 - 16 inches depth of profile, or by the advent of platy structures, or by an anaerobic layer of undecomposed mulch in the topsoil; poaching or puddling will lead to pockets of waterlogging due to smearing of the peds and rush invasion indicatesthis; weak root development in grassland that is too intensively grazed may inhibit the formation of an organic crumb topsoil resistant to treading and tearing; slaking or dispersion of cultivated topsoils may be due to exhaustion of organic matter and thus a loss of coherence in the aggregates.

(ii) Physical measurements.

The stability of aggregates is measured in terms of their stability to water, to wetting and drying and to degrees of pressure. Weak aggregates may disperse in water due to swelling, or to the expulsion of air, or to the osmotic stress set up when salts diffuse from dry soil. Hence physical measurements of aggregate stability include:

(a) measurement of the proportion of water-stable aggregates by wet sieving (Yoder 1936) or determination of infiltration rates (Dettmann and Emerson 1959) or observations on dispersivity and slaking (Emerson 1971).

(b) measurement of changes in the slope of the soil moisture characteristic curve, after taking the soil through several wetting and drying cycles. This method indicates the stability of coarse pores and Childs (1942) has used it to pick out subsoils whose structures are too unstable for mole drainage.

(c) measurement of soil porosity ie. the percent volumes of air-filled pores, water-filled pores and mineral matter at field capacity. The neutron probe densitometer is a newly developed portable device for measuring pore space of soil profiles.

(d) determination of the Atterberg limits, which indicate the effect of water on soil consistency and hence the limitations of a particular soil with respect to the timing of cultivations and bearing strength. Soil consistency studies have fallen into disuse in agriculture and need to be revived, for changes in soil consistency are accompanied by changes in soil structure and volume, particularly in soils high in sand and silt. The role of organic matter is decisive in extending the range of soft consistency over which the soil is in a suitable state for cultivations, ie. in the production of water stable aggregates. (Agric. Advis. Council 1970).

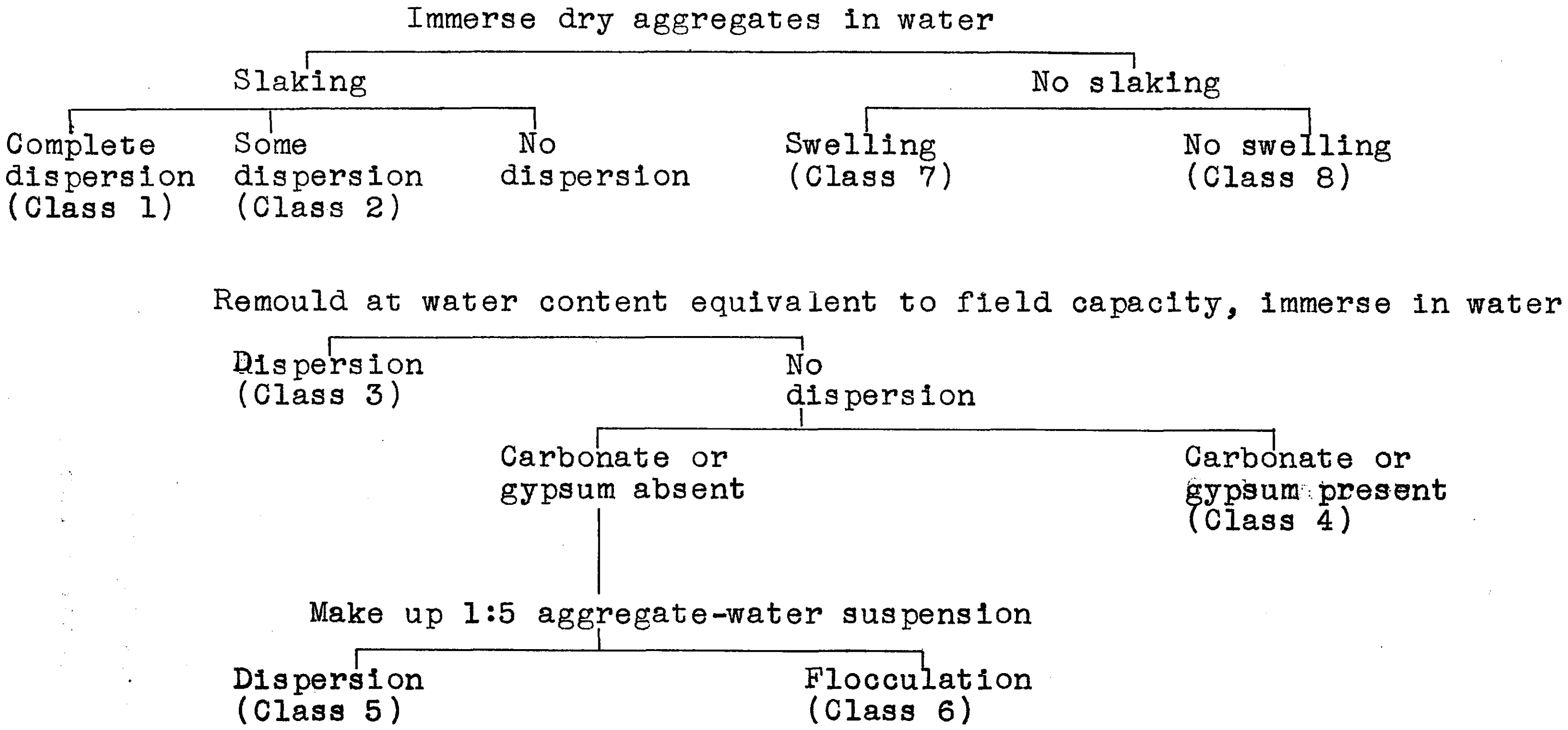
### (iii) Classification of soil aggregates.

Emerson (1967) proposed a classification of soil aggregates based upon their coherence in water, on the premise that the interaction in water of their clay particles would largely determine the structural stability of the soil. He used simple physical tests, which could be made in the field, to divide aggregates into eight classes of stability. His scheme is shown in Table 31. These stabilities were found capable of interpretation in terms of carbonate and gypsum content, cation exchange capacity, percent exchangeable sodium, clay mineral species and cultivation history.

Classes 1 and 2 which dispersed at field capacity owed their instability to high percent exchangeable sodium. The detection of class 1 aggregates in the field was particularly important for avoiding the failure of earth dams. Class 3 were soils of near neutral pH, containing clay of low to medium CEC and variable exchangeable sodium, which dispersed at field capacity when remoulded. Hence, they were sensitive to structural damage if cultivated when wet and could be improved with addition of lime or gypsum. Class 4 had aggregates stabilised by lime or gypsum. Class 5 were acid soils that failed to disperse at field capacity,

Table 31. <u>Scheme for determining class numbers of aggregates</u>.

(Emerson 1967)



but did so if the aggregate:water ratio was raised to 1:5, as might occur under heavy rains or after irrigation, or in drainage systems. Class 6 were acid soils that flocculated under these conditions due to their kaolinite content. This behaviour was independent of salt concentration and had first been noted in acid suspensions of kaolinite by Schofield and Samson (1954). Class 7 were aggregates high in organic matter, such as was found under old grassland. Organic matter would, of course, modify the aggregate stability of the other classes in their topsoils. Class 8 were portions of hard pans.

Emerson's dispersion tests showed, incidentally, that the threshold limits for ions of a particular valency quoted by van Olphen as an expression of the Schultze - Hardy law (Table 5 Chapter III p.60) could not be relied upon in practice, since the clay mineral species, water content and history of the aggregate also influenced its stability to dispersion. Table 32 records some flocculation and dispersion concentrations compiled from his results.

Such a classification for assessing soil stability is clearly valuable in the Australian situation for which it was devised. To the writer's knowledge, no

Table 32 Some threshold concentrations for the dispersion and flocculation of aggregates by uni- and divalent cations under different conditions.
(Compiled from Emerson 1967)

| Aggregate type | Treatment | Cation | Flocculation limit mM | Dispersion limit mM |
|---|---|---|---|---|
| Ca, Mg-illite or montmorillonite | aggregates shaken into suspension in water | $Ca^{2+}, Mg^{2+}$ | 0.3 - 0.5 | <0.3 - 0.5 |
| Ca, Mg -kaolinite | ditto | $Ca^{2+}, Mg^{2+}$ | flocculation | |
| K - illite | aggregates equilibriated with solution | $K^+$ | 33 | >25 <33 |
| | | $Na^+$ | 200 | >100 <200 |
| Ca - illite | aggregates remoulded ... at 80g/100g water content | $Ca^{2+}$ | 0.3 | < 0.3 |
| | ... at 56g/100g water content | $Ca^{2+}$ | 0.1 | < 0.1 |
| Class 3 aggregates ... subsoils | remoulded and suspended in 1:5 soil:water ratio | $Ca^{2+}$ | 0.3 | |
| Surface soils | ditto | $Ca^{2+}$ | 1.0 | |

similar scheme has been attempted for temperate regions. It might find useful application, particularly in drainage management; on the other hand a classification based on consistency measurements might be more appropriate.

### (iv) Aggregating agents.

The production of stable aggregates must be ascribed to a numerous variety of agents. Soil fauna work and manure the soil, the proliferation of grass roots break up and entangle it, the bacteria living free or in root rhizospheres decompose inert tissues and manufacture polysaccharide gums which bind it, fungi filaments enmesh it. The non-living components perform roles of varying importance; clays coagulated by electrolyte hold together sand and silt particles in a matrix; alumino-silicates and iron oxides by flocculation, cementation and adsorption build cohesive aggregates; components of organic matter adsorb on clay through di- or trivalent ion link to the surface, or by electrostatic adsorption, or through some kind of hydroxyl interaction in which non-specific dispersion forces are involved, creating bond strength through multiple linkages (Greenland 1965). Calcium carbonate promotes good soil structure, but the relative importance of its flocculating effect, its complexing ability, or its role in maintaining a fertile habitat for soil microflora and fauna by raising pH and supplying calcium, is unknown.

### (v) Dissolution techniques.

The selective dissolution of a specific fraction of the soil allows the role of that fraction to be assessed. Examination of the mineralogy before and after treatment, together with that of properties such as aggregate stability, surface area, ion exchange capacities and percent phosphate retention, suggest the contribution of the fraction lost, and its composition can be analysed in the extract. Recent work has sought to establish the relative importance of amorphous alumino-silicates, alumina, iron oxide and organic matter in maintaining aggregate stability. The following sections draw upon examples of this work to give a brief description of dissolution techniques and to review the results so far obtained.

## 2. Alumino-silicates and aggregate stability.

Amorphous alumina, silica and allophanic material is normally removed by some kind of alkali dissolution. The relative and total quantities of alumina and silica attacked however, depend upon the method used ie. the concentration of alkali, duration of treatment, temperature and amount of abrasion to which the material is subjected. The effectiveness of the method is further dependent on the degree of disorder in the mineral itself, and complicated by the fact that finely divided crystalline material is also susceptible to alkali attack.

When interest became focussed on the clay minerals, it was customary to remove the 'dross' of amorphous matter which interfered with their characterisation by treating them with hot 5% $Na_2CO_3$, a method Salvétat (1851) had introduced to determine soluble silica. A new procedure, said to be more efficient, was described by Hashimoto and Jackson (1960), in which allophane, interlayer alumina, gibbsite, free alumina and silica were rapidly and completely removed when 100 mg clay was boiled in 100 ml 0·5N NaOH for 2½ minutes. These conditions were critical, because prolonged boiling attacked crystalline clay, and because higher soil : solution ratios produced solubility problems and reprecipitation of silica.

Mitchell and Farmer (1962) detected allophanic material in Scottish soils after observing that the dehydroxylation peaks on DTA traces were smaller than would be expected from the X-ray analysis, while the dehydration peaks were larger than normal. This was particularly so for clays of organic horizons. They used the hot 5% $Na_2CO_3$ dissolution technique to determine the amount of amorphous material in four Ayrshire soils derived from basic rock and till. Their results are given in Table 33. (Oxides dissolved as % of original oxide). It is seen from the $SiO_2 : Al_2O_3$ ratios that the material was highly siliceous. The range within which artificial co-precipitates of silica and alumina show DTA effects resembling allophane is between 0·5 and 2·0. Ratios below and above these values indicate free amorphous alumina and silica respectively ("Soils of New Zealand" 2 p.41).

The authors had reservations in ascribing all the dissolved material to allophane, since a control experiment showed that vermiculite and chlorite released 28 and 16% of their silica and 11 and 2·5% of their alumina respectively. Thus, the vermiculite-chlorite that was the predominant clay in these Scottish soils

Table 33 **Silica and alumina dissolved from Ayrshire soil clays by hot 5% $Na_2CO_3$**

(Compiled from Mitchell and Farmer 1962)

| Soils and horizons | DTA dehydration peak | % original oxides | | molecular ratio $SiO_2 : Al_2O_3$ | % oxides dissolved as % orig. oxides | | molecular ratio $SiO_2 : Al_2O_3$ |
|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | | $SiO_2$ | $Al_2O_3$ | |
| Picket Loch A | very strong | 24•6 | 32•4 | 1•31 | 86•2 | 57•4 | 2•55 |
| Picket Loch C | medium | 38•8 | 32•4 | 2•04 | 75•9 | 54•6 | 2•36 |
| Auchans A | very strong | 32•7 | 27•3 | 2•03 | 72•2 | 42•8 | 2•86 |
| Lanfine A | medium-weak | 36•8 | 30•6 | 2•04 | 71•7 | 44•8 | 2•71 |
| Littlehill A | medium-weak | 39•0 | 26•8 | 1•54 | 56•1 | 39•2 | 2•43 |

could have been attacked to some degree, especially if finely divided. Explanations for the high silica too, might be found in dissolution of phytolith residues from grasses.

A search was made for some reagent which would differentiate between the amorphous and crystalline fraction in clay. It was thought a milder alkali treatment might succeed. A study was made of the effects of a graded dissolution procedure, in which cold 5% $Na_2CO_3$ was followed by hot extractions. This sequential method was also compared with the 0•5N NaOH method (Follett et al. 1965). Samples investigated were pure components of soil clays, a Tirau allophane, and clays from two profiles which, unlike the 1962 soils, did not on DTA evidence, contain large amounts of highly hydrated inorganic material. These, as it happened, were the end members of the South Drumboy sequence ie. Baidland peaty podzol and Dunwan humic gley. Their results are given in tables 34 and 35 together with the $SiO_2 : Al_2O_3$ ratios. The minerals and Tirau allophane were given 3 to 4 treatments with cold 5% $Na_2CO_3$ followed by 3 treatments with hot $Na_2CO_3$. The 0•5 NaOH treatment was given once. The soil clays were pretreated with ammonium acetate (Farmer and Mitchell 1963), peroxidised to destroy organic matter, washed with hot water to remove soluble oxalates and given 7 cold followed by 7 hot $Na_2CO_3$ treatments, or 6 treatments with 0.5N NaOH. The following summarises their results:-

(a) All the pure minerals except quartz and gibbsite were attacked to some extent, although less by the cold 5% $Na_2CO_3$ than the sequential treatment.

(b) The Tirau allophane was almost completely destroyed by the sequential treatment and by the NaOH. The residue contained some kaolinite. 45% of the alumina and 30% of the silica was dissolved by the cold treatment.

(c) Only small amounts of amorphous material were dissolved by cold $Na_2CO_3$ from the humic gley, but about 1/5 of the silica and 1/4 of the alumina was removed by the sequential treatment.

(d) High amounts of alumina, rising to 25.3% in the $B_3$, were extracted from the podzol by cold $Na_2CO_3$. The hot extraction had a similar effect as on the gley. The aluminous character of the podzol was shown in the low $SiO_2 : Al_2O_3$ ratios throughout the profile and by a gibbsite peak on the DTA trace of the $B_3$.

Again it is difficult from these results to know what to attribute to allophanic material. One test

Table 34 <u>Total silica and alumina contents of minerals and proportions extracted by alkali treatments</u>.

(compiled from Follett et al. 1965)

| Mineral | Original ignited 1000°C | | $Na_2CO_3$ extraction | | | | 0.5N NaOH extraction | |
|---|---|---|---|---|---|---|---|---|
| | | | cold 5% | | total cold hot 5% | | | |
| | $SiO_2$% | $Al_2O_3$% | $SiO_2$% | $Al_2O_3$% | $SiO_2$% | $Al_2O_3$ | $SiO_2$% | $Al_2O_3$ |
| kaolinite | 53.4 | 45.4 | 5.4 | 1.6 | 9.1 | 13.1 | 5.8 | 3.4 |
| illite | 54.2 | 24.2 | 7.4 | 2.6 | 11.3 | 9.6 | 6.0 | 5.2 |
| montmorillonite | 64.5 | 20.8 | 6.1 | 5.6 | 10.8 | 16.7 | 10.2 | 7.4 |
| gibbsite | 0.7 | 100.0 | nil | nil | nil | 0.2 | - | - |
| quartz | 98.4 | 0.2 | 0.2 | tr | 3.5 | tr | - | - |

Table 35 Silica and alumina dissolved from soil clays by various alkali treatments.

(Compiled from Follett et al. 1965)

| Profile | Horizon | Untreated clay ignited at 1000°C | | | $Na_2CO_3$ extraction | | | | | | 0·5N NaOH | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | cold 5% $Na_2CO_3$ | | | cold + hot 5% $Na_2CO_3$ | | | | | |
| | | $SiO_2$ % | $Al_2O_3$ % | $SiO_2$:$Al_2O_3$ | $SiO_2$ % | $Al_2O_3$ % | $SiO_2$:$Al_2O_3$ | $SiO_2$ % | $Al_2O_3$ % | $SiO_2$:$Al_2O_3$ | $SiO_2$ % | $Al_2O_3$ % | $SiO_2$:$Al_2O_3$ |
| podzol with thin iron pan | $A_2$ | 42·9 | 29·9 | 2·43 | 2·6 | 10·9 | 0·40 | 15·9 | 22·1 | 1·22 | 22·1 | 31·8 | 1·18 |
| | $B_2$ | 39·0 | 29·6 | 2·24 | 6·6 | 17·9 | 0·62 | 22·0 | 31·1 | 1·20 | 32·1 | 48·9 | 1·14 |
| | $B_3$ | 47·5 | 31·2 | 2·58 | 5·4 | 25·3 | 0·36 | 19·8 | 37·9 | 0·89 | 33·5 | 49·4 | 1·15 |
| | $C_1$ | 47·4 | 30·8 | 2·61 | 4·8 | 12·1 | 0·67 | 25·0 | 24·2 | 1·75 | 35·5 | 48·6 | 1·24 |
| | $C_2$ | 48·6 | 29·1 | 2·83 | 2·9 | 7·8 | 0·63 | 23·4 | 33·4 | 1·19 | 27·4 | 44·7 | 1·04 |
| Humic gley | Ag | 45·6 | 27·2 | 2·84 | 3·7 | 5·3 | 1·18 | 21·9 | 27·4 | 1·71 | 30·2 | 33·3 | 1·54 |
| | $B_2$g | 53·2 | 28·0 | 3·24 | 3·2 | 4·7 | 1·15 | 18·6 | 24·5 | 1·29 | 29·6 | 31·1 | 1·61 |
| | $B_3$g | 51·6 | 25·3 | 3·46 | 3·7 | 4·7 | 1·34 | 19·0 | 24·9 | 1·29 | 35·4 | 37·2 | 1·61 |
| | Cg | 52·0 | 25·2 | 3·50 | 2·5 | 3·7 | 1·15 | 18·4 | 22·5 | 1·39 | 32·2 | 30·2 | 1·81 |
| Tirau Allophane | | 42·4 | 47·5 | 1·51 | 29·8 | 45·3 | 1·12 | 65·6 | 77·1 | 1·44 | 78·6 | 76·0 | 1·75 |

N.B. extracted percentages are given as percent of total $SiO_2$ and $Al_2O_3$ in clay.

that might give a clue to the method with highest selectivity for amorphous material is the New Zealand Soil Bureau calculation in which twice the sum of the extracted $SiO_2$ and $Al_2O_3$ is taken as the allophane percent of the clay ("Soils of New Zealand" 2 p.47), as described in Chapter IV A). The calculation is not applicable to Scottish soils where clay minerals predominate, but a comparison of the results for the dissolution of the Tirau allophane might suggest which method was most selective, if one can assume correctly that it was approximately 100% allophane. Converting the percent alumina and silica to percentages of the whole clay, one gets the following allophane percent of clay:-

Cold 5% $Na_2CO_3$ : $[12{\cdot}64 + 21{\cdot}52] \times 2 = 34{\cdot}16 \times 2 = 68{\cdot}32\%$
Sequential $Na_2CO_3$ : $[27{\cdot}82 + 36{\cdot}62] \times 2 = 64{\cdot}42 \times 2 = 128{\cdot}88\%$
0·5N NaOH : $[33{\cdot}33 + 36{\cdot}10] \times 2 = 69{\cdot}43 \times 2 = 138{\cdot}86\%$

In view of the assertion that the 0·5N NaOH method gives good correlations for soils high in allophane, the large discrepancy here is disconcerting. By the result it appears that a factor smaller than 2 is necessary to take account of the loss of water on ignition. On the other hand, it had perhaps been hoped that the cold $Na_2CO_3$ would have dissolved all the allophane, and it is indeed difficult to see why some of it should be more resistant to the repeated extractions. By the calculation, about 30% clay must be accounted for. The residue contained kaolinite, but the amount may have been small, of the order of the 3% found by Birrell and Fieldes (1952), who had also found up to 5% quartz. The residue may perhaps have contained undetected amorphous hydrous felspar, common in allophane soils. If the total could be made up in this way, then the high percentages of allophane calculated for the hot alkali methods are explained. Bracewell et al. (1970) have noted the anomalously low reactivity of Tirau clay with NaF solutions in comparison with other New Zealand and Japanese allophane clays.

Fellett et al. however, did not attempt any correlation. They concluded that their results "support the concept of soil clays as a continuum from completely disordered, through poorly ordered, to well crystallized material; the range of this continuum which can be extracted depends upon the reagent employed."

This investigation was part of a wider scheme to examine the role of the alumino-silicates and iron oxides in the two soils by differential dissolution and examination of the properties before and after the successive treatments. The most striking observation at this stage was of the changes in specific surface area, shown in Table 36, and particularly the unexpected increase following the washing of the peroxidised clays. This was thought to be associated with the removal of water-soluble oxalates produced by the peroxide treatment. It is seen to be most marked for horizons high in organic matter. Specific surface areas for the podzol $A_2$ and $B_2$ for instance, increased from 4 to 58 $m^2/g$ and from 48 to 98 $m^2/g$ respectively. Earlier work by Farmer and Mitchell (1963) illuminates this problem and is described in the following note.

NOTE: It had been found advisable to inhibit the formation of insoluble calcium oxalates during peroxidation, by saturating the clay with ammonium ion. The sorbed oxalates were then removed as their soluble ammonium oxalato-aluminates and ferrates with hot water and no longer interfered with the DTA and IR traces. A significant loss of sesquioxides as oxalates was suspected (Williams et al. 1958) and the contents of the washings from peroxide treatment of the Ayrshire allophanic soils described earlier were examined. Clays from horizons highest in organic matter and allophane yielded

Table 36 Specific surface area ($m^2/g$) of soil clays after various treatments

(Follett et al. 1965)

| Profile | Horizon | Peroxidised | $H_2O$-washed | Cold 5% $Na_2CO_3$ | Successive cold and hot 5% $Na_2CO_3$ | 0·5N NaOH |
|---|---|---|---|---|---|---|
| Podzol with iron pan | $A_2$ | 4 | 58 | 87 | 91 | 96 |
| | $B_2$ | 48 | 98 | 104 | 104 | 98 |
| | $B_3$ | 49 | 73 | 96 | 91 | 92 |
| | $C_1$ | 39 | 55 | 75 | 89 | 87 |
| | $C_2$ | 43 | 56 | 75 | 87 | 91 |
| Humic gley | Ag | 36 | 82 | 80 | 85 | 99 |
| | $B_2g$ | 57 | 78 | 86 | 86 | 99 |
| | $B_3g$ | 73 | 89 | 86 | 97 | 100 |
| | Cg | 67 | 64 | 75 | 72 | 88 |

the most aluminium and oxalate. For example, the Auchans A extract contained an aluminium content corresponding to 1% of air dry clay, and 10% oxalate was recovered from the unwashed clay. It was not certain to what extent the aluminium had been complexed by the soil organic matter and to what extent it had been dissolved from the clay by oxalates formed during the peroxide treatment. The authors speculated that peroxidation effects could be "comparable with those of an oxalate extraction under ill-defined conditions."

Follett et al. took the precaution of analysing their hot water extracts. They found less than 1% $Al_2O_3$, a trace of silica and no iron, and concluded that peroxide treatment had not affected the inorganic fraction to any great extent.

The dramatic increase in specific surface area after washing leads one to assume that the aluminium oxalate complexes were binding the clay particles in a manner similar to the original binding by the unoxidised polymers, and that washing dispersed them. However, electron-optical studies showed the particles to be still undispersed in comparison to their dispersion after the $Na_2CO_3$ treatment. Specific surface areas increased after the alkali dissolution, but this increase was remarkably small, particularly with the humic gley, in view of the amount of material extracted and the increased dispersion. The authors suggested that a high proportion of the interior surfaces of the aggregates in the water-washed clays were accessible to nitrogen.

This conclusion is consistent with the explanation that an organo-allophanic material bound the clay particles, The aggregates were made porous by destruction of the organic matter, but were held together by adsorbed aluminium oxalates and free alumino-silicate till peptised or dissolved by alkali.

The sequential dissolution treatment was continued with the removal of the iron oxides. This is described in the next section, (p.235). Meantime the quest for specificity in alkali extraction was extended to the study of alumina (Jørgensen and Mitchell 1970) and flints (Jørgensen 1970). Flints have alkali reactivity and the failure of some concrete structures has been attributed to the use of flint in the aggregate material (Idorn 1967). The samples examined were microcrystalline quartz and quartz with cryptocrystalline silica. The microcrystalline quartz was attacked only slightly even in hot carbonate; the cryptocrystalline silica dissolved about 1·4% in cold carbonate and about 30% in hot carbonate at 75°C.

The alumina investigation was instructive. It will be noted in Table 34 that the gibbsite sample failed to dissolve in either cold or hot $Na_2CO_3$. Since this result conflicted with others found in the same laboratory, Jørgensen and Mitchell investigated the dissolution of alumina minerals, ranging from the highly crystalline to the poorly crystalline but excluding amorphous species. Treatments were given in 5% $Na_2CO_3$ at 25°, 50° and 75°C. and the effects of various forms of abrasion were also studied. The $Al_2O_3$ extracted was small or negligible at 25°C. but increased at the higher temperatures for the fine grained samples. Ball milling was found to increase the dissolution at 25°C. but to dissolve successively less at the higher temperatures. Thus, it appeared to have the same effect of increasing the reaction rate as was achieved by an increase in temperature. To test the consequences of this, the authors plotted the log of the $Al_2O_3$ concentration against $^1/_T$ for the unground and ball-milled samples, in order to compare the activation energies calculated from the slopes. Although straight line plots were seldom obtained, the numerical slope of the curves of the ball-milled samples was less, indicating a lower activation energy. This led to the interesting conclusion that:

> "A rapid dissolution resulting from a relatively large specific surface area associated with a highly crystalline solid is much more dependent on temperature than a high dissolution rate arising from the presence of disordered material in the sample. This is presumably because the disordered material would have a comparatively low energy of activation. A consequence of the present study is that extraction with alkali at low temperature is desirable for the preferential dissolution of poorly ordered aluminous material from soil clays."

If this conclusion is correct, perhaps it could be a key to the differential solution of allophane.

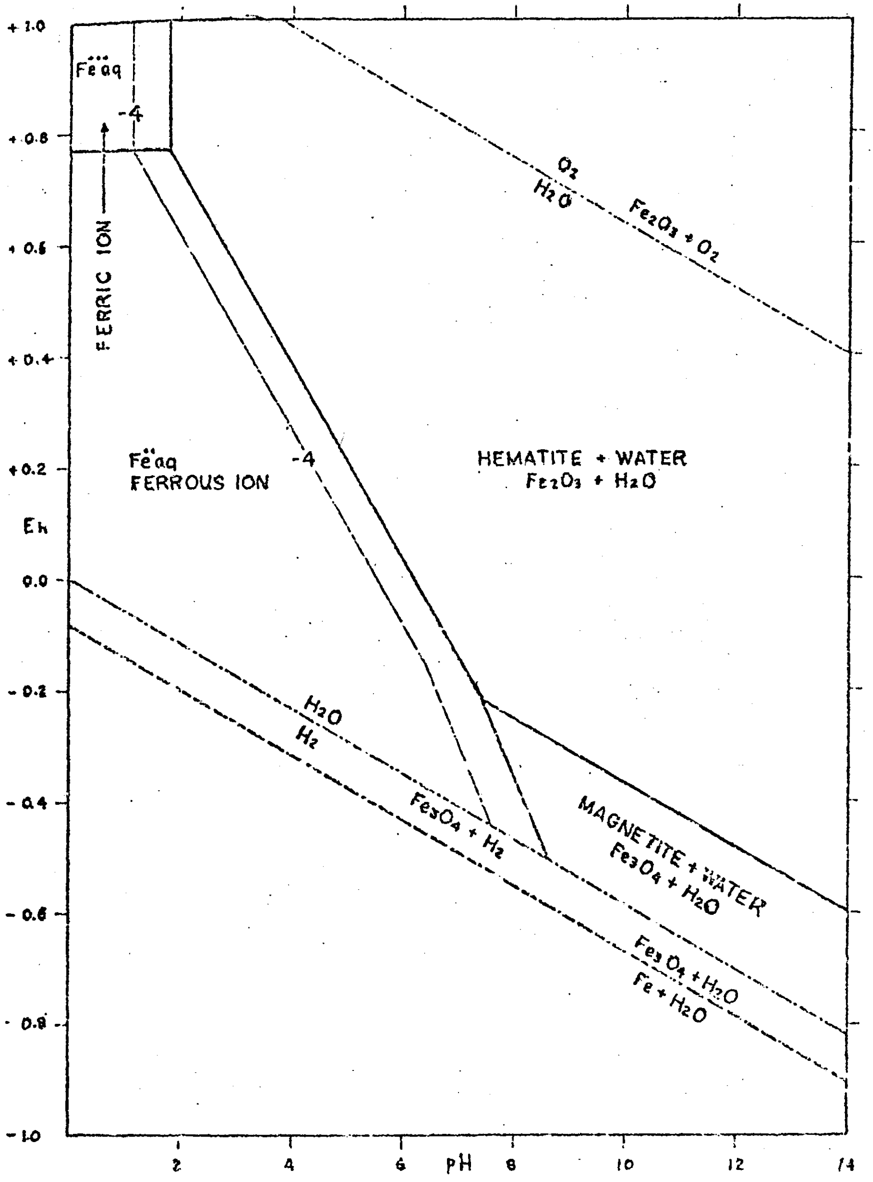
## 3. Iron oxides and aggregate stability.

It will be seen from the stability fields of ferric and ferrous oxides and hydroxides (fig. 23) that free ferric ion plays no part in the equilibria of normal soils and waters. Only under strongly acid and oxidising conditions does its activity exceed $10^{-6}$ (Garrels and Christ 1965). Gibbsite solubility becomes significant in the region pH 3 to 3:2, while disordered forms of alumina are soluble at pH values higher than this (fig.24 Hence, ferric oxide cannot be dissolved by acid without attacking crystalline clays, while the devices which remove iron in ferrous form with the aid of dilute acid or complexing agents all involve the dissolution of alumina, with associated silica, at the same time. Predissolution in alkali helps to distinguish the roles of the iron oxide and alumina or alumino-silicate in any one soil.

The most widely used methods for removing iron oxide are (a) the acidified dithionite method (Mitchell and Mackenzie 1954). This was found to dissolve all soil iron except that contained in the clay mineral lattice, and since contact with 0•05N HCl is only brief it may be the best method for selectively removing iron with minimum aluminium. (b) The dithionite/

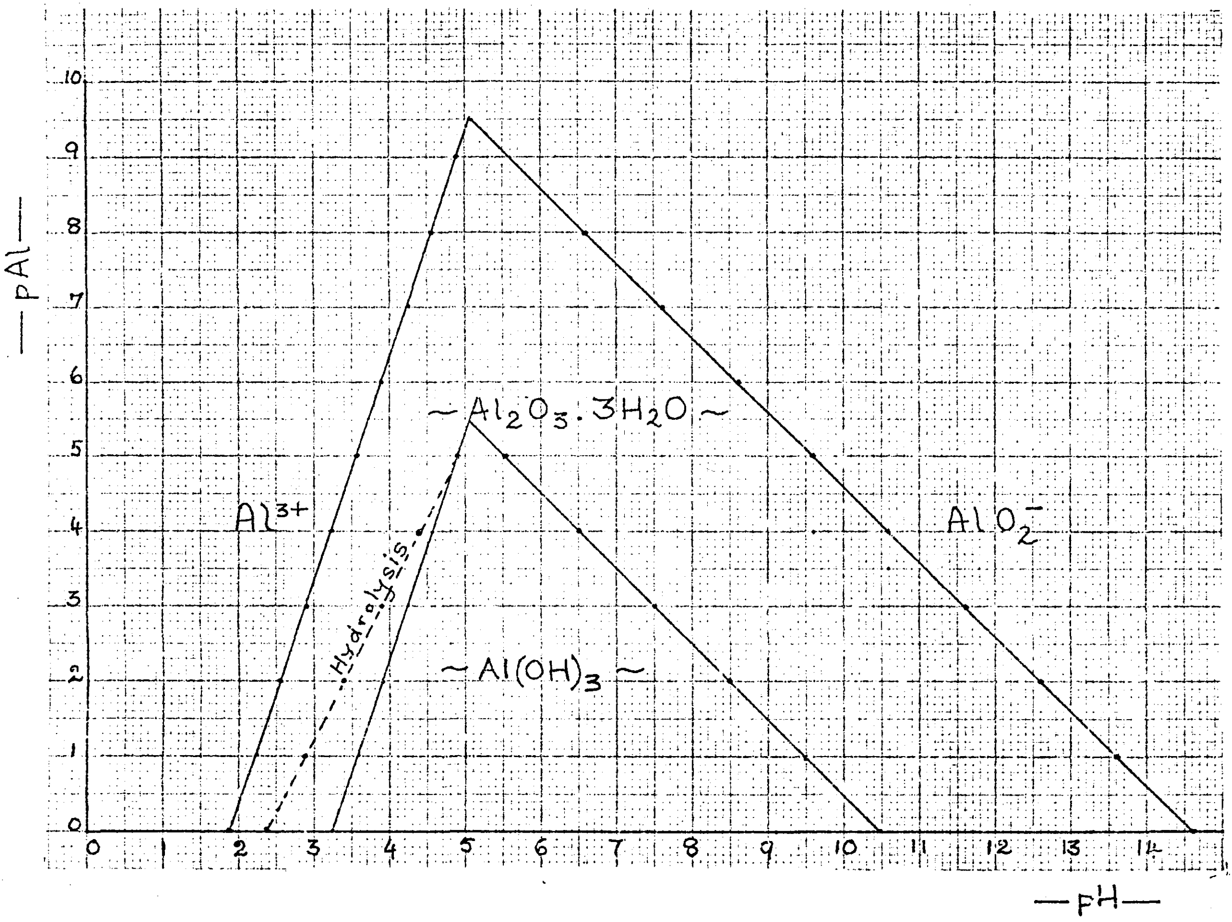
Fig. 23 Eh-pH diagram showing the domains of activity for ferric and ferrous ions.

(Garrels and Christ 1965)



Composite diagram showing stability fields of hematite and magnetite in water. Fields of ions are designated where total activity of dissolved species are $> 10^{-6}$. Fields of ions are labeled with dominant species. Contour of log [dissolved species] $= -4$ is included to show slope of activity change. Plot at 25 °C and 1 atmosphere total pressure.

Fig. 24 Stability relations for two aluminium oxides (gibbsite and aluminium hydroxide).



Solubility equations

$Al_2O_3.3H_2O_{(s)} = 2Al^{3+}_{(aq)} + 6OH^-_{(aq)}$

$pAl + 5.7 = 3pH$

$Al(OH)_{3(s)} = Al^{3+}_{(aq)} + 3OH^-_{(aq)}$

$pAl + 9.7 = 3pH$
$(Ksp = 5 \times 10^{-33})$

$Al_2O_3.3H_2O_{(s)} = 2AlO^-_{2(aq)} + 2H^+_{(aq)} + 2H_2$

$pAl = 14.6 - pH$

$Al(OH)_{3(s)} = AlO^-_{2(aq)} + H^+_{(aq)} + H_2O_{(aq)}$

$pAl = 10.48 - pH$

$Al(OH)_{3(s)} = AlOH^{2+}_{(aq)} + H^+_{(aq)}$

$K_h = 1.4 \times 10^{-5}$

$NaHCO_3$/ citrate method (Mehra and Jackson 1960). This is alleged to be the most rapid and efficient method and bases its efficiency on the raising of the oxidation potential of the system to an optimum at pH 7•3.
(c) The acid-oxalate method (Tamm 1922) in which pH is 3 to 4. This went out of favour because it was required to be done in sunlight and is now known to be a photocatalytic method (de Endredy 1963). Schwertmann (1964) however, showed that in the dark, Tamm's oxalate selectively removed amorphous iron and aluminium oxides, and McKeague and Day (1965) used this modification to differentiate amorphous from crystalline iron oxide in soil profiles. The New Zealand Soils Bureau also use the Tamm extraction to give routine information on the amounts of iron and aluminium present as amorphous compounds and hydrous oxides.

Pretreatment of soils and clays to remove iron oxide has often been found essential to allow dispersion (Dion 1944, Jeffries 1947) or to purify the clays prior to mineral analysis. Allophane soils in particular have been given this treatment (Birrell and Fieldes 1952, "Soils of New Zealand" 1968 <u>3</u> p.6). In the past decade, a major concern has been to elucidate the role of iron oxides as an aggregating agent and to determine the nature of its association with the soil clays.

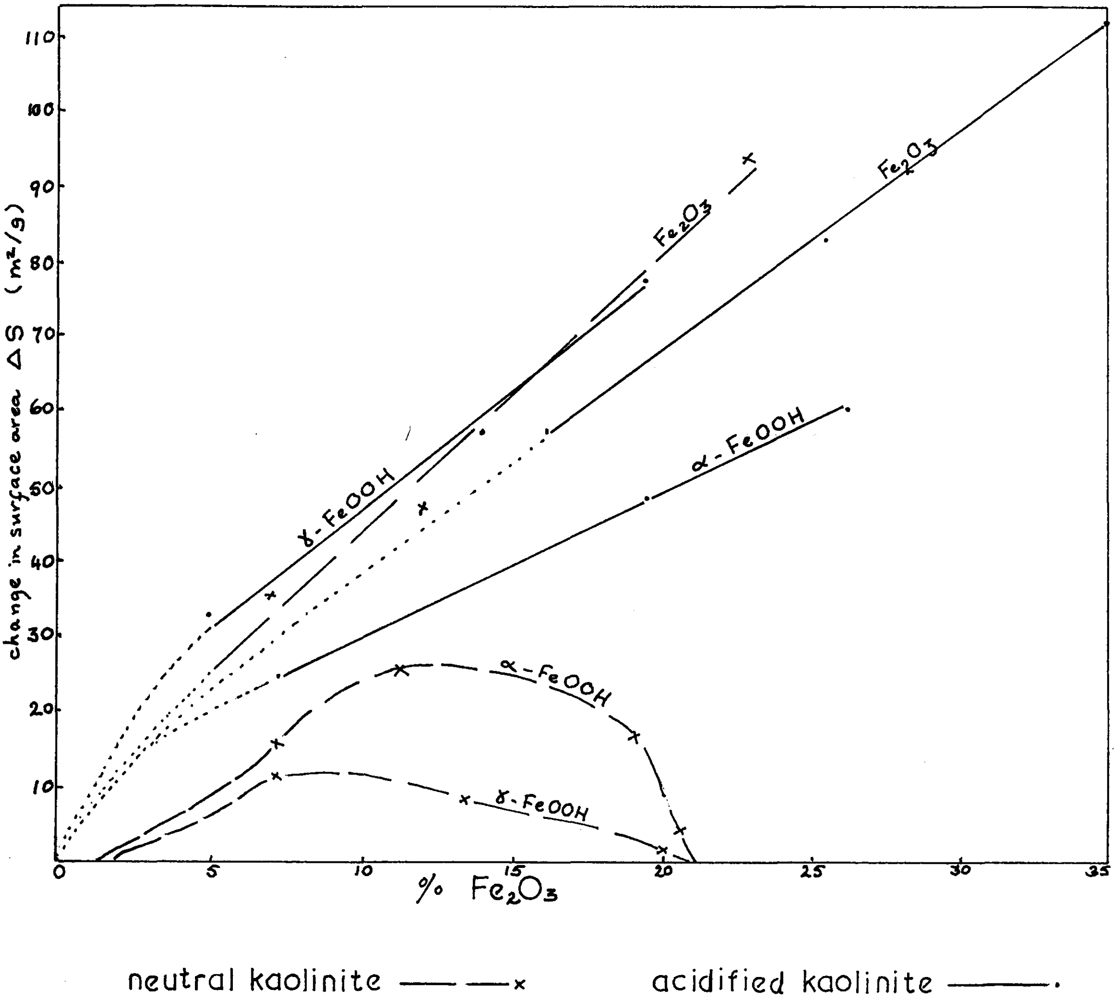
Early detailed studies were made on tropical soils, because these are often very ferruginous, and it was thought that they owed their good aggregation and porosity, or in the case of the laterites their cementation, to the iron oxides. Fripiat and Gastuche (1952) set out to establish whether iron oxide - clay complexes were formed by surface adsorption or whether there was merely an association in the matrix. They followed the changes in specific surface area and morphology (a) when soil kaolinite was deferrified and (b) when synthesised iron oxides were precipitated on the deferrified clay. Kaolinites deferrified rapidly at first, and their surface area diminished, but the rest of the iron oxide was chemically resistant and its removal produced an increase in surface area. This led them to suppose there was an amorphous and a crystalline phase. When the clay - iron oxide synthetic complexes were examined, there were remarkable differences between those whose kaolinite had been deferrified in neutral solution, by Deb's method (1950); and those whose kaolinite had been deferrified in acid solution, by Jeffries' method (1941); ie. between sodium and hydrogen clays. Neutral kaolinites adsorbed a finite amount of $\alpha$-FeOOH and $\gamma$-feOOH on their faces and the surface area first increased and then diminished as the clay flakes became cemented in the direction of the c -axis into well crystallised structures. Acid kaolinites took up an indefinite amount of those oxides and the surface area increased continuously, with the iron oxide engendering new adsorbing surfaces of porous, poorly ordered material. Amorphous $Fe_2O_3$ adsorbed in this way on both the H- and Na- kaolinites,(fig. 25).

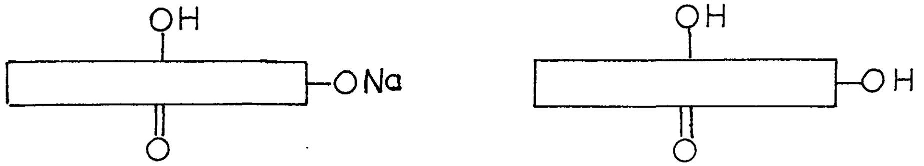
Fripiat and Gastuche concluded that there were two types of iron oxide; one chemically resistant and crystalline, which stacked the clay flakes by bonding to their surfaces, the other an amorphous material. The difference between the behavour of the acid and neutral kaolinites was thought to depend on the fact that adsorption was due to hydroxyl-hydroxyl interaction between the clay and the oxide. In acid solution, when the oxygens were protonated, this took place preferentially on the clay edges, but in neutral solution only the faces could provide the hydroxy groups for interaction.

Fripiat and Gastuche did not postulate mutual flocculation of oppositely charged colloids, and indeed

Fig. 25 Change in surface area of neutral and acidified Yangambi kaolinite when treated with $\alpha$-FeOOH, $\gamma$-FeOOH and $Fe_2O_3$.

(Compiled from Fripiat and Gastuche 1952)





– postulated mechanism –

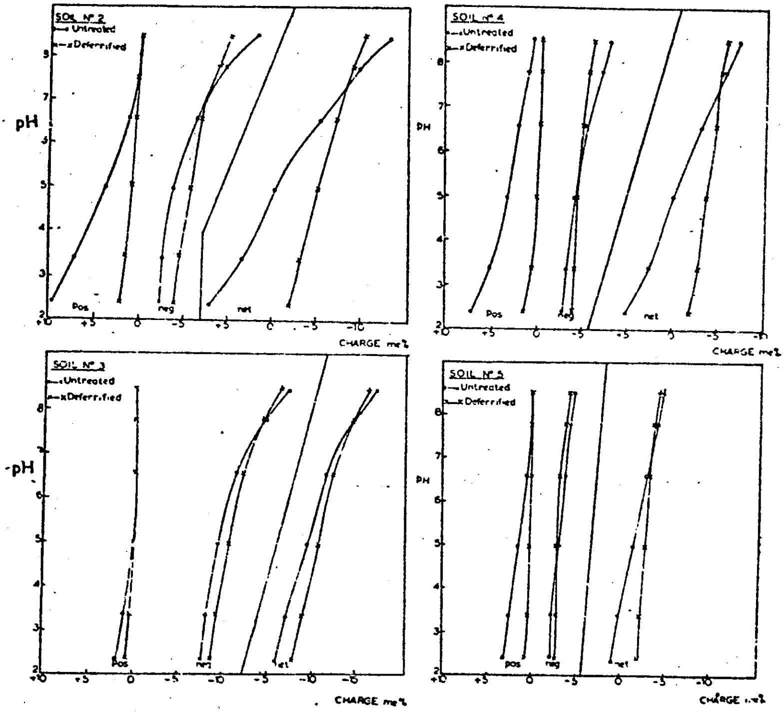
Adsorption on faces and flake cementation, via face OH only

Progressive adsorption on edges by OH - OH interaction their results were the reverse of what would be expected by that mechanism. Sumner (1961, 1963) continued this research with similar techniques, but while he supported the finding that the clay plates were surface-bonded by iron oxide, he ascribed it to the flocculation of negatively charged clay and positively charged oxide. This followed from his research into the extent to which free iron oxides contribute to the variations in positive and negative charge with pH. His examination of deferrified soil clays and of kaolinite-iron oxide complexes showed that the positive charge contribution of iron oxide decreased the nett negative charge on the clay below an isoelectric pH of 6 to 7, while above that pH, its negative charge contribution increased the nett negative charge on the clay, (fig. 26).

Sumner thus confirmed the view, that in some tropical soils at least, iron oxides were the aggregating agents. He dismissed alumina as important since only 'small amounts' were extracted by the dithionite, and suggested that aggregate stability control by alumina was likely to be confined to soils derived from volcanic ash. Organic matter was also found inessential for aggregation. Iron oxides were deduced to play opposing roles in the fertility of tropical soils: by flocculating

Fig. 26 The effect of free iron oxides on the variation of positive, negative and net electric charges with pH for some tropical soils.

(Sumner 1963)



with clay minerals they promoted soil structure, but their positive charge contribution tended to make the soils isoelectric at field pH and deplete them of plant nutrients.

Follett et al. (1965) continued the investigation of the ferruginous Darleith soils, described in Section 3 (ii), with a comparison of the effects produced by dissolution of iron after alkali pretreatment with the effects produced when this order was reversed. The results showed that a quarter to almost half the 'free' iron oxide was inaccessible to dithionite until the alkali soluble material had been removed. Alkali dissolution was seen to free a number of electron dense granules from the aggregates, and their disappearance after dithionite treatment was accompanied in general, by a decrease in specific surface area of 10 to 25%. The granules were assumed to be iron oxides, and their amorphous character, and the concurrent release of further amounts of $SiO_2$ and $Al_2O_3$ with the $Fe_2O_3$ in the extract, suggested that the iron oxides were bound up with silica and alumina in complexes.

The conclusions of this research into the two Drumboy soils were therefore, that the material binding the aggregates was for the most part, an organo-alumino-silicate complex, while the iron oxides, although amorphous, were finely particulate.

In the meantime, the belief that iron oxides were responsible for the good physical structure of tropical soils was beginning to be questioned. The evidence of many workers was strong in support of the belief, (eg. Lutz 1936, Chesters et al. 1957), but Sivarajasingham et al. (1962) and Alexander and Cady (1962) showed that the hardening process in many laterites was due to the growth of a continuous iron oxide matrix in which the other minerals were enclosed; and Deshpande, Greenland and Quirk (1964a), working with Australian red soils, reported that: "complete removal of free iron oxides by dithionite and 0•05N HCl had little effect on the structural stability of a number of soils, whereas partial extraction of aluminium oxides with 0•1N hydrochloric acid caused loss of stability." These authors countered Sumner's assumption that the positive charges were due to iron oxides with the argument that while freshly precipitated iron hydroxides had an isoelectric point about pH 7, (Mattson 1930a), the isoelectric points of aged oxides and hydroxides were much lower, and decreased with increasing crystallinity

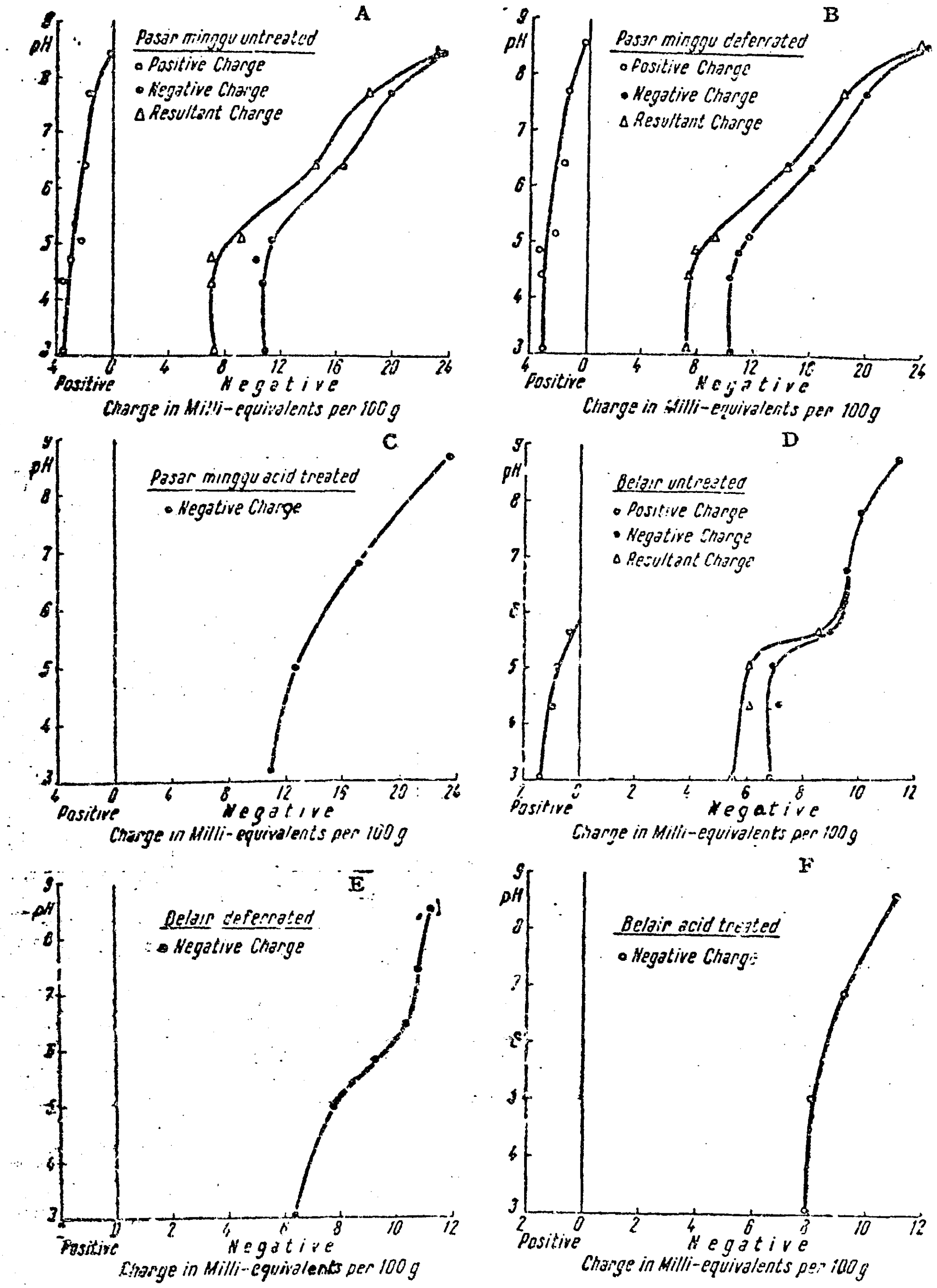
(Schuylenborgh 1950). A compilation of measured isoelectric points is given in Table 37. Moreover, soil iron oxides were often negative due to charge reversal by adsorbed anions.

These observations were confirmed by further experiments (Deshpande et al. 1964b) in which the effect of dithionite and 0•05N HCl on the charge characteristics of seven tropical soils, was compared with the effect of 0•1N HCl. The charges were determined by Schofield's method (1949). Only one of the seven soils showed more than negligible loss of positive charge with dithionite, and all the soils tested had a total loss of positive charge with the acid treatment. The major cation in the extract was aluminium. These results correlated with those obtained for aggregate behaviour, (fig.27). The authors suggested that aluminium oxide was present as finely divided, surface-adsorbed layers carrying positive charges, and that the iron oxides were present as discrete negatively charged particles. The negative charge was produced by adsorbed phosphate or some organic anion resistant to peroxidation such as oxalate.

A more detailed investigation followed (Deshpande et al. 1968), into the effect of removing iron oxide, alumina and organic matter on the aggregate stability of sixteen tropical soils, including soils of the same

Fig. 27 Effects of removing iron and/or aluminium on the charge characteristics of two lateritic soils.

(Deshpande et al. 1964b)



Positive (0—0) negative (•—•) and resultant (x—x) charges on Pasar Minggu lateritic red earth; *A* — after peroxidation only: *B* — after peroxidation and deferration with dithionite and 0.05N HCl; *C* — after peroxidation and treatment with 0.1N HCl; Belair lateritic podsolic soil; *D* — after peroxidation only; *E* — after peroxidation and deferration with dithionite and 0.05N HCl; *F* — after peroxidation and treatment with 0.1N HCl.

Table 37 Variations in the pH of isoelectric point for iron oxides and hydroxides.

| pH | Oxide | Source |
|---|---|---|
| 7·15 | hydroxide pptd. from $FeCl_3/NaOH$ | Mattson 1930a |
| 7·05 | hydroxide pptd. from $Fe_2(SO_4)_3/NaOH$ | Mattson 1930a |
| 6-7 | synthetic $\alpha$-FeOOH, $\gamma$-FeOOH and $Fe_2O_3$ precipitated on kaolinite | Sumner 1963 |
| 6·8 | $\alpha$-FeOOH | van Schuylenborgh (1950) |
| 5·7 | $\gamma$-FeOOH | van Schuylenborgh (1950) |
| 4·3 | $Fe_2O_3$ | van Schuylenborgh (1950) |
| 3·2 | well crystallised goethite | van Schuylenborgh (1950) |
| 2·1 | well crystallised hematite | van Schuylenborgh and Sanger (1950) |

type under grassland and cultivation. The treatments and their relative selectivities are given in Table 38. Aggregate stability was determined by permeability and wet sieving methods (Williams et al. 1966), and the relative permeabilities for two soils are depicted graphically in fig.28a,b. The results of the experiments are summarised as follows:-

(a) Aggregates were most effectively disrupted when organic matter was destroyed. In fig. 28 the ratio

$$\frac{\text{permeability after t hours}}{\text{permeability initially}},$$

was used as a measure of aggregate stability following treatments with dithionite and acid, periodate/borate or pyrophosphate. Pyrophosphate and periodate/borate completely disrupted the aggregates of the cultivated soils and pyrophosphate virtually destroyed those of the old pasture. The dithionite had little effect on the aggregates from the pasture, but decreased the permeability of the cultivated soil. The decrease could not unequivocally be ascribed to loss of iron oxide however, because the dithionite also removed some organic matter.

(b) Soils treated with dithionite/$HCO_3$/citrate lost stability, but treatment with $Na_2SO_4$/$HCO_3$/citrate led

Fig. 28a Relative permeability of aggregates from an Australian red earth under natural grassland after treatment with various reagents.

(Deshpande et al. 1968)

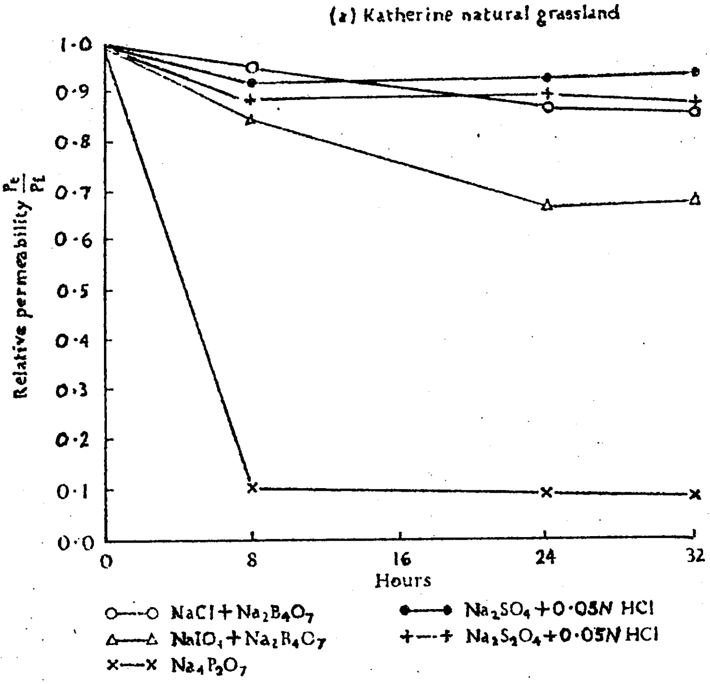


Fig. 28b Relative permeability of aggregates from a cultivated Australian red earth after treatment with various reagents.

(Deshpande et al. 1968)

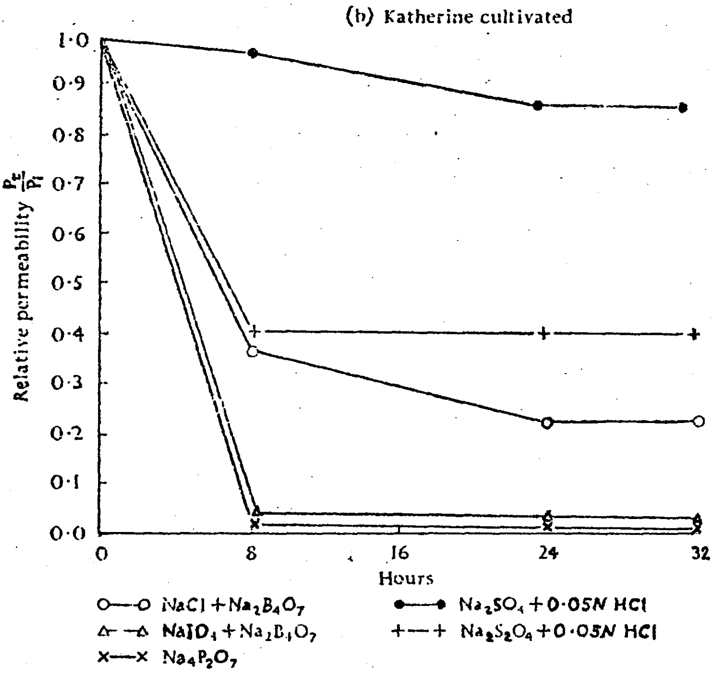


Table 38 Extractants and their controls used in experiments to detect soil aggregating agents.

(Compiled from Deshpande, Greenland and Quirk 1968)

| Extractants and Controls | Material extractable |
|---|---|
| 1. Dithionite and 0•05N HCl wash | Iron exide, alumina and silica. Some organic matter. |
| 2. $Na_2SO_4$ and 0•05N HCl wash | Alumina and silica. |
| 3. Dithionite /$NaHCO_3$/citrate | Iron oxide, alumina and silica. Some organic matter. |
| 4. $Na_2SO_4$/$NaHCO_3$/citrate | Alumina and silica. |
| 5. 0•1N HCl | Alumina and silica. |
| 6. 0•02M Na-periodate and 0•2M Na-borate | cis-glycol polymers, mainly polysaccharides, alumina and silica. |
| 7. 0•02M NaCl and 0•2M borate | Alumina and silica. |
| 8. $Na_4P_2O_7$ | Organic matter, chelated metals. |

to comparable loss, and since this control removed some organic matter and aluminium, the original stability was more likely due to these than iron oxide.

(c) Dithionite and acid treatment generally resulted in a decrease in specific surface area, suggesting the removal of discrete iron oxide; while the 0•1N HCl treatment produced larger surface areas, suggesting that aluminium oxides or allophane had bonded surfaces together.

(d) In a subsequent paper, Greenland, Oades and Sherwin (1968), showed electron-optically that the iron oxides were present as small granules, similar to those observed by Follett et al. (1965). They tended to be attached to the edges of the kaolinite plates or halloysite tubes in the manner of the negatively charged gold sols described earlier. There was no association with the clay faces. Face association was only observed when iron oxides were freshly precipitated on kaolinites. Their faces accepted a coating of spherical particles providing the pH was below 5. Above pH 5 and on aging, the particles coagulated.

The interesting conclusion to be drawn from these results is of the crucial role played by organic matter, even when this was present in very low amounts. The

Katherine old pasture and cultivated soils were quite typical and had 1•1 and 0•5% organic carbon respectively, yet the influence on soil permeability and aggregate stability was decisive. Next in importance were the aluminous materials; but in these soils at least, iron oxides were the bound rather than the binding material.

## 4. Organic matter and aggregate stability.

The importance of organic matter in creating crumb structured top soils is well known, but the mechanism of its interaction and the identity of those constituents which produce the aggregation is uncertain. Some interesting work on this has been done in the last decade and the following account is presented in chronological order, so that it can be shown how the problems were tackled and how the very conflicting evidence was resolved. There was much to support the suggestion that polysaccharides and other carbohydrates might fulfil or partially fulfil the aggregating role. Carbohydrates have widespread occurrence in soil as plant residues and bacterial products and may constitute 5 to 20% of the organic matter (Mehta et al. 1961), their ability to cause aggregation had been demonstrated, and their long chained polymers with hydroxy groups capable of interacting with clay seemed an ideal binding material. Mehta et al. (1960) however, pointed out that these correlations did not prove that polysaccharides were the cause and aggregation the effect. Creation of good structure with synthetic soil conditioners for instance, had been found to increase the biological activity of soil and thus its polysaccharide production. Hence they sought to establish whether or not polysaccharides were the aggregating agents by treating soil aggregates with chemical reagents that would destroy polysaccharides only.

The soil they examined was the topsoil of a brown earth from oak woodland and contained traces of calcium carbonate which were removed. Synthetic aggregates were made by grinding the same soil and then restoring aggregation with various polysaccharides. The soil and synthetic aggregates were subjected to: (a) Periodate and alkali treatment: this would selectively cleave and degrade cis-glycol polymers ie. the majority of polysaccharides. (b) An eight hour HCl hydrolysis: this would depolymerise most polysaccharides to their sugar components, but some other organic materials would also be destroyed. (c) Chlorine dioxide oxidation: this would attack lignin and humus,but leave polysaccharide untouched. Aggregate stabilities were determined by wet sieving (Yoder 1936).

The results were unexpected. The periodate and hydrolysis treatments disrupted the synthetic aggregates but did not affect the natural soil. The $ClO_2$ treatment disrupted the natural soil but not the synthetic aggregates. Two rendzinas gave the same results. The nature of the agent aggregating the soil was unknown, except that it was not polysaccharide.

Greenland, Lindstrom and Quirk (1962), extended this degradative approach to other soils, on the premise that aggregating mechanisms might vary between one soil type and another, and be influenced by cultivation history and even season. Top and subsoils of red brown earths, solonised brown soils and rendzinas with carefully selected cultivation histories were treated with periodate and borate, and their aggregate stability before and after treatment was measured by wet sieving and permeability techniques (Dettmann and Emerson 1959). The results of the experiment for red brown earth surface soils are shown graphically in fig. 29a,b and the authors' findings are summarised as follows:-

(a) Continuous wheat and wheat/fallow rotation topsoil aggregates lost all their stability after treatment. Soils from fallow plots retained least stability. Hence these soils were stabilised by periodate-sensitive materials.

(b) The stability of topsoil aggregates to periodate treatment increased with each increment of pasture. The stability of an eleven year old pasture was largely due to periodate-resistant materials.

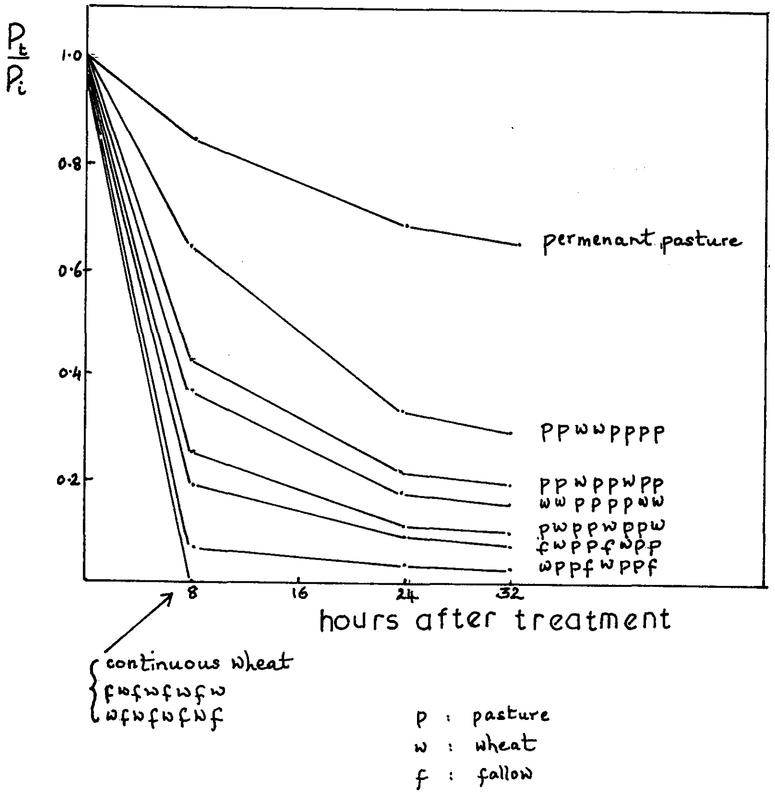
(c) The periodate-resistant materials were destroyed by cultivation. It was thought they might be due to fungal mycelium.

(d) Subsoils were mainly aggregated by periodate-sensitive material.

(e) Periodate treatment had less effect on the solonised brown soil and none on the rendzina except

Fig.29a <u>The effect of various rotational systems on the aggregate stability of a red brown earth: change in permeability with time.</u>

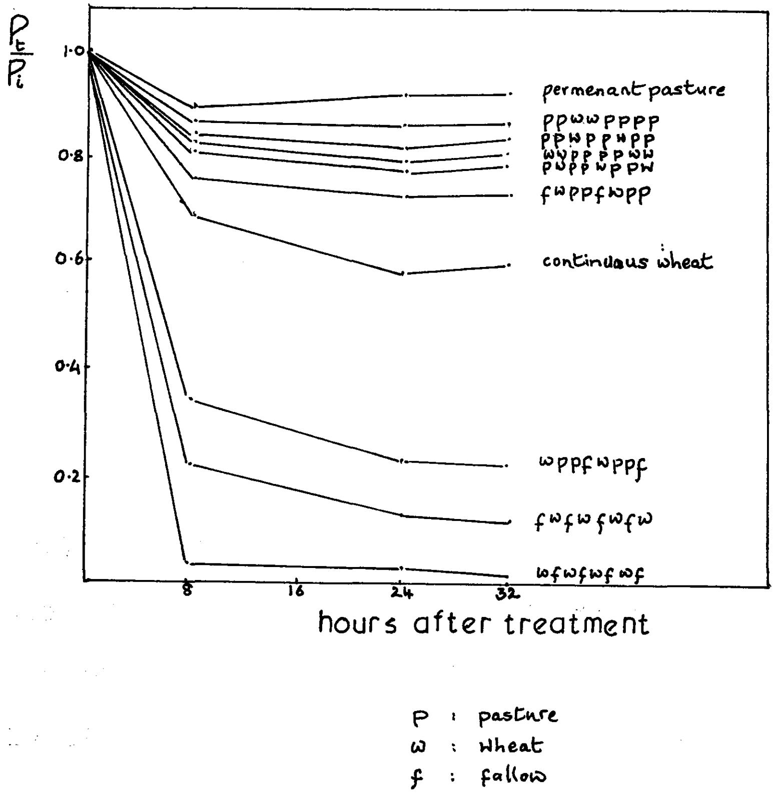
(Greenland et al. 1962)



Test : after treatment with 0.02N $NaIO_4$ and 0.2N $Na_2B_4O_7$.

Fig.29b <u>The effect of various rotational systems on the aggregate stability of a red brown earth: change in permeability with time.</u>

(Greenland et al. 1962)



Control : after treatment with 0.02N NaCl and 0.2N $Na_2B_4O_7$.

in one case where there had been intensive cropping. The stability was thought due to the calcium carbonate content of the soils.

At this stage a reservation should be noted with respect to the selectivity of periodate for polysaccharides. Mehta et al. had used acid hydrolysis as an alternative method for detecting them, but the periodate test itself and on its own, is only valid for those polysaccharides with cis glycols and there are a few that do not possess them. They include laminarin, a polysaccharide found in both seaweeds and plants; chitin, or N- acetyl glucosamine, present in fungal cell walls and insect exo-skeletons; certain highly acetylated pectins, such as are found in sugar beet; and certain branched polysaccharides. In addition, the complexing of metals by polysaccharides, as in magnesium fructoses, aluminium pectates and iron dextrans may, and to an unknown extent, limit the ability of periodate to gain access and oxidise the glycols.

It is conceivable therefore, that the periodate-resistant materials found under old pastures were of a special type, or firmly chelated by metal cations, or for some other reason of limited access to periodate.

Clapp and Emerson (1962), furthered these studies with a more detailed investigation of soils containing periodate-resistant aggregating materials ie. grassland and forest soils. They assumed that the mechanisms for clay-organic matter linkage included both hydrogen bonding of clay to polysaccharides and co-ordination with di- and tri- valent cations, and tested this assumption by applying periodate, pyrophosphate and pyrophosphate plus periodate treatments to aggregates from a variety of topsoils. Periodate treatments were for 6 or 24 hours. The aggregate stabilities were monitored by observations on their slaking and dispersion when immersed in a dispersing reagent for 72 hours. The results were found as follows:-

(a) Cultivated aggregates dispersed after 6 hours periodate treatment. Grassland aggregates dispersed almost 50% after 24 hours, provided they contained no $CaCO_3$.

(b) Grassland aggregates were unaffected by pyrophosphate alone and cultivated aggregates only slightly affected, but when this treatment was followed by periodate oxidation, there was complete degradation of all aggregates, except those containing high calcium carbonate. If calcium carbonate soils were pre-leached with 0.1N HCl, they too lost stability on treatment.

(c) Two forest soils were resistant to all combinations of treatment.

These results are of great interest. It appears from the 24 hour treatment of grassland soils with periodate that the reagent required more time in which to gain access, and this could have been due to the presence of chelated metals. The inability of the pyrophosphate to destabilise the aggregates until it was followed by periodate treatment suggests very strongly that in these soils, aggregation was due to polysaccharides, rather than to humic acids co-ordinating with clay by metal ion linkages. This was not the view of Clapp and Emerson, who suggested that the pyrophosphate extracted 'exchangeable cations' which co-ordinated organic polymer and clay. The writer believes that the most probable mechanisms would be:-

(a) That non-exchangeable di- or tri-valent ions such as $Ca^{2+}$, $Al^{3+}$, $Fe^{3+}$ were held in a clay-organic complex similar to that proposed by Edwards and Bremner (1967). This situation would appear to apply in the red brown earth Katherine grassland soil (Greenland et al. 1962), described in Section 3, where pyrophosphate was the most efficient extractant of stabilising material.

(b) That aggregates were stabilised almost entirely by polysaccharides and that a considerable proportion of these were complexing metal cations. This is commonplace with plant polysaccharides. Fructosans, for example, extracted from cocksfoot, have been found with up to 20% associated inorganic matter, and 10% is an average yield of ash from grasses (H.J. Duncan pers. comm.). Thus, the polysaccharide glycol groups could have been made inaccessible to periodate by complexing per se, or the glycol-metal complex could have bonded in turn to clay, and provided an additional co-ordinating mechanism to the hydroxy-hydroxyl interactions of clay and polysaccharide.

(c) The confirmation of the finding of Mehta et al. (1960) that the forest soil aggregates were not stabilised by polysaccharide, and the discovery that they were not stabilised primarily by links through polyvalent metals, suggests perhaps that tannates may be involved. The instability of the aggregates to $ClO_2$ oxidation, and the work by Handley (1954), Bloomfield (1953, 1955) and Davies et al. (1964) and others on the supply of phenolic constituents to forest soils, supports this possibility.

The strong stability of calcium carbonate soils and their ability to withstand high cultivation pressures is well known, although the reason for this is little understood. However, the fact that Greenland et al. (1962) noted some deterioration in the aggregate stability of an intensely cultivated rendzina could be cautionary, in view of the fact that the Agricultural Advisory Council's report (1970) claims that continuous cultivation of the calcareous soils of southern England can be carried on indefinitely without injurious effects. To the writer's knowledge it is not known whether calcium flocculation is sufficient to maintain structure or whether there is a lower limit of organic matter content below which structural problems might arise, even for rendzina soils. The Yangya soil quoted had a relative permeability $\frac{P32}{Pi}$ of 0.4 and a carbon content of 1.34% which was below the range of 1.71 to 3.06% for the other rendzinas.

The next step was to isolate the polysaccharides from the soils of various type and management history; in order to discover whether they differed in amount, origin, molecular weight, composition and difficulty of extraction. The methods used for their extraction and isolation are described in Chapter VI. Oades (1967) found for some Australian soils, that the proportion of organic matter in the form of carbohydrate depended on soil type, and not on cropping history or season, and that the decrease in carbohydrate under cultivated systems was accompanied by a parallel decrease in organic matter. Oades and Swincer (1968) and Oades, Swincer and Greenland (1968), working on a red brown earth, found that there was 3 times as much carbohydrate, and 2 to 3 times as much carbohydrate of molecular weight $>$ 100,000, in the pasture soil as in the cropped soil. Moreover, the pasture had 4 times as much microbial polysaccharide as plant polysaccharide. This was indicated by the proportions of mannose, arabinose, ribose, fucose and rhamnose, the bacterially dominant sugars, to galactose and glucose, the plant dominant sugars.

## 5. Aggregation in allophane soils.

The New Zealand allophane soils have been described as 'fluffy'. They are well aggregated and have good drainage but their structure is easily damaged. In the field it is found that: "the aggregates are friable and easily broken when dry. Rubbing when moist is apparently able to break weak linkages between silica and alumina so that the material yields in a manner and for a reason analagous to the yielding of wax near its melting point." ("Soils of New Zealand" 1968 2 p34).

The allophane pumice soils have low plasticity, but because of the vesicular nature of the grains, a high water holding capacity. After partial drying however, water is taken up reluctantly, so that the feel of an air-dry sample when moistened may suggest even less clay than indicated by mechanical analysis. Reworking of these soils causes substantial breakdown of the vesicular particles leading, in effect, to a different soil. The allophane yellow brown loams are slightly different in that they have high liquid and plastic limits. The natural water content is usually above the optimum and the plastic limit, so that considerable drying is required before they can be handled in an engineering context. After air drying however, many of them behave like sandy soils and can then be compacted satisfactorily ("Soils of New Zealand"

2 p.157). The unusual water-holding properties of the soils is attributed to the way in which part of the water is held in the interior of the allophane 'gel', so that it can only be removed with difficulty. In an agricultural context, this confers valuable water storage capacity and coarse textured soils classed as sands, sandy silts and sandy loams have available moistures ranging from 10 to 30% of soil volume.

In allophane topsoils, the presence of organic matter strengthens the fragility of the aggregates and extends the range of soft consistency to allow a latitude in operations. The importance of an adequate organic matter content has already been seen in Chapter II 2 where the effects of its exhaustion on the structure of some market garden soils in North Island were described. The return of these soils to fertility by putting them under grass may take some time, because although allophane soils are noted for their rapid build up of organic matter, they are also remarkable for the comparative slowness with which it is broken down. Jackman (1964) pointed out that ploughing inverts the soil and accelerates the immobilisation of N, S and P, and he recommended that where the soil was deficient in any of these, as in the allophane soils, ploughing should be infrequent, so as to disturb the topsoil as little as possible and maintain the organic matter in a near steady state.

The Tirau, Egmont and Taupo soils have 10•6, 12•3 and 10•1% organic carbon in their top few inches. The Scottish Darleith soils have deep $A_1$ horizons, and unusually high 'loss on ignition' values have been recorded (D.B. Patterson, pers. comm. 1971).

These field observations of the affinity of allophane for organic matter were confirmed by Wada and Inoue (1967) who used rotted clover leaf extracts to study its uptake by allophane and montmorillonite soil clays over a period of nine months. The montmorillonite was saturated after taking up 6•5 mg carbon/g soil clay, while the allophane remained unsaturated, with an estimated capacity of 28-44 mg carbon/g soil clay. The montmorillonite also lost organic matter more rapidly by mineralisation and leaching. Further differences were found in that montmorillonite showed fairly strong preferences for certain constituents in the extract, and a higher percentage of the adsorbed carbon was re-extractable by polyphosphate, while the allophane showed less preference in adsorption and the carbon was less extractable by pyrophosphate.

High organic matter uptake by allophane is to be expected if the mechanisms of clay-organic matter interaction discussed in Section 4 are correct. It should have an affinity for polysaccharides by virtue of its array of surface hydroxy groups allowing multiple linkage by hydrogen or van der Waals bonding, and it should have an affinity for the complexing constituents in humus and polysaccharide on account of its exposed and susceptible aluminium. These reactions taking place on the large surface areas of the particles would allow organic matter to be adsorbed in considerable amounts. In addition, as discussed in Chapters III 4 (iii) and VII 2, the positive charge of the aluminium in the complex, would flocculate allophane with the organic matter.

## CHAPTER VI : THE EXTRACTION OF ORGANIC MATTER FROM SOILS.

### 1. Factors governing the choice of method.

The method chosen for the extraction of organic matter from soils depends upon the end in view. Possibilities might include (a) maximum recovery (b) characterisation of organic matter constituents (c) identification of the organic-clay bonding mechanism (d) isolation of a fraction in order to conduct experiments.

(a) Maximum yield. Classical methods for extracting organic matter have used sodium hydroxide, and it is still the best single extractant known. Recoveries of up to 70% are commonplace. It is unsuitable from the point of view that degradation of the material and interaction of the oxidised products can give rise to artefacts. Phenols for example, become polymerised into condensed and unidentifiable products, and these may precipitate out other substances such as protein.

(b) Characterisation of organic matter constituents. If it is intended to identify the original constituents, a method is required which is both mild and selective. Such methods are low yielding and therefore suffer from the disadvantage that the material may be non-representative.

(c) *Identification of the organic-clay bonding mechanisms*. Hydrogen bonding mechanisms may be suggested by the material extracted in acid; and di- and tri-valent metal bonding by the material extracted with complexing agents such as fluoride, EDTA or pyrophosphate.

(d) *Isolation of a fraction for experiments*. The most common type of experiment is the adsorption experiment, in which the relative adsorptive capacities, or the character of the adsorption isotherms are studied for different clays with a specific fraction of organic matter, or for different fractions of organic matter on a specific clay. For example, Finch et al. (1966) isolated soil polysaccharide to study its adsorption on kaolinite and on $H^+$saturated and untreated montmorillonite

The discussion of extractants in section 2 is confined to polysaccharide extractants, since only polysaccharides were examined in the experimental work. The writer has used the results of a study of a red brown earth by Swincer et al. (1968) to illustrate comparative yields by various methods consistently.

## 2. Extractants of Soil polysaccharides.

### (i) Flotation.

Separation of the 'light fraction' of partly decomposed plant remains can be made by some densimetric procedure such as that described by Ford and Greenland (1964) or Ford, Greenland and Oades (1969). This is useful both because much of the material is cellulose and therefore resistant to most extraction procedures, and because it may account for a high proportion of the soil carbohydrate. Swincer and Oades (1968) recovered two fifths of soil carbohydrate in this fraction.

### (ii) Hot water.

Shaking of soil in water at 70-100°C. has been used to extract polysaccharides, the advantage lying in the ease of purification afterwards, since very little humic material is liberated. Up to one quarter of soil carbohydrate may be released. (Swincer et al. 1969). The disadvantage lies in the degradation of polymers by hydrolysis.

### (iii) Alkalis.

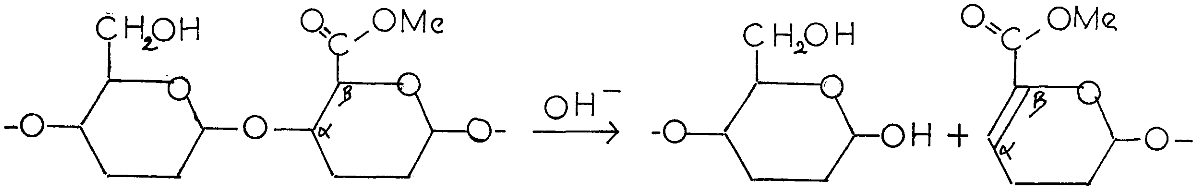
The efficiency of alkali extraction depends upon

the fact that both clay and organic matter are peptised and released to a large extent from their adsorption sites. This is brought about by the overall negative charge repulsion, the breaking of hydrogen bonds and the dissolution of some active aluminium. On the whole, alkali is regarded as a fairly safe solvent for polysaccharides in that glycoside bonds are stable to it under mild conditions, such as cold 0·5 N NaOH. Swincer et al. (1968) extracted 30% of total soil carbohydrate in this way in a sixteen hour extraction. Disadvantages include: heavy contamination with humic material, so that the polysaccharides must be purified by methods described in section 3; possible contamination with dissolved silica, which must be removed by its precipitation; and the unknown degree of alkali degradation to which the heterogeneous mixture of polysaccharides may be subjected. It is obviously impossible to monitor these effects unless the original structures are known in the first place. No confident statements can be made on the quantities and composition of polysaccharides extracted in alkali, for the degradation could by quite serious and yet go undetected. This is because the stability of the glycosidic bonds may be undermined by (a) reducing groups
(b) $\beta$-elimination reactions. In addition, oxidation

and interaction with other components may occur.

(a) Reducing groups: reducing sugars are rapidly converted into saccharates in the presence of dilute alkali, and although masked in the polysaccharide polymer, a slow stepwise degradation may occur at the reducing end of a molecule, giving rise to a 'peeling' reaction which is only brought to an end when the release of the saccharate is inhibited by un unfavourable glycosidic linkage. In the absence of oxygen and at low temperature this reaction is slow, but in the presence of oxygen, the destruction is faster and the products more complex and difficult to predict. Soil extractions are particularly hard to control, because trace quantities of $Fe^{3+}$ or $Cu^{2+}$ in alkaline environments will rapidly oxidise reducing sugars irrespective of the exclusion of oxygen from the system. Choudri and Stevenson (1957) proposed that addition of $SnCl_2$ to the soil suspension would reduce this risk.

(b) $\beta$-elimination: a second mechanism for the rapid depolymerisation of some polysaccharides can be explained on the basis of $\beta$-elimination reactions; for if an electron withdrawing group such as $-C=O$ or $-C\equiv N$ is attached to the $\beta$ carbon of the constituent, then this constituent is readily released. Polysaccharides with a carbonyl group β to a glycosidic bond depolymerise rapidly, with conversion of the released reducing sugar to saccharinic acid. Pectins with a methyl ester at C 6 behave in this way and it is considered inadvisable to extract them at a pH above 6. (H.J. Duncan, pers. comm.) The mechanism is illustrated below:-



(c) Oxidation: other oxidising reactions of individual sugars can occur in the presence of oxygen or electron accepting agents such as $Cu^{2+}$ and $Fe^{3+}$.

(d) Interactions: interaction of the polysaccharide with other components of the organic matter via covalent bonds or metal ion linkages may produce artefacts in unknown amounts.

(iv) Dilute mineral acids.

Inorganic acids are relatively more efficient in extracting polysaccharide than humic material and moreover they tend to hydrolyse the bond between the two components. Hence, acid extracts are fairly readily purified. Any tendency of the polysaccharides themselves to hydrolyse can be prevented by carrying out the extraction at 3°C. (Barker et al. 1965, 1967). Use of hydrogen fluoride may increase the yield by dissolving the clay silicates, but fluoride interferes with subsequent analysis. The great disadvantage in the acid extraction method is the low recovery and its non-representative character. Swincer et al. (1968) extracted only 9% of the total soil carbohydrate in 1NHCl after 16 hours at 20°C. However, it was found a very useful pretreatment to the 0•5N NaOH extraction and stepped up the yield of the latter from 30 to 41 percent.

The reason for the low yields lies in the fact that uronic acid polymers and most of the neutral polysaccharides are either insoluble or considerably less soluble in dilute acid than they are at pH 7 and above. Hydrogen bonding between the unionised carboxylic acid groups brings about the polymers' precipitation. The exceptional behaviour of pectin can be explained in terms of its methyl ester groups which limit hydrogen bonding and make this polysaccharide soluble.

### (v) Organic reagents.

A number of organic reagents have been used to extract polysaccharide. Swincer et al. (1968) extracted 29% of the carbohydrate with a dimethyl formamide preparation. Their most successful extractant was a combination of acetic anhydride and concentrated $H_2SO_4$ which yielded 76% of the carbohydrate. When this was used in sequence with 1N HCl and 0•5N NaOH pretreatments, carbohydrate yields of up to 94% were obtained for a variety of soil types. These organic reagents however, degraded the polymers, and were not recommended for polysaccharide characterisation.

### (vi) Complexing reagents.

It is obviously desirable to extract organic matter under the mildest possible conditions ie. at room temperature and near neutral pH. Complexing reagents such as pyrophosphate and EDTA have been used for this purpose but in a review by Swincer et al. (1969) yields of carbohydrate were said to be less than 5%. It is predictable that best recoveries may be obtained where clay and organic matter are co-ordinated by some polyvalent metal linkage, and an illustration of this is suggested if one analyses the results of a study by Schnitzer et al. (1958). This is given in some detail because of the information that can be gleaned in a number of respects.

The authors were comparing the effectiveness of a range of extractants for the removal of organic matter from the $A_0$ and $B_{21}$ horizons of a Canadian podzol. The extractants, extraction pH and percentage of carbon extracted are shown in Table 39. 2g samples of the $A_0$ and 10g samples of the $B_{21}$ were stood overnight in 10 and 50ml respectively of extractant, centrifuged at 2000 rpm for 5 minutes and the supernatants filtered. The residues were washed and centrifuged repeatedly until the supernatants were colourless, and these washings were added to the extracts. The table shows very low per cent carbon extractions for the $A_0$ horizon except for the 0•5N NaOH which recovered 24•8%. The $B_{21}$ horizon produced astonishingly high percentages. The alkali reagents NaOH, $Na_2CO_3$, $Na_3PO_4$/pHi 12 yielded 96•3, 92•3 and 93•6% respectively. The complexing reagents pyrophosphate/pHi 7, NaF/pHi 7 and EDTA/pHi 4•2 yielded 82•6, 88•7 and 86% respectively. Borate/pHi 9•2 yielded 80•8%, HF/pHi 2•2 83% and HCl only 11•2%.

The credibility of the absolute values of these high amounts will be discussed shortly, but the complexing and alkali extractions of the $B_{21}$ can still be taken as very efficient. This should be attributed, in the writer's view, to a high allophane content in

Table 39 Extraction of organic matter from the $A_o$ and $B_2$ horizons of a podzol by various extractants.

(Compiled from Schnitzer et al. 1958)

| Extracting solution | pH initial | pH After extraction | | Percentage of carbon extracted | |
|---|---|---|---|---|---|
| | | $A_0$ | $B_{21}$ | $A_0$ | $B_{21}$ |
| 0·1M $Na_4P_2O_7$ | 7·0 | 5·2 | 6·2 | 5·5 | 82·6 |
| 0·1M $Na_3PO_4$ | 12·0 | 7·3 | 9·4 | 9·1 | 93·6 |
| 0·1M $Na_2B_4O_7$ | 9·2 | 7·7 | 8·1 | 7·7 | 80·8 |
| 0·5M NaF | 7·0 | 6·4 | 10·3 | 4·4 | 88·7 |
| 0·5M NaCl | 5·5 | 2·9 | 3·9 | 2·5 | 2·2 |
| 0·5M $Na_2CO_3$ | 11·2 | 9·5 | 9·9 | 8·3 | 92·3 |
| 0·5M NaOH | 13·1 | 12·6 | 13·1 | 24·8 | 96·3 |
| 0·5% HCl | 1·4 | 1·7 | 2·9 | Tr | 11·2 |
| 0·5% HF | 2·2 | 2·1 | 4·0 | Tr | 83·1 |
| 0·2M EDTA | 4·2 | 3·7 | 4·2 | Tr | 86·0 |

the podzol subsoil, as is normally found. Active aluminium was thus complexed by fluoride, pyrophosphate and EDTA, with displacement of the organic matter. In alkali, organic matter was peptised and its extraction assisted by dissolution of mobile aluminium. The success of the borate extraction could be explained on the grounds that it displaced cis-glycols from interacting with the clay surface by forming a borate complex. This in turn, suggests that polysaccharides predominated in the horizon. Greenland et al. (1962) observed that subsoils contained a greater proportion of their organic matter as carbohydrate than topsoils.

The high yields of the $B_{21}$ need an explanation especially in view of the fact that the soils were merely stood overnight and not shaken, and that only one extraction was made. The authors' report that the extracts were found by X-ray diffraction to contain some clay suggests that the extraction was incomplete. Washed extracts centrifuged at only 2000 rpm for 5 minutes would almost certainly have contained colloidal clay and allophane in particular. Moreover, the percent ash contents were very high, ranging from 23% for HCl to 41•9% for the pyrophosphate, and this must have contained clay as well as extracted oxides. The authors also found large and variable amounts of dialysable material suggesting that very low molecular weight materials were extracted. The ratios C in dialysed residue: C in dialysate ranged from 0.5 to 4.0 but without any consistent pattern relating to the extractant. The ratio was 1.5 for NaOH and 4.0 for $Na_2CO_3$. The writer would have suspected that the dialysate contained small glycerol-like artefacts leached from the dialysis bags, similar to those described in the chapter on artefacts in Part Two of this research, but apparently the dialysate concentration was found by subtraction so that at present no explanation can be put forward.

This last study might encourage the prediction that fairly high yields of organic matter, including polysaccharide, could be extracted under mild conditions at pH 7.0 by a complexing agent from a soil high in allophane. Such an extraction would allow analysis of representative, undegraded polysaccharide; and by comparing the results with those of a parallel NaOH extraction, the degree of alkali degradation in the soil situation could be assessed.

## 3. Purification of polysaccharide extracts.

Purification involves the separation of the non-polysaccharide material and the removal of salts and metal cations. The humic acid fraction has usually been precipitated from an NaOH extract with HCl. Swincer et al. (1968) however, recommended leaching the extract through a coarse $H^+$ Dowex 50 resin. This took up the metal cations, trapped the precipitated humic fraction and released the purified carbohydrates. Only 1% of the total carbohydrate was lost in this way compared to an 8% loss when the humic acid fraction was precipitated with HCl.

The most commonly used method of secondary purification to remove salts, solvents and small molecules has been dialysis is visking tubing against distilled water. Considerable losses have been noted. Swincer et al. (1968) report: "About 40% of the carbohydrates in the fulvic acid fraction were lost during dialysis in visking tubing against distilled water. Half of this carbohydrate was recovered in the dialysis water, presumably as low molecular weight fragments, but not as monosaccharides. The other half was sorbed on the tubing and could not be recovered by washing (Clapp 1957; Müller, Mehta and Deuel 1960)."

Other purification procedures include: leaching through acid-washed animal charcoal, which leads to low recoveries; precipitation, as with ethanol, or with cetylammonium bromide, neither of which are specific for polysaccharides; gel filtration, which separates high molecular weight polysaccharides from both humic acid and low molecular weight polysaccharides, but cannot separate these from each other. A recommended procedure is to pass the extract through Polyclar AT, a strong adsorbent of polyphenolic compounds. Swincer et al. (1968) obtained 95% carbohydrate recovery in this way when the pH was lowered to 2.

## 4. Fractionation of polysaccharide extracts.

The most successful fractionations are those based either on molecular size ie. gel filtration (Oades and Swincer 1968, Swincer et al. 1968), or on differences in charge density ie. anion exchange chromatography. This last method has given the best defined fractionations so far reported for soil polysaccharides. It was suggested by Mehta et al. (1960) and has been used successfully by Barker et al. (1965, 1967) and Finch et al. (1966).

## 5. Measurement and characterisation of polysaccharides.

Colorimetric methods can give estimates of the carbohydrates extracted from the soil when preceded by hydrolysis of the polymers to monosaccharides. Hydrolysis conditions vary for the carbohydrate fractions, but polysaccharides in general can be recovered as monosaccharides after hydrolysis for 2 hours in 72% $H_2SO_4$ at 20°C. followed by boiling for 16 hours in 1N $H_2SO_4$. the sugars can be determined by a colorimetric method such as the phenol-sulphuric method or the anthrone method. These determinations are limited in accuracy because equimolar solutions of different sugars vary slightly in their colour intensity.

After desalting, the sugars can be identified by paper chromatography or gas liquid chromatography.

# CHAPTER VII: THE ION EXCHANGE PROPERTIES OF ALLOPHANES AND NON-CRYSTALLINE MATERIAL.

## 1. The anomalous behaviour of allophane colloids.

### (i) Introduction.

In this chapter the observed ion exchange properties of allophane clays as established by experiment are described. These properties have been interpreted along certain lines by modern workers in this field. The writer has found however, in almost every respect, that it has been a great advantage to turn to the studies of synthetic and soil colloids made by Sante Mattson some forty years ago, and that only in the light of his interpretations can the apparent vagaries of allophane behaviour be understood. It has been found necessary to present these aspects of his studies on the laws of colloidal behaviour in considerable detail both in order to illuminate the current work on allophanes, and because much of his contribution to soil science appears to have been overlooked in recent years.

### (ii) Ion uptake by physical adsorption.

Allophanes have a pH dependent charge, with an isoelectric point in the range of field pH. Perhaps it was this which encouraged an early view that they had low cation exchange capacities. Birrell and Fieldes (1952) found on the contrary, that they were relatively high. Egmont clay had a CEC of 54 me/100g, comparable to the CEC values reported by Mattson (1926a,1928b,1931a). The conflicting evidence was resolved by Birrell and Gradwell (1956) who discovered that high or low cation exchange capacities could be obtained depending on the method used. The results were controlled by the strength and pH of the leaching solution, the cation species, and the alcohol:water ratio of the washing liquid. When the entrained salts were washed with water, a high percentage of the adsorbed cations were removed. Since none of these variations were believed to have a major effect on the CEC determinations of crystalline clays, the authors predicted that some kind of adsorption mechanism other than base exchange was occurring, and tested their hypothesis with equilibrium experiments to measure ion uptake.

It was found that when cation uptake was plotted against reduced concentration, the curves resembled portions of gas adsorption isotherms and fitted the BET equation for multilayer physical adsorption of gases on solid surfaces. The influence of surface area on adsorptive capacity was shown, it was thought, both by its increase with increasing salt concentration and by its dependence on the size of the hydrated cation, the order of uptake being of the pattern $Ba^{2+} > NH_4^+$ $Na^+ > Li^+$ . The physical adsorption of the ions was further demonstrated in their susceptibility to hydrolysis or desorption by water. Table 40 and fig. 30 illustrate these results with two allophane soils. The adsorption isotherm for montmorillonite is also given.

A pH effect was superimposed on the adsorption patterns, in that the cation exchange capacities rose with a rise in the pH of the leaching solution. There was also some indication that anions were taken up as well as cations (Table 41 ). The effect was slight for chloride at low concentrations, but increased in the stronger solutions; a near normal solution of barium acetate however took up Ba: OAc in the ratio 4:1. It was concluded that the physically adsorbed ions constituted an interference, and that "where the presence of such amorphous material is suspected in soils, the conventional CEC methods should be supplemented by equilibrium methods to test the significance of the CEC results."

Wada and Ataka (1958) investigated both the physical adsorptive and the pH effects. They concluded

Fig. 30 Variation of BET adsorption isotherms for Tirau clay with the adsorbed cation and anion species.

(Birrell and Gradwell 1956)

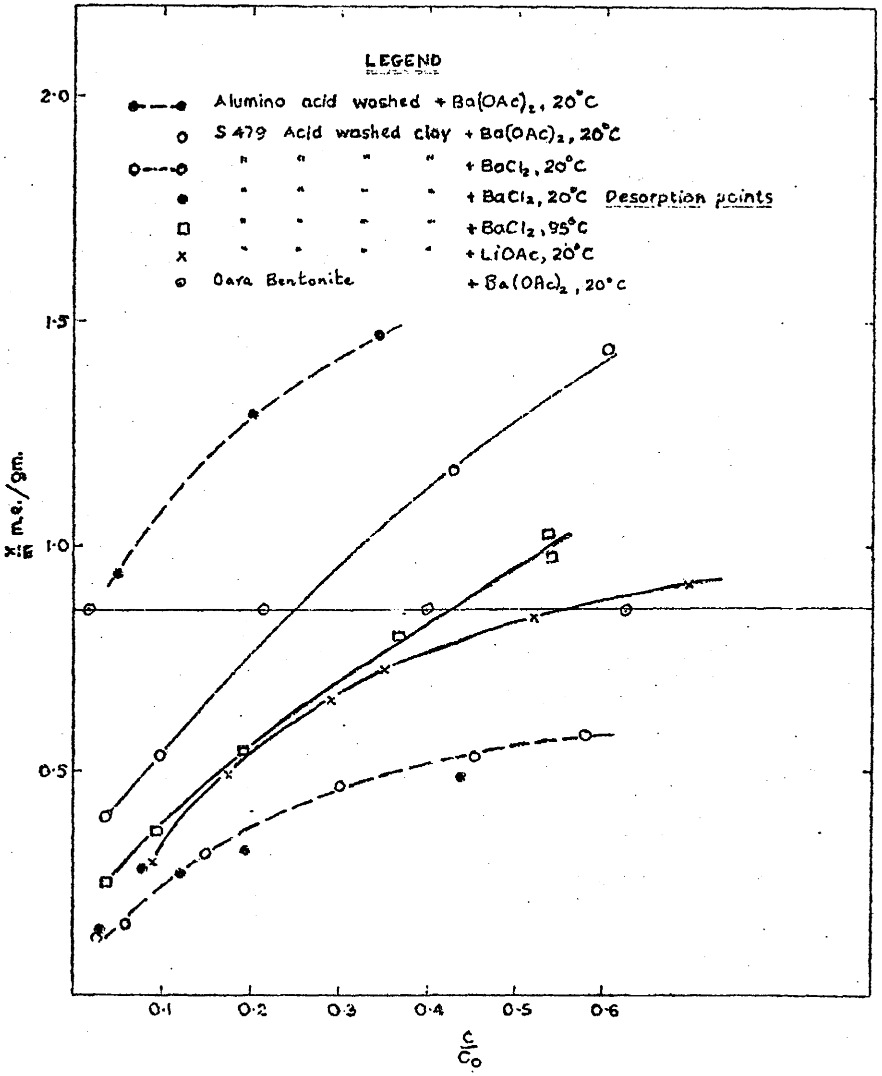


Table 40 <u>The effects of (a) the strength of the leaching solution and (b) alchol or water washing on CEC determination of water-sorted ash allophane soil</u>.

(Compiled from Birrell and Gradwell 1956)

| Normality of $NH_4OAc$ solution | CEC me/100 g | |
|---|---|---|
| 100 ml. | 50 ml washing alcohol | 22 ml washing water |
| 1.74 | 42.5 | 8.0 |
| 0.87 | 39.9 | n.d. |
| 0.438 | 34.7 | n.d. |
| 0.087 | 22.1 | n.d. |

Table 41 Ion adsorption at 20°C. for Tirau allophane soil (NaOH dispersed) at pH 7, for Ba $(OAc)_2$ and $BaCl_2$.

(Birrell and Gradwell 1956)

| Normality of original salt | Barium uptake me/100 g | Acetate uptake me/100 g |
|---|---|---|
| 3•166 | 230 | 131 |
| 2•477 | 207 | 92 |
| 2•018 | 191 | 78 |
| 1•072 | 170 | 43 |
| 0•485 | 147 | 29 |
| 0•096 | 128 | 16 |
| | Barium uptake | Chloride uptake |
| 1•995 | n.d. | 68 |
| 1•00 | 120 | 2 |
| 0•50 | 110 | 0.2 |
| 0•253 | 108 | nil |
| 0•065 | 94 | nil |

that in allophanes there were two mechanisms of uptake operating simultaneously: one was a non-coulombic salt adsorption in which both cation and anion was taken up in almost equal amounts. It was independent of pH but dependent on concentration. The other was a coulombic reaction, largely independent of concentration but dependent on pH. Measurements of uptake of ammonium chloride by the Schofield method (1949) showed that cation uptake perdominated at high pH and anion uptake predominated at low pH.

It thus appears that the high 'apparent' cation exchange capacities for allophanes are correlated with their good water storage properties. The mechanism of the water adsorption is still in debate. Allophanes have a great capacity to adsorb polar liquids, while at the same time about two thirds of their interior surface are inaccessible to nitrogen gas. The specific surface area of a Choyo clay for example, was measured as 481, 474, 434 and 169 $m^2/g$ when glycerol, water, ethylene glycol and $N_2$ respectively were used as adsorbent (Aomine and Otsuka 1968). In this differentiation between the behaviour of their interior and exterior surfaces, allophanes resemble montmorillonite. Their capacity to adsorb water per unit area however, is greatly in excess of montmorillonites, particularly at low relative humidity % (Aomine and Otsuka 1968). Fripiat (1964) suggested that since the charge density on the allophane clay was normal for clay, the greater adsorption of water might be due to the large amount of OH on the surface together with a unique pore size.

There is some discrepancy between the findings of Birrell and Fieldes ("Soils of New Zealand" 1968 2 p.40) on glycol adsorption and those of the authors above, for Birrell and Fieldes state that the BET method gave higher specific surface areas than the glycol desorption method of Dyal and Hendricks (1950). This is of some importance in the interpretation of the adsorption isotherms of Birrell and Gradwell (1956). They measured the specific surface area of a Tirau clay as 270 $m^2/g$ by the BET method, and then calculated that the hydrated barium ion would give a monolayer coverage at 0.72 me/g. Barium uptake at 1.3 me/g for N $Ba(OAc)_2$ at pH 7.7 suggested multilayer coverage. But if, as according to Aomine and Otsuka, the surface accessible to nitrogen was only 1/3 of the total surface, then monolayer coverage would not have been achieved even at 2 N $Ba(OAc)_2$, and the fit of the adsorption curve to the BET equation must have been due to some other influence.

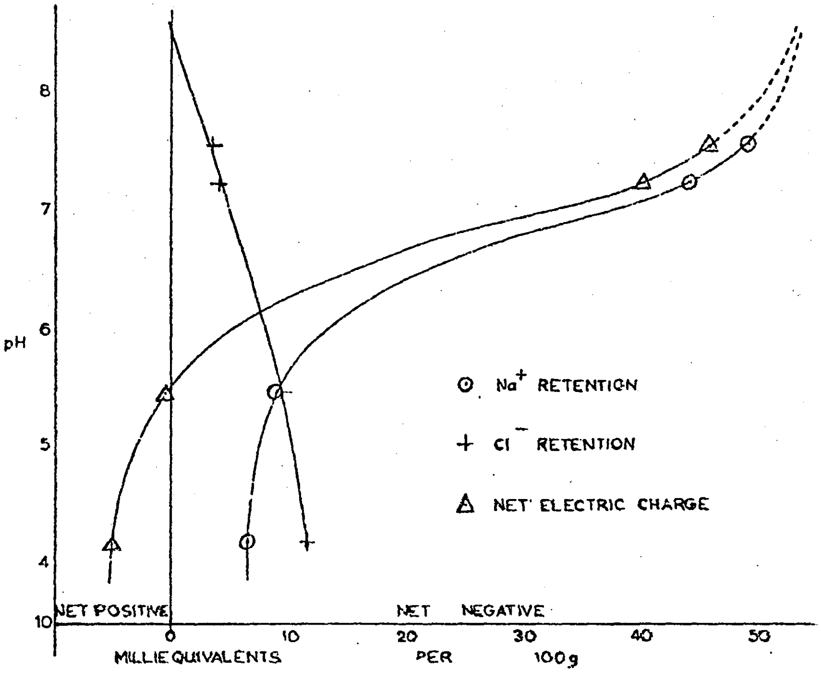
### (iii) The pH dependent charge of allophane.

Fieldes and Schofield (1960) and Birrell (1961) investigated the effects due to the pH dependent charge on allophane. Fieldes and Schofield were interested in the possibility of characteristic activity of specific sites. Birrell's interests were in cation exchange capacities and ion fixation.

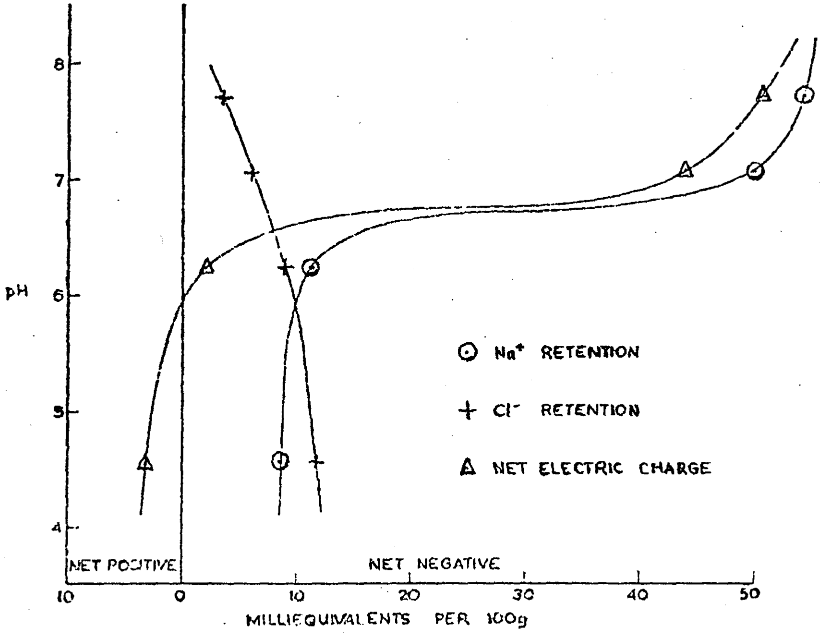
Fieldes and Schofield studied the variation in ion uptake with pH. Samples of allophane and other soil clays were leached with 0•2N NaCl solution adjusted to different pHs until the leachate approached a desired steady value, and the amounts of $Na^+$ and $Cl^-$ retained by the clay was measured after their displacement with ammonium nitrate solution (Schofield 1949). Their results are reproduced in figs. 31 and 32. Allophane clays had a nett positive charge at low pH; a pH of exchange neutrality, assumed to be zero charge, at pH 5•5 (Taupo) and 6•0 (Egmont); and thereafter a nett negative charge which increased to high values in a strongly buffered region between pH 6•5 and 7•5. Soils containing layered clays, such as the Taiti soil derived from greywacke and the Rothamsted soil, had characteristic nett negative charge at all pH values. Whatatiri gibbsitic clay exhibited both positive and negative nett

Fig. 31 Variation of electric charge with pH for two New Zealand allophane soils.

(Fieldes and Schofield 1960)



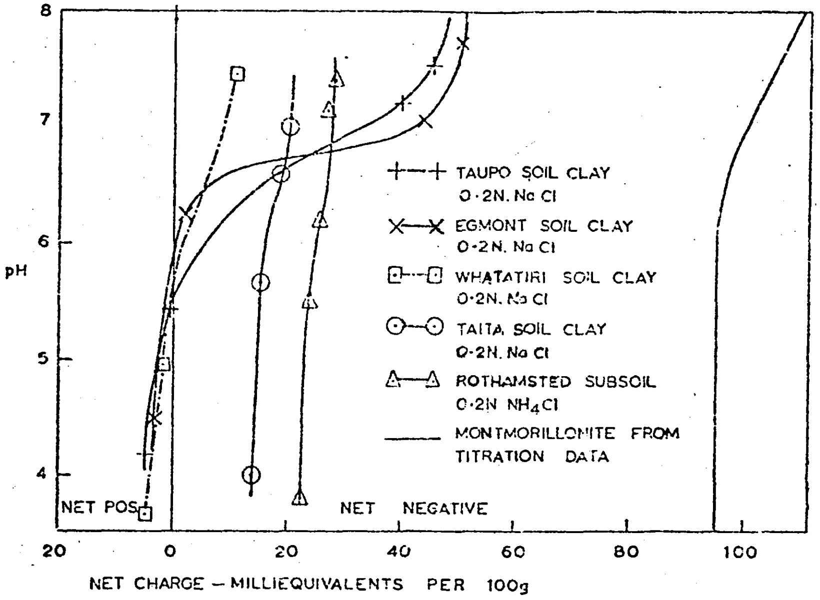
Electric charges on Taupo soil clay in 0·2N NaCl at different pH.



Electric charges on Egmont soil clay in 0·2N NaCl at different pH.

Fig. 32 Net electric charges on various materials at different pH values.

(Fieldes and Schofield 1960)



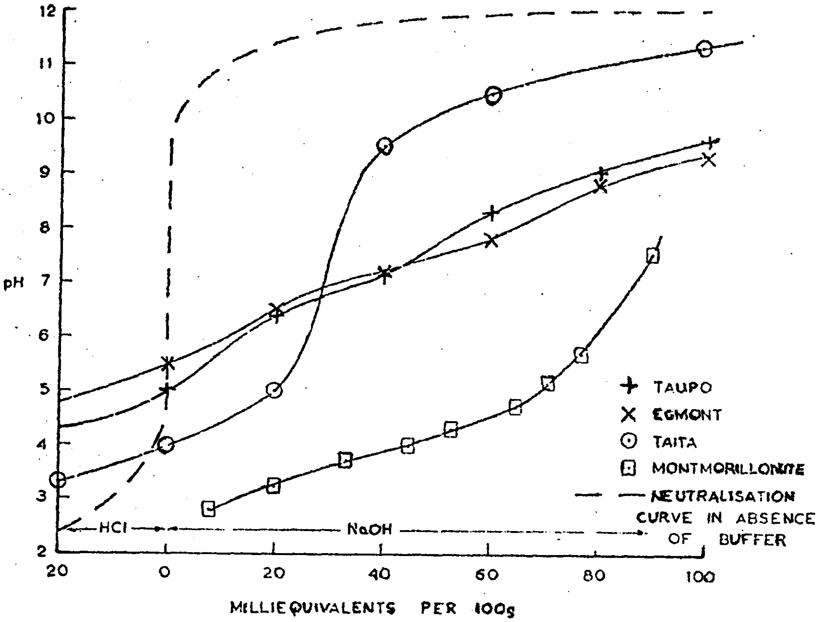
charge like the allophanes, but had no buffer range. The buffering effects were reproduced when the clays were titrated with alkali (fig. 33).

Fieldes and Schofield noted that high variable negative charge was a property of colloids with high aluminium content, and that this produced analogous behaviour in alumino-silicates of the Permutit type in which high $Al_2O_3 : SiO_2$ ratios were favoured to promote increased cation exchange capacities. Since these resins and allophane clays gave similar reversible buffer curves to those obtained from carboxylic acid resins, it was conceivable that the cation exchange properties of the alumino-silicates were due to dissociation at specific sites in the manner of carboxyl acid groups. From these premises they postulated a theory which would account for the general behaviour of allophane including (a) increased cation retention with increasing pH (b) anion retention and the order of affinity of the allophane for different anions (c) reversible loss of water at 105°C. The fact that gibbsite had no variable charge also required an explanation.

The authors suggested that variable charge was due to the behaviour of specific sites originating from broken bonds of aluminium in tetrahedral co-ordination.

Fig. 33 Titration curves of allophane and other clays in 0.2N NaCl.

(Fieldes and Schofield 1960)



Tetrahedral sites were involved because these were thought to predominate in allophanes and also because clays such as gibbsite, did not show the same behaviour. In detail, the theory proposed that a broken bond of the type: $\mathrm{Al}_{\overline{\underline{iv}}} - \mathrm{OH} - \mathrm{Si} \longrightarrow \mathrm{Al}^{o}_{\overline{\underline{iv}}} + {}^{o}\mathrm{OHSi}$ would give rise to an uncharged aluminium with an incomplete octet. This octet could be filled by co-ordination with an oxygen. If the oxygen came from a water molecule, then in the pH range 6 to 7•5, dissociation of a proton would allow the site to act as a cation exchanger. If the oxygen came from an anion, then the degree to which it was 'fixed' would depend on the degree to which it stabilised the linkage with aluminium. Since aluminium's contribution of valence to the bond was 3/4, an anion which could best make up the difference that satisfied the -2 valence of oxygen would be one with a contribution of 5/4, such as molybdate or phosphate. Hence, these were the anions most strongly held and the notable ability of allophane soils to fix phosphate and molybdate was explained.

This theory will be contrasted later with the theories and observations of Sante Mattson. In the meantime it should be noted that the buffer curves of the allophanes between pH 5•0 and 7•5 (fig.32 and 33) closely resemble the 'third buffer range' curves described by Schwertmann and Jackson (1965), and discussed in Chapter II 12 p. 48 (figs. 5a - d ). Their curves were constructed from NaOH titrations of the suspensions after the clays had been treated with potassium fluoride. The buffering was thought to arise from the production of proton donor groups which had developed on the disrupted surfaces, and to be of the type $XAlOH_2^{0.5+}$, where X is the sesquioxic or alumino-silicate mineral. Since both halloysite and gibbsite are octahedrally co-ordinated, the similarity strongly suggests that the buffering between ~ pH 5·0 and 7·5 has an origin common to them all and is due simply to the presence of amorphous material, and not to any specifically co-ordinated site. It is of interest to note here however, that both the Fieldes and Schofield theory and the Schwertmann and Jackson explanation are variations of the alumino-silicic acid theory of cation exchange put forward by Kerr (1928) and disputed by Mattson. In addition, and whatever the mechanism, this strong buffering in the region of soil pH has great practical significance when lime requirements are being considered.

(iv) Cation exchange capacity determinations.

Birrell (1961) determined the CEC of Tirau clay in a variety of ways in order to devise a method which would best reflect the 'real' cation exchange capacity and give a good correlation of percent base saturation with the water-suspension pH. Base saturation values for soils containing allophane had appeared abnormally low in relation to the pH values of water suspensions of the soils, when the method of leaching with 2N $NH_4OAc$ at pH 7 and washing with alcohol was used (N.B. this was twice the standard concentration). For example, Tirau soil had a water suspension pH of 5.9, but this method yielded a CEC of 34 me/100g and a percent base saturation of only 20%. If however the CEC was taken as the sum of the cations $Ca^{2+} + Mg^{2+} + Al^{3+} + H^{+}$ in the leachate of an unbuffered N KCl extract initially at about pH 6, then the CEC was 6.8 me/100g and the base saturation was 66%. This appeared to the authors a more reasonable value for a soil of pH 5.9.

A second source of discrepancy giving rise to a low percent base saturation occurred when the pH of the leaching solution was raised. For example, replacement of the KCl solution by $BaCl_2$ buffered at 8.1, increased the CEC to 26.5 me/100g, 22 me $H^{+}$ was released, and the % base saturation fell to 17%. It was recommended that the CEC of soils should be determined by leaching with KCl at pH 6, since this eliminated salt adsorption effects and effects due to the negative charge developed in the buffer range above the isoelectric point. The New Zealand Soil Bureau must have found the conventional method more realistic, for profile CEC determinations were made with N $NH_4OAc$ leaching solution and alcohol washing ("Soils of New Zealand" 1968 <u>3</u> p.7).

### (v) Ion fixation.

On the premise that at low pH anion uptake predominated, Birrell (1961) postulated that fixation of ions could occur when allophanes were treated with suitable concentrated salt solutions. Wada (1959) obtained the phosphate mineral taranakite after treating allophane with M ammonium phosphate solution at pH4. Birrell (1961) found the uptake of sulphate from potassium sulphate solution at pH 3.5 was about double the uptake of potassium and that, of the sulphate retained by the allophane in a form insoluble in water, 53% was soluble in N/2 NaOH. In a similar manner, in alkaline solution Birrell fixed cations that were only recoverable by leaching in acid. A Tirau clay + silt fraction in contact with 4M potassium acetate for 3 weeks at 30°C and pH 9, yielded a product that contained 6.4% $K_2O$, and more than 4/5 of the potassium was non-exchangeable. At pH 10 in M potassium acetate, the sample lost 12% material including considerable alumina.

## 2. Ion uptake and exchange, the ideas of Sante Mattson.

### (i) Historical perspective.

When Mattson produced his papers on the Laws of Colloidal Behaviour 1929 to 1931, the differentiation of clay colloids into amorphous and crystalline substances was only just being made from observations of the X-ray diffraction patterns of the clay minerals (Hendricks and Fry 1930, Kelly et al. 1931). Mattson differentiated soil colloids chemically, on the basis of their acidoid-basoid ratios and their cation-anion constituents; and electro-kinetically from electrophoretic measurements. The validity of his conclusions are not affected, in the writer's view, by the fact that many of the soil colloids he investigated were crystalline or mainly crystalline. The same laws of colloidal behaviour apply to them, and the major distinction between them and the non-crystalline soil and synthetic colloids is in their relative inertness and slow response to the fluctuations and changes in the soil environment. In them the properties of the reactive colloids studied by Mattson are greatly muted by their ordered nature and resistance to disruption. Perhaps it was the pre-occupation over the past thirty years with crystalline clays which allowed neglect of Mattson's discoveries.

Today however, it is recognised that the contribution of the 'active' amorphous fraction to soil processes is most important, even when such clay is present in very small amounts (Mitchell et al. 1964). It is now both helpful and necessary to return to Mattson's view of the colloid complex and to use his coherent theory as a guide to observation and experiment.

(ii) Cation adsorption.

It will be recalled from Chapter III 4 (iii) that Mattson's experiments on the effects of $SiO_2 : Al_2O_3$ ratios on the charge of the alumino-silicate showed that the more siliceous the colloid the greater the electrongativity and the lower the pH of the isoelectric point. From this it follows that cation adsorption is due to the influence of the silica or acidoid component, while anion adsorption is due to the influence of the alumina or basoid component, and cation and anion capacities are increased by increases in the silica (acidoid) or alumina (basoid) ratios of the complex respectively.

This relationship is illustrated in Table 42 (Mattson 1931 a), where the cation exchange capacities obtained for isoelectric precipitates of alumino-

Table 42 Cation adsorption and exchange by isoelectrically precipitated aluminium 'silicates', 'phosphates' and 'humates'.

(Compiled from Mattson 1931a)

| Composition | Ratio | Isoelectric pH | Exchangeable Ba me/g | Exchangeable Ba me/mM$SiO_2$ |
|---|---|---|---|---|
| $SiO_2 : Al_2O_3$ | 2.62 | 4.7 | 1.03 | 0.14 |
| | 1.63 | 6.25 | 0.47 | 0.09 |
| | 1.09 | 6.6 | 0.30 | 0.07 |
| | | | $NH_4$ me/g | $NH_4$ me/mM $PO_4$ |
| $P_2O_5 : Al_2O_3$ | 0.86 | 4.9 | 1.84 | 0.34 |
| | 0.77 | 5.6 | 1.47 | 0.27 |
| | 0.49 | 6.45 | 0.87 | 0.22 |
| | 0.24 | 6.65 | 0.30 | 0.12 |
| | | | Ba me/g | Ba me/g humus |
| Humus : $Al_2O_3$ | 1.30 | 4.5 | 1.83 | 2.62 |
| | 0.53 | 5.15 | 1.05 | 2.33 |
| | 0.26 | 5.5 | 0.60 | 1.97 |
| | 0.14 | 6.2 | 0.41 | 1.54 |
| | 0.07 | 6.8 | 0.33 | 1.05 |

Table 43 <u>Cation adsorption and exchange by natural soil colloids</u>.

(Mattson 1931a)

| Golloid | Composition $SiO_2 : R_2O_3$ | CEC | |
|---|---|---|---|
| | | Ba me/g | Ba me/mM $SiO_2$ |
| Bentonite | 3.81 | 1.10 | 1.37 |
| Sharkey | 3.18 | 0.80 | 0.09 |
| Sassafras | 1.89 | 0.33 | 0.05 |
| Norfolk | 1.63 | 0.21 | 0.03 |
| Aragon | 0.55 | 0.16 | 0.06 |

silicates, -phosphates and -humates are set down. The silicate and humate complexes were leached with 500 ml 0•5N $Ba(OAc)_2$ followed by 10 ml $BaCl_2$, washed with hot water and leached with $NH_4Cl$. The phosphate complexes held on to barium too tightly for ammonium to displace it efficiently, and so these were leached with 500 ml $NH_4OAc$, followed by 10 ml $NH_4Cl$, washed with 90% methanol and leached with $BaCl_2$. One notes that the ammonium ions were expected to hydrolyse, but the barium ions were not. It is seen that in addition to the trends described above, the adsorptive capacity of the acidoid increases: humate > phosphate > silicate as observed in Chapter III 4 (iii) g. A similar series of CEC values was obtained when the basoid $Fe_2O_3$ was substituted for $Al_2O_3$. They differed in that the greater electronegativity of the ferric complex lowered the isoelectric pH and hence increased the cation exchange capacities for a given acidoid: basoid (or ampholytoid) ratio. Table 43 shows the same trend for a selection of soil clays. Mattson concluded:

"It would seem that this general relationship can best be accounted for on the assumption that the acidoid and ampholytoid constituents exist in partial combination with one another in the form of compounds which are at the same time both acidic and basic, and that the uncombined acidoid valencies constitute the seat of cation adsorption and exchange whereas the free basoid mol fraction is responsible for the adsorption of anions."

This statement, the writer believes, is the key to understanding.

Two further experiments will amplify the argument. Mattson (1928b) electrodialysed 1g Sharkey clay of $SiO_2 : Al_2O_3$ ratio 3.18. 71 me of exchangeable bases per 100g clay were removed, together with 0.0247 g $SiO_2$ and 0.0022g sesquioxide. The subsequent cation exchange capacity was 60.7 me/100g. An alumino-silicate with a ratio > 3 was thus unstable on removal of the divalent ions, for the silica was then in excess of that proportion which the sesquioxides were able to neutralise at the pH prevailing. Hence the silica dissolved. This mechanism was discussed in Chapter III 4 (iii) p.75.

The argument was demonstrated from the other direction when the sesquioxide surface layer of some heavily leached subtropical soils was removed by peptising them in hot saturated $AlCl_3$ solution. All the colloids had $SiO_2 : R_2O_3$ ratios $< 2$ and Table 44 shows how the treatment increased them. The $SiO_2 : R_2O_3$ ratio of Norfolk clay went up from 1·63 to 2·19. Its cation exchange capacity was enlarged 100%, but its power to adsorb anions such as $Cl^-$ and $SO_4^=$ from acid solution was totally destroyed (Mattson 1927b, 1931a).

These treatments were severe but they illustrate the dynamic concept of the Mattson colloid, in which the valences of the complex shift in response to variation in pH of the leaching solution and its electrolyte content. The displacement theory is based upon the fact that "an amphoteric colloidal complex does not represent a constant quality even at the same pH. The exchange capacity depends upon the manner in which the valencies are linked within the complex. Any treatment, physical or chemical, may bring about a shifting in the bonds." (Mattson 1931a)

These arguments are significant in understanding the cation exchange capacities of allophanes in the field. It would be a mistake for example, to predict that an acid soil with allophane, such as is found at South Drumboy, would have a pH below the isoelectric point of allophane, and this component must therefore have a low CEC and lower the nett CEC of the soil clays;

Table 44 $SiO_2 : R_2O_3$ ratio of soil colloids before and after treatment with a hot, saturated $AlCl_3$ solution.

(Mattson 1931 a)

| Treatment | $SiO_2 : R_2O_3$ ratios of soil colloids | | | | | |
|---|---|---|---|---|---|---|
| | Aragon | Cecil | Norfolk | Orangeburg | Chester | Sassafras |
| None | 0·55 | 1·34 | 1·63 | 1·71 | 1·79 | 1·89 |
| $AlCl_3$, 3 days | 2·08 | 1·81 | 2·19 | 1·98 | 2·08 | 2·13 |

because on Mattson's evidence, an acid allophane soil would be siliceous and would indeed take up silica as the pH fell. Such a soil, particularly if it was also combined with humate, might have a comparatively high CEC. Moreover, if it was limed, the calcium ion uptake would ensure that the siliceousness of the allophane was maintained. On the other hand, an aluminous soil would have a low CEC particularly if the pH was near neutral, and this accounts for the observed sterility of many tropical soils (Orchard and Darby 1956), which Sumner (1963) ascribed to iron oxides, and which Deshpande et al. (1964, 1968) are probably more correct in attributing to aluminium or allophane.

### (iii) Anion adsorption.

The sites of anion adsorption, according to Mattson, are the partially displaced basoid valencies. Strongly adsorbed anions themselves become an acidoid constituent and may displace less active acidoids in the manner that phosphate displaces silica. Tables 45 and 46 (Mattson 1931 b) show the influence of $SiO_2 : R_2O_3$ ratios on the ion uptake of two clays: the Nipe, which was ferruginous and had a ratio 0•31, and the Sharkey with a ratio 3•18. At pH 5•8 the Nipe adsorbed 2•4 me $Cl^-$/100g, while the Sharkey adsorbed none at all. At

Table 45 Adsorption of $NH_4$, Cl, $SO_4$ and $PO_4$ ions by electrodialysed Nipe Colloid $SiO_2 : R_2O_3$ = 0·31 (3g in 100 ml).

(Mattson 1931 b)

| me added | | me per gram adsorbed | | Cataphoresis $\mu$/sec.lv./cm. | pH |
|---|---|---|---|---|---|
| $NH_4$ | $Cl^-$ | $NH_4$ | $Cl^-$ | | |
| 2·242 | 2·00 | 0·039 | 0·00 | -1·30 | 7·25 |
| 2·121 | 2·00 | 0·021 | 0·003 | -0·30 | 6·7 |
| 2·00 | 2·00 | 0·014 | 0·011 | 0·47 | 6·1 |
| 2·00 | 2·10 | 0·012 | 0·024 | 0·82 | 5·8 |
| 2·00 | 2·20 | 0·006 | 0·038 | 1·51 | 5·3 |
| 2·00 | 2·40 | 0·007 | 0·059 | 1·78 | 4·05 |
| | $SO_4$ | | $SO_4$ | | |
| 2·242 | 2·00 | 0·042 | 0·00 | -1·44 | 7·2 |
| 2·121 | 2·00 | 0·032 | 0·007 | -1·32 | 6·9 |
| 2·00 | 2·00 | 0·017 | 0·029 | -1·08 | 6·65 |
| 2·00 | 2·10 | 0·017 | 0·046 | -0·87 | 6·25 |
| 2·00 | 2·20 | 0·012 | 0·066 | -0·61 | 5·9 |
| 2·00 | 2·40 | 0·011 | 0·105 | 0·00 | 5·0 |
| | $PO_4$ | | $PO_4$ | | |
| 2·00 | 3·00 | 0·109 | 0·297 | -2·02 | 7·5 |
| 2·00 | 4·20 | 0·093 | 0·408 | -1·78 | 6·75 |
| 2·00 | 5·40 | 0·077 | 0·465 | -1·68 | 6·1 |
| 2·00 | 6·60 | 0·055 | 0·561 | -1·51 | 5·5 |
| 2·00 | 7·80 | 0·028 | 0.750 | -1·00 | 4·6 |
| 2·00 | 9·00 | 0·017 | 0·921 | -slight | 3·8 |

Table 46 Adsorption of $NH_4$, Cl and $PO_4$ ions by electrodialysed Sharkey Colloid $SiO_2/R_2O_3 = 3{\cdot}18$ (2•8g in 100 ml)

(Mattson 1931 b)

| me added | | me per gram adsorbed | | cataphoresis μ/sec. lv./cm. | pH |
|---|---|---|---|---|---|
| $NH_4$ | Cl | $NH_4$ | Cl | | |
| 4•178 | 2•00 | 0•661 | 0•00 | -2•16 | 6•8 |
| 3•089 | 2•00 | 0•376 | 0•00 | -1•68 | 5•6 |
| 2•00 | 2•00 | 0•111 | 0•001 | -1•01 | 3•2 |
| 2•00 | 2•20 | 0•090 | 0•001 | -0•60 | 3•1 |
| 2•00 | 2•40 | 0•081 | 0•001 | -0•43 | 3•0 |
| 2•00 | 2•80 | 0•066 | 0•004 | -0•25 | 2•8 |
| | $PO_4$ | | $PO_4$ | | |
| 3•210 | 3•00 | 0•674 | 0•324 | -2•25 | 6•5 |
| 2•605 | 3•00 | 0•592 | 0•363 | -2•18 | 6•1 |
| 2•00 | 3•00 | 0•448 | 0•387 | -2•05 | 4•8 |
| 2•00 | 4•50 | 0•332 | 0•474 | -1•92 | 4•0 |
| 2•00 | 6•00 | 0•245 | 0•606 | -1•68 | 3•3 |
| 2•00 | 9•00 | 0•164 | 0•810 | -1•23 | 2•9 |

pH 4·6 and 4·8, the Nipe adsorbed 75 me P/100g, and the Sharkey 38·7 respectively. The Nipe's ability to take up cations was improved by its uptake of phosphate, for at pH 6·1 it adsorbed 1·4 me $NH_4^+$/100g in the chloride solution and 7·7 me $NH_4^+$ in the phosphate solution. It was also of interest that the phosphate, unlike the sulphate and chloride, was taken up from alkaline solution by both soils.

One puzzling anomaly in anion exchange was solved. It had been noted that Sharkey clay with a $SiO_2 : R_2O_3$ ratio 3·18 adsorbed more phosphate from neutral solution than Norfolk clay with a ratio 1·59, although in acid solution the Norfolk clay adsorbed more. The ability of sesquioxides to adsorb phosphate from acid solutions is well known and the explanation lies in the suppression of hydroxyl competition at low pH, but the displacement of the silica by the phosphate meant that this reaction was less affected by pH. It was then found by experiment that in neutral solutions, phosphate displaced very little silica from clays rich in sesquioxide but displaced it strongly from clays rich in silica, like the Sharkey or bentonite.

Studies in the desorption of silica on phosphate application appear to have been made only recently, and they endorse this finding. Kafkafi et al. (1970) made an investigation "to examine the hypothesis that slow reactions of phosphate with soils involve desorption of silica from clay surfaces." Equilibriation of two soils with phosphate solutions for eight months gave results which led the authors to conclude that the slow adsorption of non-exchangeable phosphate was regulated by the slow release of displaced silica.

(iv) The relationship between the isoelectric pH and the pH of exchange neutrality (Mattson 1931 a and b)

The isoelectric pH of an amphoteric colloid is that pH at which it dissociates cations and anions in equal numbers (Michaelis 1922). For the alumino-silicates this depends on the $SiO_2 : Al_2O_3$ ratio and on the nature and concentration of the ions in the solution with which the complex is in equilibrium. The more electronegative the colloid, the greater the dissociation of cations and the lower the pH at which the electropositive component is able to dissociate an equal number of anions. Strongly adsorbed or weakly dissociated anions such as phosphate, contribute to the electronegativity and lower the isoelectric pH, whereas weakly adsorbed or strongly dissociated anions like chloride have negligible effect. This is illustrated in Table 45, where the Nipe colloid has an isoelectric pH 6•1 in the chloride system and less than 3•8 in the phosphate system.

The pH of exchange neutrality, on the other hand, is that pH at which the colloid adsorbs equal amounts of cations and anions. When the cations and anions are strongly dissociating and contribute little to the electronegativity or positivity of the colloid, then this pH is very close to the isoelectric point, and it is probably safe to assume, as the Schofield method of measuring charge assumes, that the pH of zero charge is the pH of equal ion uptake. When the cation or anion however, is weakly dissociating or strongly adsorbed, then the pH of exchange neutrality is displaced in the opposite direction to the displacement of the isoelectric pH. A sulphate ion for example, by contributing to the electronegativity, will increase the adsorption of cations and displace the point of exchange neutrality to a higher pH. Hence Birrell (1961) found the pH for equivalent uptake of cations and anions was 5•4, 6•0 and 6•9 for KCl, $K_2SO_4$ and KOAc respectively, but it would be incorrect to equate this, as was done, with zero nett charge. The Nipe colloid measurements in

Table 45 illustrated the difference: the pH of exchange neutrality was 6.1, 6.65 and > 7.5 for chloride, sulphate and phosphate systems respectively, while the isoelectric points were 6.1, 5.0 and < 3.8 pH. The practical importance of this type of study has already been discussed in Chapter III 5 p.80 in connection with the control of flocculation in water purification. A more extended investigation into anion species control of isoelectric precipitation of aluminium hydroxide was made by Marion and Thomas (1947).

A significant distinction between the amphoteric colloids and those with a 'permenant' negative charge is in their behaviour when placed in salt solution or in water so that their salts diffuse ie. when their pH is taken. The pH of a suspension in a neutral salt solution depends on the $SiO_2 : Al_2O_3$ ratio. Most clays show an exchange acidity, because their electronegativity ensures that more cations dissociate than anions and hence more hydrogen ions than hydroxyls, although the clay should first be electrodialysed for accurate measurement. If the colloid has a low $SiO_2 : Al_2O_3$ ratio, the electropositive contribution allows more anions than cations to be dissociated, and hence more hydroxyls than hydrogens, so that the suspension shows exchange alkalinity. Table 47 illustrates this point. The Sharkey suspension has exchange acidity down to pH 2•8, the bentonite to $<$ 1•2, but the Nipe suspension has exchange alkalinity to above 6•05. Mattson concludes:

> "The pH at equilibrium, of a suspension of an amphoteric soil in a neutral salt solution can be no measure of its degree of 'unsaturation' or of 'lime requirement.... An acid soil having a high sesquioxide content will either show an apparent exchange acidity which is smaller than the real or it will show a negative exchange acidity when in equilibrium with a salt solution .... There is therefore no correlation between the pH and the degree of base saturation, as has recently been conclusively shown by Pierre and Scarseth (1931)" (Mattson 1931 a and b)

Thus soils whose clays have a low $SiO_2 : Al_2O_3$ ratio and a low CEC have a higher pH when completely unsaturated with bases than do soils whose clays have a higher ratio and higher CEC. The latter soils when unsaturated react the most acid.

It can now be seen why the pH measurements of the Tirau and other allophane soils were high in relationship

Table 47 <u>Exchange reactions of soil colloids in N NaCl solutions at various pH values</u>. (pH adjusted by HCl. 0.5g colloid in 10 ml).

(Mattson 1931b)

| | pH after equilibrium with colloids | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample | Nipe | | Sassafras | | Sharkey | | Bentonite | |
| $SiO_2 : Al_2O_3$ | 0.31 | | 1.89 | | 3.18 | | 4.0 | |
| Original NaCl solution pH | pH | Diff. | pH | Diff. | pH | Diff. | pH | Diff. |
| 7.9 | 6.8 | -1.1 | 4.2 | -3.7 | 2.95 | -4.95 | 2.3 | -5.6 |
| 6.85 | 6.6 | -0.25 | 4.2 | -2.65 | 2.95 | -3.9 | 2.3 | -4.55 |
| 5.55 | 6.05 | 0.5 | 4.2 | -1.35 | 2.9 | -2.65 | 2.3 | -3.25 |
| 4.4 | 6.0 | 1.6 | 4.2 | -0.2 | 2.9 | -1.35 | 2.3 | -2.1 |
| 3.6 | 5.9 | 2.3 | 4.15 | 0.55 | 2.9 | -0.7 | 2.2 | -1.4 |
| 2.2 | 4.25 | 2.05 | 3.5 | 1.3 | 2.8 | 0.6 | 1.8 | -0.4 |
| 1.5 | ... | ... | ... | ... | ... | ... | 1.2 | -0.3 |
| pH of 1:10 water extract | 6.0 | ... | 4.7 | ... | 3.6 | ... | 2.7 | ... |
| pH of 1:10 suspension | 6.65 | ... | 4.63 | ... | 3.73 | ... | 2.60 | ... |

to their percent base saturation when the CEC was determined by the standard method. Birrell was persuaded the method was faulty, but an examination of the pH values obtained in the profile analysis (Table 16 p. 150 ) is of interest. At the lowest depth of sampling, and furthest removed from the influence of organic matter, the pH of the soil in water suspension was 6·7 while in N KCl it was 5·4. The original pH of the deionised water and salt solutions would have been 5·7 in the presence of atmospheric $CO_2$. If one assumes no extraneous source of alkalinity, the KCl must have dissociated $H^+$ and $OH^-$ ions in almost equal proportions. This is a rough calculation because the other dissociated cations and anions should be considered, but Birrell (1961) however, obtained a value of pH 5·4 for the pH of equivalent uptake of $NH_4^+$ and $Cl^-$ ions, and it is reasonable to assume that the pH of this point will not be very different for KCl. Hence the Tirau soil exhibits in N KCl an exchange acidity so slight in comparison with crystalline clays, that it appears to be base saturated.

This behaviour would be expected in view of Mattson's explanation that "for a given pair of ions the pH of exchange neutrality will be higher the greater the quantity (or activity) of the basoid in the colloid and will be lower the greater the quantity (or activity) or the acidoid in the colloid." The $SiO_2 : Al_2O_3$ ratio for Tirau clay has been given variously as 2.2, 1.75 and 1.52 (Table 16, Birrell and Fieldes 1952, Follett et al. 1965 respectively), hence a considerable contribution of exchange alkalinity would be looked for, and soil pH would not be taken as a measure of base saturation.

(v) Mechanism of ion uptake.

Mattson's theory of the mechanism of ion uptake was that "the adsorption of the cations was due to and followed the adsorption of the anions" (1928b). Cation uptake of salts whose anions are strongly dissociated is governed of course, by the electronegativity of the acidoid anion itself; and it has already been demonstrated that addition of the strongly adsorbed anions to the complex increases the electronegativity and thus the cation uptake. In alkaline solution the anion of importance is the hydroxy ion and it was his observations on its behaviour (1922) that led him to dispute the current theory that cation uptake was due to the existence of an alumino-silicic acid (Kerr 1928) and state that it was due to and followed the adsorption of the anions. An experiment in which he saturated an electro-dialysed Sharkey clay with $Ca(OH)_2$ and weighed the ignited product showed that both cation and hydroxyl had been adsorbed (1928b). In alkaline solutions it was observed that sesquioxides became acidoids and adsorbed quantities of bases, exceeding in this respect the soil colloidal materials having the greatest quantities of silica. Mattson (1930a) states:

> "The combination formed is commonly assumed to be in the form of an aluminate, thus:-
>
> $$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$
>
> There is however, no proof of this. The combination is more likely to be in the form of simple addition such as $NaAl(OH)_4$. This seems to be the way in which bases combine with soil colloids."

The $Al(OH)_4^-$ ion is indeed now the accepted formula or simplified formula for alumina in basic solution. The polymeric species are not certain, but in order for them to be negative, they must either take up more hydroxy groups or lose protons. If they take up hydroxy groups, Mattson's thesis is correct, if they lose protons, the alumino-acid or alumino-silicic acid thesis is correct. It may however be that the argument rests in a difference in point of view: if one is looking at the surface, one sees the proton donor reaction of Schwertmann and Jackson (1965),

$$XAlOH_2^{0.5+} + OH^- \rightleftharpoons XAlOH^{0.5-} + H_2O;$$

if one is looking at the complex, one sees uptake of hydroxyl. It is probable in fact, that both reactions are occurring. Polymerisation suggests however, that hydroxyl uptake is of major importance. This can be seen if one turns to the critical coagulation plot of Matijević et al. (1961a)for aluminium salt solutions in the presence of halide sols (fig. 19 p.107 ). It was earlier described how the polycation adsorbed on the colloid in the region ~ pH 5 to 7·5 was calculated to be $Al_8(OH)_{20}^{4+}$, with an OH:Al ratio of 2·5. This is the region of the third buffer range. There is another plateau to the coagulation curve in the region of pH 9 to 10, at a concentration of 0·3 mmoles/l, corresponding to the formation of a divalent polymer:

$$Al_8(OH)_{20}^{4+} + 2OH^- \rightleftharpoons Al_8(OH)_{22}^{2+}.$$

Matijević et al. suggest "it is possible that the addition of OH⁻ ions into the complex continues giving, eventually, the neutral $Al_8(OH)_{24}$."

Thus far however, does not explain the cation uptake mechanism itself which Mattson interpreted in terms of the structure of adsorbed water. All chemically inert materials, as disparate as charcoal, quartz, humus and the noble metals, he argued, charge themselves electronegatively in water. The explanation for this lay in the nature of water itself, its dissociability into $H^+$ and $OH^-$ ions and the strong adsorption properties of the $OH^-$ ion (Mattson 1922). Adsorption of the hydroxyl to the surface led to a weakening of the basic and a strengthening of the acidic properties of water. Adsorbed water therefore was both structurally and chemically different from ordinary water and exhibited the properties of an acid. The dissociation he perceived of protons from molecules held on clay surfaces has been confirmed by Mortland et al. (1963), Mortland (1968) and Fripiat (1968). Mattson continued (1928b):-

> "When a neutral salt is added the process is the same (as when a base is added), the H ions are displaced and in addition, a certain quantity of base is adsorbed, resulting in each case in the liberation of free acid. An additional quantity of base is adsorbed because the increased osmotic pressure of the cations relieves the stress which must exist in the form of an outward pull on the

> OH ions because of the tendency of the cations to diffuse and distribute themselves in the solution. The higher the concentration of the cations the more extensive therefore the adsorption of the OH ions. This means that the neutral salts are subject to hydrolysis in the presence of adsorbents which strongly adsorb the OH ions. In the presence of such adsorbents, salts of strong bases must behave as do salts of weak bases, that is they must be subject to hydrolysis."

This explanation may interpret the well known effects of the depression of pH in alkaline soils by the soluble salts present, and of the rise in pH by up to a unit or more when the salts are removed by irrigation.

In his dictum, 'the cation follows the anion', Mattson appears to be stating a general truth, because there are analagous situations in the uptake of ions by plants, and in the leaching of ions from the soil. Uptake of cations into the plant is now thought to be governed by anion metabolism in the plant (Kirkby 1969). Leaching of cations from the soil is controlled by the supply of anions in the soil solution, and in this way a limit of acidity is reached (Nye and Greenland 1960).

## 3. Allophane and the Mattson concept of colloidal behaviour.

Having in mind now, a concept of the Mattson colloid with its sensitivity to changes in the surrounding electrolyte and its ability to take up or release anions and cations in response to these changes by partial or complete displacements of the acidoid or basoid valencies, the behaviour of allophane, which was found so anomalous in the context of the behaviour of crystalline clay, becomes the logical behaviour. The 'apparent' cation exchange capacity, and the 'physical' adsorption of ions of both species can be explained in terms of the fact that changes in the concentration of the leaching solution lead to changes in the colloid itself, and changes in the cation and anion species of the solution, lead to changes in the colloid itself. Mattson points out that if NaCl is substituted for $NH_4Cl$ in the leaching solution: "we are dealing with the same colloid but not the same complex and this distinction cannot be overstressed" (Mattson 1931 b).

Consider the adsorption isotherms of Birrell and Gradwell (1956), for the uptake of barium acetate, barium chloride and lithium chloride on Tirau clay (fig.30 p.280and Table 41 p.282). At a concentration

$\sim$0·1N, pH 7, chloride uptake was nil, but the acetate uptake was $\frac{1}{8}$ the uptake of barium. At $\sim$ N concentration there was a small chloride adsorption, and the acetate uptake was about $\frac{1}{4}$ the barium uptake. At $\sim$ 2N concentration, the chloride uptake was 6·8 me/100g, while the acetate uptake at 78 me/100g was nearly half tha barium uptake. At every stage the barium uptake from the acetate solution was greater than from the chloride solution. These results can be interpreted in terms of the strong dissociation of the chloride ion and relatively strong association of the acetate ion. At low concentration the barium ion would be adsorbed on electronegative sites due to silica and the developing negative alumina sites, so that chloride is not taken up; but even at low concentration, the acetate is sufficiently associated to become in some degree, incorporated as an acidoid constituent, with fractional displacement of the other acidoid valencies, thereby increasing the electronegativity and the cation uptake. At 2N concentration this effect has become very marked indeed. The chloride ion however, only becomes associated, at this pH, when the osmotic pressure becomes excessive. In this connection it would be interesting to look for the hydroxy uptake mechanism predicted by Mattson. Birrell and Gradwell showed that exchangeable $H^+$ remained constant in the acetate CEC leachate. No figures were given for chloride leachates.

Fig. 30 demonstrates that lithium in acetate solution was adsorbed less than barium from acetate solution, but more than barium from chloride solution. This is predictable from its position in the Hofmeister series. In other words, the effect that Birrell and Gradwell suggested was due to surface area coverage was due to the electrokinetic properties of $Li^+$, although both effects originate in its large hydrated radius. It has already been noted that the surface area could have been three times as large as that calculated from $N_2$ adsorption, in which case the monolayer would not have been saturated (Section I p.284).

The behaviour of the amorphous colloids to cation exchange capacity determinations is thus not anomalous, nor does it give misleading results. It merely underlines the necessity for consistency in method, which applies to the CEC determinations of all clays, and illustrates more emphatically M.L. Jackson's caveat: "The cation exchange capacity varies according to the nature of the cation employed, the concentration of the salt, the equilibrium pH, the stored condition of the soil. The measurement should not be thought of as exact but as an equilibrium measurement under the conditions chosen." (Jackson 1962).

The displacement theory thus accounts for the adsorption and exchange properties of cations and anions in allophane soils. It also accounts for the observations on ion fixation made by Wada (1959) and Birrell (1961), described in Section I (v). In these cases the fractional displacement of silica was carried forward to a complete displacement, so that in the acid solution of M ammonium phosphate, phosphate displaced and led to dissolution of silica, ammonium was taken up, and a new phase taranakite, or ammonium aluminium phosphate separated; while in the alkaline solution of KOH, hydroxyl was taken up, together with potassium, and the complex began to be destroyed, with loss of 12% material and discharge of alumina into solution.

It has been said that soil clays can be conceived "as a continuum from completely disordered, through poorly ordered, to well crystallised material" (Follett et al. 1965); in the same way there is a continuum in their properties ranging from the highly reactive non-crystalline alumino-silicates whose shifting valencies, variable electronegativity and low energy barriers react to and accommodate changes in the soil solution, to the highly crystalline, strongly electronegative, relatively inert clay minerals, whose fixed valencies constitute larger barriers to change.

# CHAPTER VIII : PHOSPHATE RETENTION AND AVAILABILITY IN SOILS CONTAINING ALLOPHANE.

## 1. Correlation of phosphate sorption with Tamm oxalate Al and Fe.

One of the major concerns in crop nutrition is phosphate availability. This may determine the cultivation practice, the crop sown, the rotational system, and the economics of fertiliser application. It is well known for example, that phosphate is most available near neutral pH; that oats are a crop which can extract poorly available phosphate; that certain crops are useful in the rotation for their ability to mobilise phosphate; and that the value of adding phosphate fertiliser may be small, if for some reason the soil is making phosphate unavailable faster than the plant can use it, or on the other hand, if the crop can make satisfactory growth from the reserves of phosphate present.

Measurements of available phosphate by chemical extractions are designed to correlate with the known order of crop responsiveness to phosphate fertilisers, but since these relationships vary with soil types, it is important in soil management to know the forms in which phosphate is held in the different soils, its degree of retention, and the way in which it can best be mobilised.

An illuminating study was made by Williams et al. (1958), who sought to find which soil characteristics gave the best correlations with phosphate sorption for a range of Scottish soils of acid type. Excellent correlations were obtained with Tamm oxalate extractions of iron and aluminium, in particular with aluminium. Soils so treated normally lost 90% of their adsorptive powers. The role of clay minerals, when denuded of their amorphous coatings, was shown to be a relatively minor one. The oxalate extract contained not only aluminium and iron, but also silicon and organic matter. Since almost as good correlations were found with 'loss on ignition' and percentage carbon values, these were thought to reflect a relationship between organic matter and active iron and aluminium. The authors concluded:

"This almost certainly means that in these acid surface soils the active iron and aluminium are present mainly as humate complexes, and that these comprise a fairly constant proportion of the total organic matter. The combinations involved probably range from specific metallo-organic compounds to more definite complexes of the type studied by Mattson and his co-workers (1931, 1950). Phosphate and humus acidoids are mutually replaceable and iron and aluminium humates sorb phosphate over a wide pH range. Their sorption capacity, isoelectric point and pH of maximum adsorption vary inversely with the acidoid (humus)/basoid (Fe,Al) ratio, and are higher for aluminium compared with corresponding iron complexes. An interesting possibility, however, is that although aluminium is mainly responsible for the magnitude of sorption, iron may be important in determining the strength of retention."

These results suggest that the phosphate sorption properties of the soils were mainly due to allophanic material, of the type investigated in detail by Follett et al. (1965) where it was found strongly associated with organic matter, and where iron was present as a subsidiary amorphous component. This was described in Chapter V 2. p.211.

## 2. Effect of drainage on phosphate levels and on allophane content.

In another study, Williams and Saunders (1956) surveyed the distribution of phosphorous between particle size fractions and within the profiles of various soil types. This particularly brought out the difference in phosphate status between freely drained and poorly drained soils and was shown to be connected with organic phosphate levels. A decrease in total P with depth was noted for all the soils, and reflected a fall in organic P, but this decrease was accentuated in gleyed soils where the supply of organic P was much lower and fell more abruptly with depth. The cause of this was seen to lie in the lower returns to the soil from poor plant growth and restricted root development on the one hand, and on the other in the probability of greater losses of organic P, due to the fact that the higher pH and lower aluminium content of poorly drained soils in comparison with freely drained, are less favourable for the stabilisation of organic phosphates (Black and Goring 1953).

These findings are confirmed by field observations (a) that gleyed soils are consistently deficient in available phosphate, which more than any other factor accounts for the widespread infertility of the Scottish uplands; (b) that aluminous materials such as allophane are low in gleyed soils.

NOTE. Until very recently the only known source of natural inorganic phosphate in soils was apatite. Norrish (1957) identified soil phosphate minerals of the Crandellite type ($Ca\ Al_3\ (PO_4)_2\ OH_5H_2O$). They were found to be of wide distribution but the degree of their occurrence is unknown. They may be important for the experimental fact that they become amorphous and relatively soluble when heated to ~ 400°C. The conventional method for determining organic P involves pre-heating to 550°C. (Saunders and Williams 1955) and thus their presence could lead to erroneous results.

## 3. Phosphate retention in New Zealand allophane soils.

Saunders (1965) used methods similar to those of

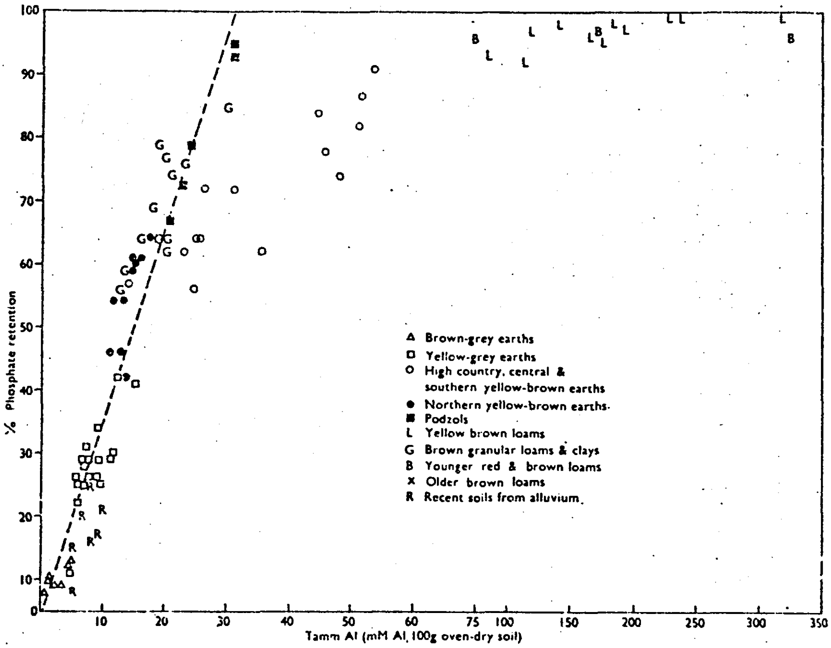
Williams et al. (1958) in a survey of New Zealand soils for phosphate retention. Phosphate sorption was measured after shaking 5 g soil for 24 hours with 25 ml NaOAc – HOAc solution buffered at pH 4·6 and 0·032 M with respect to $KH_2PO_4$. This was equivalent to 500 mg P/100 g soil. Subsoils as well as topsoils were examined in order to evaluate the effect of organic matter content. Fig. 34 for topsoils shows the same correlation with Tamm oxalate aluminium as was found with the Scottish soils, and indicates the pervasive influence of the amorphous clay fraction on phosphate retention. A similar distribution occurred for subsoils. Tamm iron was also well correlated. Soils high in allophane however, differed from other soils in certain respects:

(a) They retained less phosphate per unit of Tamm Al extracted. This is seen in the distribution of the brown and yellow brown loams, and was only marginally affected when the phosphate concentration was increased five times. Table 48 shows that phosphate retention in these soils was more than 90%. Podzol subsoils were not in this category, for their 81% retention correlated with the Tamm Al.

(b) Considerable amounts of silica was dissolved by the Tamm oxalate.

Fig. 34 Contrasting relationship between phosphate retention and Tamm Al for some allophane soils and other soil groups in New Zealand.

(Saunders 1965)



.—Relationship between phosphate retention and Tamm Al for subsoil samples (P added at 500 mg P/100 g soil).

Table 48 <u>Tamm Al, Fe and Si and Phosphate retention for topsoils and subsoils from New Zealand profiles</u>

(Compiled from Saunders 1965)

| Soil Group | Horizon | Mean %P retention | Mean Tamm Al mM/100g | Mean Tamm Fe mM/100g | Mean Tamm Si mM/100g |
|---|---|---|---|---|---|
| Yellow brown loams and brown loams | A + AB | 94 | 111 | 29 | n.d. |
| | B + C | 97 | 180 | 41 | 53•0 |
| Brown granular clays and loams | A + AB | 65 | 22 | 21 | n.d. |
| | B + C | 69 | 19 | 14 | 4•2 |
| Older red and brown loams | B + C | 74 | 22 | 92 | 4•0 |
| Podzols | A + B | 18 | 6 | 2 | n.d. |
| | B + C | 81 | 26 | 17 | 2•0 |
| Yellow brown earths | A + AB | 54 | 23 | 15 | n.d. |
| | B + C | 72 | 36 | 15 | 6•3 |
| Yellow grey earths | A + AB | 24 | 8 | 8 | n.d. |
| | B + C | 28 | 9 | 8 | 3•7 |
| Brown grey earths | A + AB | 10 | 4 | 7 | n.d. |
| | B + C | 9 | 2 | 4 | 1•5 |

(c) Phosphate retention was as great in topsoils as in subsoils.

Saunders reaffirmed the opinion of Williams et al. (1958) that the site of phosphate adsorption was the acidoid component of a complex gel; a phospho-silico-hydroxy humate of iron and aluminium, as proposed by Mattson et al. (1950) and in his earlier papers that have been described (1930, 1931). He suggested that the lower P retention per unit of Tamm Al indicated strongly that some of the aluminium of the gel complex was rendered inactive by combination with silicate, which was displaceable by oxalate but blocked retention of phosphate. The extent of the retention would depend on the degree of cross linking in the alumino-silicate and on its $SiO_2 : Al_2O_3$ ratio and would decrease with the crystallisation of the allophane to kaolinite. It might also depend on other anions such as hydroxyl and humate, since these together with silicate had all been shown capable of reducing phosphate retention when present in sufficient concentration, although they differed in this ability (Dean and Rubins 1947, Swenson, Cole and Seiling 1949).

The fact that phosphate retention was as high in topsoils as in subsoils was unexpected. It was thought to be due to the stability of the organic matter and to the power of phosphate to displace humate from iron and aluminium under the prevailing conditions.

The analyses for total, citric soluble and sorbed phosphate are given for the Tirau, Egmont and Taupo soils in Tables 14, 15, 16 p. 148-150, together with the Tamm Al and Fe values. Since citric-soluble P values reflect high availability at > 12 mg P/100g, and deficiency at < 2 mg P/100g, it is seen that all three soils have satisfactory P in the top few inches, but the Tirau and Taupo have marginal deficiency at a rooting depth of eight inches. It may perhaps be assumed from the data that these two soil profiles were under poorish pasture and had not been fertilised, so that the high availability at the surface was due to the organic matter. The above figures suggest that the allophane has the ability not only to retain but to fix phosphate, and this indeed is its reputation. It would have been of interest however, to know how far the phosphate sorbed in the experiments was available and how rapidly it was fixed; and it would be important to discover from field trials whether the equal ability of topsoil and subsoil to retain phosphate was matched by an equal ability to fix it. Almost certainly they would have behaved differently because of the greater activity of the microflora in the topsoil. One could not predict in the short term however, that the organic matter would necessarily have an ameliorating effect, because as has been noted for allophane soils, immobilisation can exceed mineralisation (Jackman 1964).

## 4. The silication hypothesis.

Saunders' thesis that phosphate adsorption and availability levels in volcanic ash soils was related to the degree of silication of the allophane, was examined by Cloos et al. (1968) from a study of phosphate uptake by synthetic alumino-silicates of varying ratio. The resulting availabilities were also measured. Table 49 gives the results which confirm Saunders' view that phosphate uptake and fixation both increase with a decrease in $SiO_2 : Al_2O_3$ ratio. The authors postulated that in siliceous allophanes, aluminium is present as $Al(OH)_2^+$ and as relatively soluble small hydroxy-aluminium complexes, which confer a high

Table 49 Adsorbed P, Available P and availability degrees for alumino-silicates of varying ratio after shaking with 0·04M $KH_2PO_4$ solution at pH 4·5.

(Compiled from Cloos et al. 1968).

| Sample ratio $\frac{SiO_2}{Al_2O_3}$ | Days of shaking | P-adsorbed % | P-available % | $\frac{Pav.}{Pads.}$ % |
|---|---|---|---|---|
| 4·60 | 3 | 2·44 | 1·55 | 63·5 |
| | 19 | 4·16 | 2·45 | 58·9 |
| | 33 | 4·60 | 2·60 | 56·5 |
| 1·73 | 3 | 4·83 | 2·60 | 59·9 |
| | 23 | 6·92 | 3·25 | 48·6 |
| | 34 | 6·92 | 3·95 | 57·1 |
| 0·36 | 3 | 4·34 | 2·30 | 47·5 |
| | 21 | 6·68 | 2·90 | 42·1 |
| | 35 | 6·92 | 3·10 | 44·8 |

availability of P on the clay; allophanes of medium or high aluminium content however, contain large amounts of poorly soluble polynuclear hydroxy aluminium compounds, with a high power of P adsorption and a low availability level. Their % P retention figures however, do not appear to the writer to support this claim. The siliceous alumino-silicate retained 36.5% P initially and this rose to 43.5% after 33 days shaking with phosphate solution. Their highly aluminous material retained 47% rising to 55.2% after 33 days.

Their theory is interesting because it suggests that siliceous allophanes may show greater degrees of aluminium toxicity than aluminous allophanes. This is shown not to be the case however from experimental evidence described in the next section.

## 5. The amphoteric nature of soils in relation to aluminium toxicity.

Mattson and Hester (1933) studied the correlation between injury to plant seedlings and the amphoteric properties of acid soils with widely varying silica: sesquioxide ratios. Aluminium toxicity had been reported to appear at different pH values in different soils, and the authors pointed out that this was to be expected, because the pH at which aluminium ionised and became soluble varied with the isoelectric point of the clay complex. When the isoelectric pH was high for instance, the basoid group was relatively more active and the aluminium more readily liberated and liable to create toxicity.

In their experiments, wheat seedlings were planted in electrodialysed samples of Sharkey, Sassafras and Nipe soils. The $SiO_2:R_2O_3$ ratios of these soils was 3.18, 1.89, 0.31 and the pH of their exchange neutrality 3.7, 4.6 and 6.2 respectively. The pH of the soils was varied by additions of HCl or $Ca(OH)_2$. Good growth and injury to the seedlings were noted. Growth weights, soluble sesquioxide and percent $Ca^{2+}$ saturation of the soil (at pH 7.0) were measured. Tables50 and 51 are compiled from their results.

It is seen that for the Sharkey soil the lowest pH of good growth was 3.6, while for the Sassafras it was 4.4. Only a trace of sesquioxide was dissolved at these respective points, but when the Sassafras was at pH 3.6, considerable sesquioxide (5.2 mg) was dissolved. The authors' own tables showed that the Sharkey soil was toxic until it was saturated with 10% $Ca^{2+}$, but the Sassafras allowed good growth in unsaturated condition. Their figures for the Nipe soil are not given, because while injury appeared at pH 4.8, it was due to manganese and not aluminium.

The pH of injury could be altered by addition of basoid or acidoid constituents to the soil, as would be predicted from the Mattson concept of the clay complex. Thus, addition of $Al(OH)_3$ raised the pH of injury of the Sharkey soil to 4.4 - 4.5, and addition of silicic acid lowered the pH of injury of the Sassafras soil to 3.0 - 3.4. The pH of injury was similarly lowered on addition of humic acid or phosphate.

One of the aims of the study was to ascertain the effect of fertiliser salts on the development of aluminium toxicity. The effect of adding a Shive's

Table 50 <u>Development of wheat seedlings in electrodialysed Sassafras soil under varying conditions</u>.

(Compiled from Mattson and Hester 1933)

| Treatment | lowest pH good growth | soluble $R_2O_3$ mg | % saturation with $Ca^{2+}$ | dry wt. growth mg | pH of injury | soluble $R_2O_3$ mg | ml 0.1N HCl added | dry wt. growth mg |
|---|---|---|---|---|---|---|---|---|
| eletro-dialysed only | 4.4 | 0.4 | - | 35.6 | 3.6+ | 5.2 | 5 | 21.0 |
| silicated | 4.0 | 0.8 | - | 51.8 | 3.4 | 43.6 | 10 | 11.0 |
| nutrient salts added | 4.6 | 2.6 | 10 | 98.2 | 4.5 | 4.4 | - | 70.0 |
|  |  | $SiO_2 : R_2O_3 = 1.89$<br>pH of exchange neutrality = 4.6 |  |  |  | $R_2O_3$ : mg/100g soil, principally $Al_2O_3$ |  |  |

### Table 51 Development of wheat seedlings in electrodialysed Sharkey soil under varying conditions.

(Compiled from Mattson and Hester 1933)

| treatment | lowest pH good growth | soluble $R_2O_3$ mg | % saturation with $Ca^{2+}$ | dry wt. growth mg | pH of injury | soluble $R_2O_3$ mg | ml 0.1N HCl added | dry wt. growth mg |
|---|---|---|---|---|---|---|---|---|
| electro -dialysed only | 3.6 | trace | 10 | 41.2 | 3.4 | 1.6 | - | 26.6 |
| aluminated | 4.8 | 4.4 | - | 49.1 | 4.5 | 9.2 | 10 | 15.4 |
| nutrient salts added | 4.4 | 6.0 | 40 | 107.0 | 4.1 | 6.0 | - | 67.2 |

$SiO_2 : R_2O_3 = 3.18$

pH of exchange neutrality = 3.7

nutrient solution containing $K_2SO_4$, $Ca(NO_3)_2$ and $MgCl_2$ was to modify the pH of injury drastically. This was raised to 4.1 in the Sharkey case and 4.5 in the Sassafras case, while the % $Ca^{2+}$ saturation required to prevent toxicity became 10 - 40 for the Sharkey and 0 - 10 for the Sassafras. The result was attributed to displacement of the strongly associated $OH^-$ ions by the dissociating anions of the salts and the subsequent ionisation of aluminium in greater quantities.

These experiments explained the observations of Burgess and Pember (1923) that organic matter counteracted the toxic effects of aluminium and of Pierre (1931) that soils of relatively high percentage base saturation at low pH values yield, in general, less aluminium in solution than soils of low percentage base saturation. It was concluded that the toxic effects of aluminium could be counteracted by organic matter, silication and high percent base saturation, and enhanced by the lack of these and also by the presence of soluble salts. This may have relevance to the management of the Darleith soils, if the postulate that they are prone to give rise to aluminium toxicity is correct.

## 6. Phosphate problems in forestry production on basalt soils.

Many of the soils available to the Forestry Commission for planting in Scotland are of poor quality, comprised of peaty gleys, humic gleys, peats, and podzols with thin iron pan. The brown forest soils are a minor and much sought-after component, because their rooting depth, good structure and better fertility give rise to expectations of a high yielding crop with resistance to wind throw. It was therefore a great disappointment to find that spruce, and sitka spruce in particular, did not do well on the basalt brown forest soils. Some of these soils have been planted in Blairadam Forest, Fife, where pockets of them had developed on the carboniferous sandstone-age lavas. In west Argyll however, on the extensive outcrops of tertiary basalt in Morvern and on Mull, there are much larger areas of brown forest soil and the plantations there represent a serious loss of capital in their present state of poor growth.

The trouble was tentatively diagnosed as phosphate deficiency and it was thought it might be due to the fixing powers of the soils' high iron content (G. Pyatt, D.B. Patterson pers. comm. 1968). The writer suggested however, from observations on the South Drumboy soils, that if there was phosphate fixation, it could be due to allophane. A pilot experiment in which phosphate retention was measured on a sample of Dunlop $B_3gx$ confirmed this prediction (R. Lindsay B. Sc. project 1969). It was later learned that the situation was more complex. Lab. analyses showed that while the spruce needles were phosphate deficient, the soils themselves contained satisfactory levels of acetic-soluble phosphate (D.B. Patterson, pers. comm. 1971). This led the writer to postulate aluminium toxicity as the cause of check. Unfortunately, the short time available precluded wider field studies, but the writer is much indebted to D.B. Patterson, Site Survey Officer for the Forestry Commission, for his comments and for making available a copy of the Commission's report on a pilot Survey of Fiunary Forest (1971); and also to J.S. Bibby of the Scottish Soil Survey for his observations on the Mull plantations. These are incorporated in what follows:

The pilot survey was directed by D.B. Patterson (1970 - 1971), and its object was to examine the poor and variable growth rates associated with basalt soil types. It was conducted in a part of Fiunary Forest, and correlations were made with J.S. Bibby's soil survey on Mull, where the basalt soils were being mapped as Darleith association soils. Brown forest soils and podzols are similarly affected, but analytical data correlating soil and crop growth was confined to the brown forest soils, or 'normal brown earths' as they are designated. The normal brown earths were dark reddish brown with fine sandy loam to sandy clay loam textures, usually with a very strong subangular blocky structure and friable consistence becoming firm, but not indurated, in the C horizon. Slight or moderate gleying in the B and C reflected varying degrees of imperfection in the drainage, but their situation on steep slopes allowed them to be classed as free draining Darleith series. The soil depths varied from 45 to 100 cm depending on their slope situation. Nevertheless, even in their deep phases the soils all exhibited shallow rooting often with a sharp interface between the top of the B and bottom of the A, where rooting ceased.

"It is unusual to record pronounced rooting deeper than the upper B horizon, approximately 25 cm from the surface. This characteristic is found in Norway spruce plantations of 14m top height, in recently established plantations and in old birch scrub. Bracken roots also show little ability to penetrate the soil deeper than the upper B horizon. Rooting in iron pan soils is predominantly in the Eg with little penetration into the B even though the pan is discontinuous. Deeper rooting takes place in the gleys to the B/C interface." (Fiunary Forest Survey 1971).

It has already been noted that allophane has not been found in gley soils. The Fiunary gleys show P deficiencies but only of the type characteristic of poorly drained soils and crops respond to phosphate application. Hence, the ability of the spruce to root in the unfavourable gley environment as far as the B/C interface, together with the vivid description of the demarcation of the roots by the interface in the brown earth of the A and B horizon, reinforces the writer's conviction that the spruce suffer from aluminium toxicity, and seek protection in the organic rich A horizon, where organic matter masks the aluminous sites and/or lowers the pH of injury. It must be admitted that allophane field tests have not been done on these particular soils, but the Campsie tertiary basalt soils give a strong sodium fluoride reaction. Moreover, the Fiunary soils have "abnormally high loss on ignition values for the brown earths' A horizons, over 35%, much higher than morphological assessment would indicate" (D.B. Patterson pers. comm. 1971), which supports the assumption that they have high allophane content.

As far as the crop was concerned, the Survey found that leading shoot increments were very low in the first 15 to 20 years. Table 52 gives the needle analysis by weight and P% for brown forest soils that were subdivided into vegetation and cultivation categories. It is seen that only the previously-cultivated soil produces a crop with satisfactory needle weight and

Table 52 **Foliage analysis and crop growth of Sitka Spruce on tertiary basalt (Darleith association) brown earths at Fiunary Forest.**

(Compiled from Forestry Commission survey data June 1971).

| Brown earth sub-type | — Needle analysis — | | | | | | yield class |
|---|---|---|---|---|---|---|---|
| | Weight mg OD | Weight rating | P % OD | P rating | N rating | K rating | |
| once cultivated | 6.37 | * * * | 0.155 | * * | * * * | * * * | 10 - 18 |
| bracken/holcus/bluebell (fertilised at planting?) | 4.32 | * | 0.177 | * * * | * * * | * * * | 7 - 10 |
| | 3.75 | * | 0.232 | * * * | * * * | * * * | |
| | 4.22 | * | 0.203 | * * * | * * * | * * * | |
| | 3.95 | * | 0.209 | * * * | * * * | * * * | |
| bracken/grass/calluna | 3.33 | * | 0.090 | * | * * | * * * | 4 to check |
| | 3.57 | * | 0.086 | * | * * | * * * | |
| | 3.37 | * | 0.090 | * | * * * | * * * | |
| | 3.50 | * | 0.212 | * * * | * * * | * * * | |
| calluna | 3.32 | * | 0.085 | * | * | * * * | check |
| | 2.93 | * | 0.085 | * | * | * * * | |

Ratings: * * * adequate —— * * marginally adequate — * low.

| NB Healthy growth —— | mg OD weight | N | P | K —— % OD |
|---|---|---|---|---|
| > 5 yrs | 8 | 1.5 | 0.21 | 1.1 |
| < 5 yrs | 4 | 1.9 | 0.23 | 0.8 |

yield class. The report concluded that extra dosages of phosphate could not be recommended until the cause of the phosphate deficiency had been established.

J.S. Bibby stated that the most important of his observations was the "cultivation effect." On the inbye land inside the head dyke, there were 'spruce cathedrals' of crops making excellent growth, with large volumes of rooting into the B horizon. Outside the head dyke, on the hill pasture, there was a spectacular fall in growth, with yields dropping from 220 to 140 hoppus feet, and rooting growth so shallow, the trees could be lifted out. The cultivation effect was complicated by the fact that the head dyke often separated the brown forest soils from the podzols, so that the brown forest soil behaviour was masked by the unknown factor introduced by cultivation. Cultivation of course, has long since ceased and its effects have not maintained any significant difference in pH, which is about 5·6 in both soils. J.S. Bibby suggested that the factor inhibiting root development was structural. The soils were as easy to dig on the unimproved as on the inbye land, but he thought there was some physical impediment to rooting.

## 7. The aluminium toxicity hypothesis.

Clues to the problem consist in (a) phosphate deficiency (b) rooting depth restricted to the A horizon (c) cultivation effect (d) presence of allophane. If the cultivation effect arises from its influence on the soil allophane, then the cause of the improvement could lie in its past (i) higher returns of organic matter (ii) liming (iii) ploughing of the soil. If the 'cultivated' soil is richer in organic matter than the 'uncultivated soil, one may propose that the effect of humate is to mask the aluminous sites and to lower the isoelectric pH of the complex so that the pH of injury is also lowered (Mattson and Hester 1933). If the 'cultivated' soil was once supplied with lime, then one may propose that its long term effects are felt not in terms of pH, for the pH of both soils are said to be the same ( $\sim$ 5.6) but in silication of the complex; for according to Mattson (1930a) addition of calcium induces uptake of silica as described in Chapter III 4 p.77. This again would mask aluminous sites and lower the pH of injury. Finally ploughing of the soil would have increased the depth of organic matter distribution.

One notes that the lowest pH of good growth of the Sassafras soil (Table 50 p.337) was 4.4. Hence if the allophane coatings on the clay fraction of these Mull and Fiunary soils were of comparable $SiO_2 : Al_2O_3$ ratio, then the environment of the tree root might well be within the region of the pH of injury. Such soils would give rise to aluminium toxicity effects. Exceptions would be those soils or horizons where the allophane complex was modified by uptake of organic matter or silica as in A horizons or by inheritance of some older land use effects.

One of the visible signs of aluminium toxicity is a pattern of root branching which resembles corralloid roots with mycorrhizal associations and is due to the development of laterals of similar diameter close to the apical meristems (Clarkson 1968). Wright (1943) and Wright and Donahue (1953) suggested that the aluminium toxicity mechanism was an internal precipitation of aluminium in the root, inducing phosphate deficiency. Clarkson (1968) observed that aluminium treatment inhibited root elongation and cell division, and that it interfered with the distribution of phosphorylated intermediates within the cell in such a way as to depress respiratory metabolism.

If the premise of aluminium toxicity is correct and the situation is to be overcome, then either the aluminium must be immobilised or the tree must be protected. Immobilisation of the aluminium requires adsorption on the aluminous sites by humate, hydroxyl or silicate ie. by incorporating organic matter or liming. Sitka spruce may not take kindly to too much lime, but perhaps it would be an opportunity to plant hardwood on these brown forest soils. Protection of the tree might involve the growing of a species, or a variety, resistant to aluminium. It is possible indeed that the exchange complex on the spruce root surface is more acidic than that of other tree species and exacerbates the problem, and it would be useful to know the trees that grew on these soils in the natural forest. On the other hand, the tree might be protected by some symbiotic association with fungi or microflora able to chelate trivalent aluminium or to raise the pH of the root environment. Such an association might again necessitate a different crop. The problems of economics and practicality must be borne in mind. There is the question of saving the crops already planted and of utilising the unplanted land, so that different solutions may be required. Incorporation of organic matter or liming might prove effective answers, but on the other hand some simple observation in the field may suggest an ecological solution at low cost.

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# PART TWO

# EXPERIMENT AND DISCUSSION

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## SUMMARY OF THESIS.

High amounts of allophane as measured by the sodium fluoride test were found in the brown forest soils and B horizons of podzols developed on basalt and basalt till. A hydrologic sequence of the Darleith association was examined and the soils' strong aggregation, high organic matter levels and phosphate retention were found due to their allophane content. Allophane was found also in the C horizons of podzols of other material.

C horizons flocculated on ultra-sonic vibration but were dispersed in ammonia. All horizons however, when vigorously peroxidised, behaved like allophane soils and remained flocculated in alkaline suspension. The relative tendency of a soil to flocculate appeared to depend on the number of aluminous sites exposed ie. on the amount of allophane and its $SiO_2 : Al_2O_3$ ratio. This correlation was supported by analysis of the alumino-silicate extracted with (a) cold 5% $Na_2CO_3$ (b) cation exchange resin (c) 1% citric acid, and by the rise in suspension pH on NaF treatment.

NaF released more Al, and $Na_2CO_3$ more Al and much more Si when added to dry soil than to suspensions, and this was attributed to energy provided by the heat of wetting.

Successful dispersion of flocs, as measured by mechanical analysis, was obtained for a New Zealand Tirau B horizon and the peroxidised Scottish soils by :

(1) Vibrating in HCl at pH 4.3. This was only possible for Tirau B, with negligible clay mineral present.

(2) Vibrating in zirconium or thorium nitrate solution and pH controlled at 4.3. Adsorption of the hydrolysis products (polycations) on the negative colloids, reversing their charge, was the dispersion mechanism.

(3) Shaking with Na-exchange resin, followed by hand shaking in ammonia. The resin took up large quantities of alumina and silica and some iron, in addition to bases.

(4) Vibrating in alkaline silica sol.

(5) Vibrating in sodium hexametaphosphate. Peroxidised Darleith soil dispersed in calgon. Tirau B was partially dispersed in $(NaPO_3)_6$ at pH 7.5.

(6) Repeated washing of alkaline flocs followed by shaking in NaOH (efficiency not yet measured).

(7) Dialysis at soil pH gave partial dispersion of Tirau B.

Alkaline flocculation of allophane could be explained in terms of (a) alumina groups (b) their capacity to adsorb hydroxyl (c) the presence of free electrolyte. Dispersion was achieved by any mechanism which interfered with one of these, viz. by:- masking alumina groups with organic matter or silica; 'destroying' hydroxyl with $H^+$ ions; or removal of electrolyte. This interpretation is inherent in Mattson's 1922 paper, in which adsorbed hydroxyl ions were shown to be flocculating agents, and a bridging mechanism dependent on electrostatic linkages between them and divalent cations in the free electrolyte was envisaged.

A review was made of the concepts of aggregation, coagulation and flocculation. Experiments showed the validity of the distinction between 'coagulation' by electrolytes and 'flocculation' by polyelectrolytes was unsubstantiated. It was suggested that aggregation could be interpreted in terms of the double layer Verwey-Overbeek theory, but flocculation required another explanation. Mattson's work, together with his postulate of the crucial role of the hydroxyl group should be reappraised.

The unusual cation exchange properties of allophane described in the work of New Zealand and Japanese soil scientists were re-interpreted in the light of Mattson's experiments with amphoteric colloids. Anomalies were explained in terms of the acidoid-basoid complex.

Sodium fluoride was used to extract allophane-held organic matter. Optimum conditions were established at pH 6 to 7. Approximately 30% of total polysaccharide was extracted, or allowing for non-humified cellulose, about 50% of soil 'combined' polysaccharide. It appeared to be representative in composition. Sodium fluoride extraction of soils high in allophane offers a technique for the systematic study of virtually unaltered organic matter.

N.B. Plastic artefacts interfered with organic matter studies: (a) Moist soils stored in plastic bags became impregnated with mobile hydrocarbons.
(b) Dialysis tubing dissolved out reducing substances. These gave high values to polysaccharide analyses and interfered with sugar chromatograms.

The Forestry Commission finding that spruce checked on basalt brown forest soils, and that the needles showed phosphate deficiency although the soils appeared to contain adequate phosphate, led the writer to postulate that aluminium toxicity was the cause of the phosphate deficiency. Large amounts of alumina were dissolved by 1% citric acid. Mattson and Hester (1933) showed that the pH of injury to wheat seedlings was raised in soils of low silica-sesquioxide ratio due to the greater mobility of aluminium. If the toxicity hypothesis were correct, the condition could be ameliorated by adding organic matter to mask aluminous sites and lower the pH of injury, or by liming. An alternative crop might thrive better than spruce. No allophane reaction to the NaF test was found on Darleith soils under hardwood, even where it was strong in the adjoining grassland.

# CHAPTER IX : FIELD SURVEY.

## 1. Experimental notes.

### (i) Horizon nomenclature.

Horizon nomenclature used in this work is as follows:-

| | |
|---|---|
| $A_o$ | horizon of organic matter lying on the surface of the mineral soil. |
| A | uppermost mineral horizon, in which the organic matter is intimately mixed with the inorganic matter. |
| $A_e$ | eluviated layer, which when present, lies below an A or $A_o$ horizon. The minerals are bleached, due to the removal of iron oxides, and may be grey from a coating of organic matter. It is designated $A_2$ by the Scottish Soil Survey. |
| $B_I$ | iron pan, if present. It is designated $B_1$ by the Scottish Soil Survey. |
| $B_2$ | usually a brighter brown than either the A or C horizon, due either to relative enrichment in iron oxides derived from A, or more intensive oxidation and weathering of iron oxides than is occurring in C. |

$B_3$ subdivision of the B horizon. In Scottish soils it is usually an indurated horizon. Induration is signified by x eg. $B_{3x}$.

C weathering parent material. This may also be a $C_x$ or indurated horizon.

R rock.

Moderate gleying, as shown by mottled soil colours of red or brown and yellow or grey, is signified by g as in $B_{2g}$. Intensive gleying, where all or most of the iron is in ferrous form by G as in CG. Subscripts are used where it is necessary to subdivide a major horizon in which differences in colour, texture and so on occur, as in $C_1G$, $C_2$.

### (ii) Sampling.

Samples were at first collected in plastic bags and stored moist by putting a test tube of water into each bag and sealing it from the atmosphere. While this is not a recommended procedure for the subsequent determination of available nutrients, it was done because the students' soils course began in midwinter, and their first step was to handle the soils they were going to analyse. However, as described in Chapter XVI the bags leaked some of their plastic components and suffused the soil with hydrocarbons. This was detected during the extraction of organic matter. Hence, all soils were subsequently collected in brass sieve holders, and wherever possible, sieved and air-dried the same day.

### (iii) Allophane test.

This test was made on all horizons of the Drumboy soils and was used in field work elsewhere as a matter of routine. Small samples of soil from each horizon were placed on filter paper that had been pre-soaked in phenolphthalein indicator and dried. A drop of saturated sodium fluoride solution was added to the soil and the degree of development of alkaline pink after the elapse of a few minutes gave an indication of the allophane content (Fieldes and Perrott 1966). Organic rich soils tended to be slower in developing colour. Care was taken where lime had been applied to topsoils, to avoid contamination by the sodium carbonate that would be formed.

## 2. South Drumboy.

Drumboy hill lies to the east of the A77 Glasgow-Fenwick road and just within the border of north Ayrshire. It rises to 876 feet and is bounded on the south and east by Soame burn (fig.35 ). The Geological Survey has mapped the high ground as trachyte with hill peat, and the lower ground at some 750 feet as Dalmeny basalt with boulder clay drift (Ordinance Survey of Scotland 1950, 1952). Outcrops of basalt occur on the east side of the burn and trachyte and tuff on the upper slopes and hill top. The trachyte outcrops are misleading however, because in 1970/71 Kings and Co. Ltd., Glasgow, quarryowners, began to prospect the hill with a view to the extraction of trachyte for road metal. They made a number of borings, some more than 100 foot depth, and found that most of the rock beneath the peat is porphyry.

A transect of a hydrologic sequence of Darleith association soils was made from the top of Drumboy hill down its southern slope towards the burn (fig.35 ) Fresh pits were dug for each soil type once or twice a year from 1967 to 1971. Five of the seven members of the series mapped by the Scottish Soil Survey were included in the transect:-Baidland (peaty podzol with

Fig. 35 Sketch map of South Drumboy area, North Ayrshire (OS 495485).

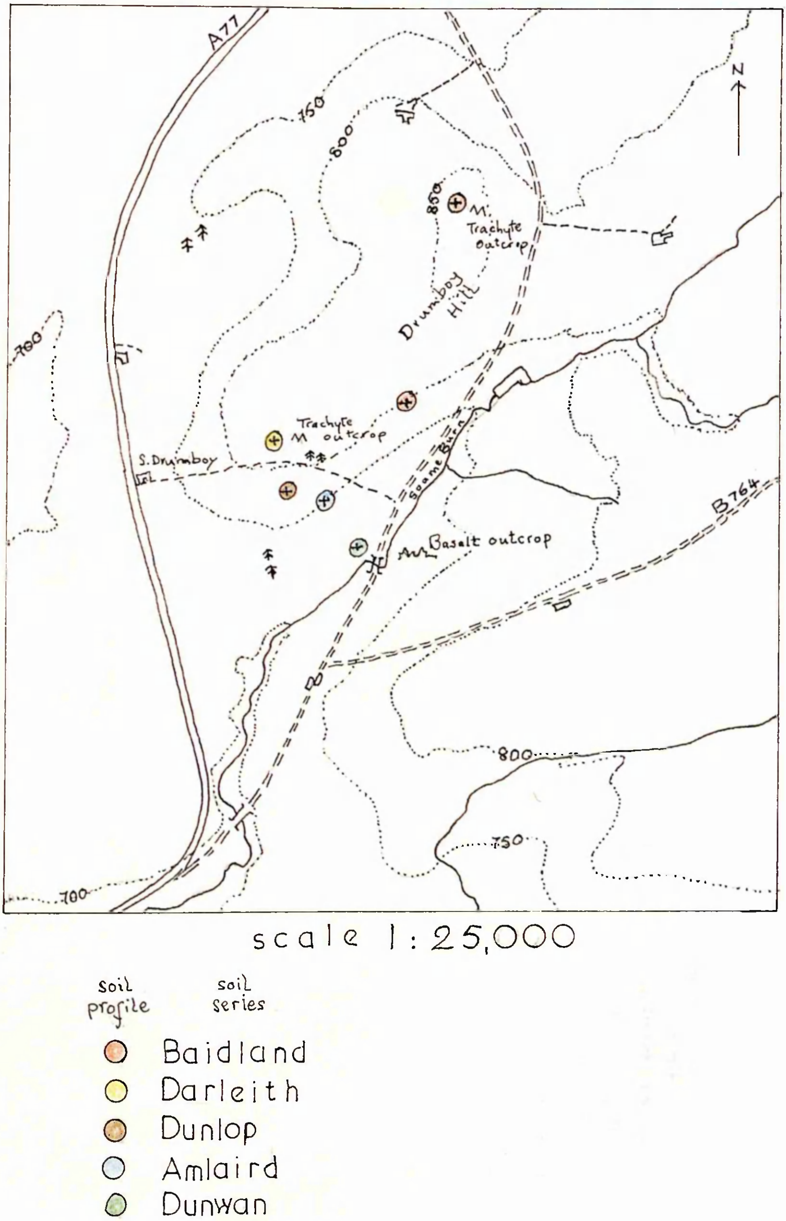
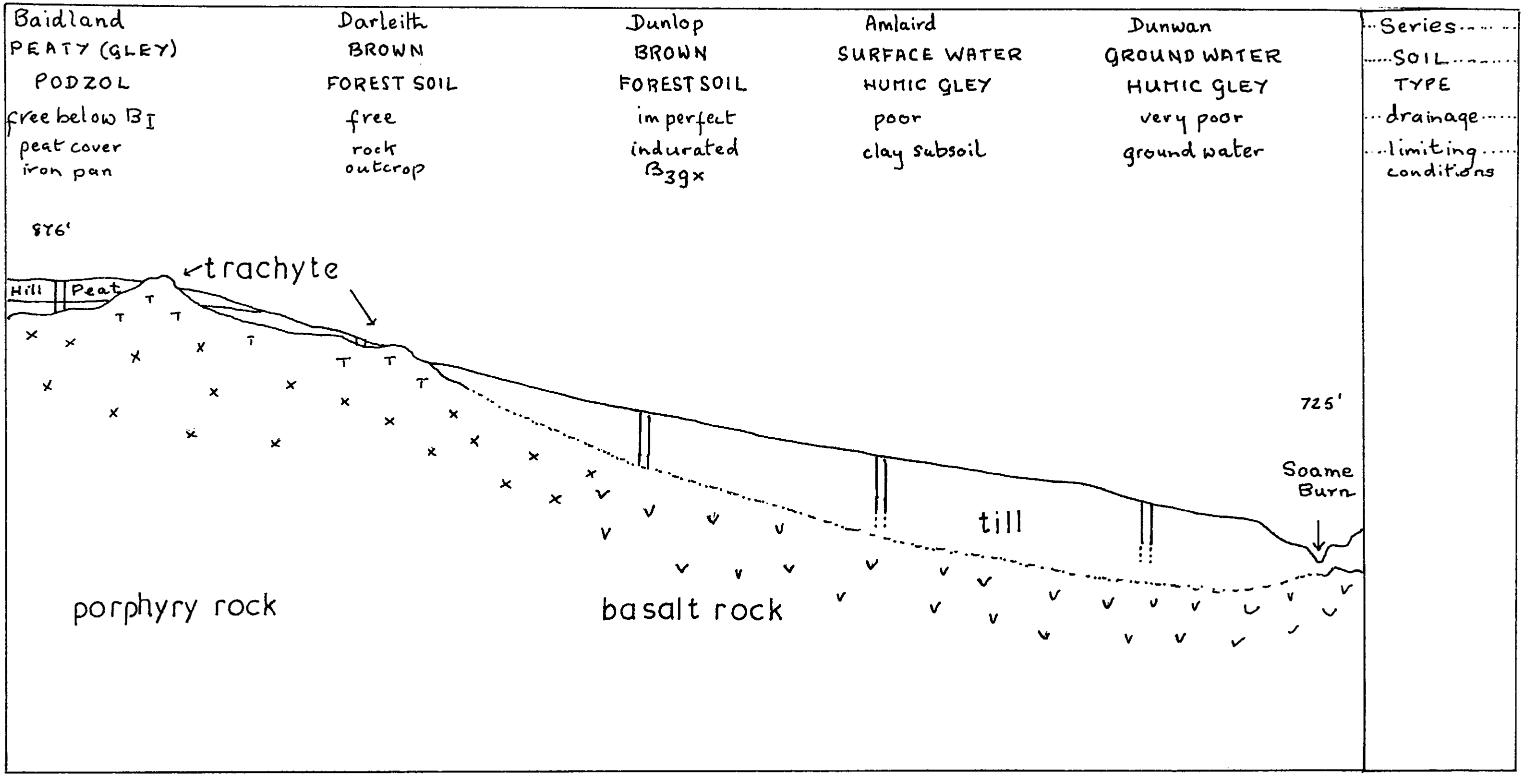


Fig. 36 Hydrologic sequence of South Drumboy soils.



thin iron pan), Darleith (freely drained brown forest soil), Dunlop (imperfectly drained brown forest soil), Amlaird (surface water humic gley), Dunwan (ground water humic gley). The sequence is shown in fig. 36 and illustrates the strong topographic control in the development of soil types.

## 3. Soil and site descriptions at South Drumboy.

**Baidland series** (peaty (gleyed) podzol with thin iron pan).

The Baidland and Darleith series are both developed on shallow loamy till, or in their shallow phases on trachytic or porphyritic rock. Baidland however, is an organic soil, since higher altitude, increased rainfall and lower temperatures have led to accumulation of humus. The writer found peat deposits varying from 1 to 3 foot. Borings by Kings quarry men passed through up to 20 foot, although these might have been made in the neighbouring Myres series. A thin iron pan was generally detected, and where strongly formed it is overlain by a gleyed $A_e$ horizon. Drainage below the pan is normally free, except on the lower slopes where a $B_{3x}$ horizon impedes it. An example of this latter profile is given. It was obtained from an eight foot deep 20 yard long trench which Kings' submanager Mr. Lochart, and the site foreman Mr. Cameron, kindly left open for use in a soils excursion.

Profile description (peaty gley podzol with thin iron pan, heath vegetation)

| | |
|---|---|
| Slope | level |
| Aspect | nil |
| Altitude | 876 feet |
| Vegetation | Deschampsia flexuosa (wavy hair grass), Sphagnum spp., Polytrichum commune, Molinia caerulea (purple moor grass), Eriophorum angustifolium (cotton grass), Vaccinium myrtillus (bilberry), calluna vulgaris (heather). |

Drainage class free below iron pan.

| Horizon | Depth ins. | pH | NaF reaction | Description |
|---|---|---|---|---|
| $A_o$ | 30-0 | 3.3 | nil | Peat |
| $A_{eg}$ | 0-3 | 4.4 | nil | Grey gleyed sandy loam |
| $B_I$ | at 3 | | nil | Thin iron pan, intermittent |
| $B_2$ | 3-8 | 4.4 | strong | Brown |
| C/R | 8 | 5.0 | nil | Weathering porphyry rock |

All profiles dug were similarly shallow. The dominant vegetation is wavy hair grass which has been neglected by the sheep and grows in large unpalatable tufts. The molinia component is small and the leaf blades in August were all bitten down. This is of interest in view of the opinion that sheep reject molinia.

Profile description (Peaty podzol with thin iron pan, grass vegetation)

| | |
|---|---|
| Slope | gentle |
| Aspect | southeast |
| Altitude | 800 feet |
| Vegetation | Nardus stricta (matgrass), Festuca ovina (sheep's fescue), Agrostis tenuis (brown bent), Anthoxanthum odoratum (sweet vernal), Galium saxatile (heath bedstraw), Potentilla erecta (tormentil), Juncus conglomeratus (rush), Rumex acetosella (sheep's sorrel). |

Drainage class imperfect

| Horizon | Depth ins. | NaF reaction | Description |
|---|---|---|---|
| $A_o$ | 8-0 | nil | Peaty humus |
| $A_{eg}$ | 0-4 | nil | Bleached greyish loam, only occasionally present |
| $B_I$ | at 4 | nil | Thin iron pan, very intermittent; mainly round stones |
| $B_{2g}$ | 4-8 or deeper | very strong | Ochreous brown loam, friable, humus stained, occasionally gleyed. Very variable depth and texture. |
| $C_x$ | 8-30 | slight | Very indurated. The hardened matrix holds assorted stones including flat sandstones. Sandy, biscuity; many of the stones can be crushed by pressure of finger and thumb and consist in gravel and sand indurated together |
| R | 30- | nil | Weathering porphyry rock, very sandy and stony. A vein of barytes cuts through the bottom of the trench. |

Agriculture. The Baidland series provides rough grazing for sheep. It is very exposed, although at one time it had a small woodland which would have provided shelter. The 'heath phase' has only a minor heather component and is considerably wet underfoot at all times. It would require intensive drainage to dry it out. The 'grassland phase' supports a better pasture. Its iron pan is intermittent, but the deep excavation clearly showed the limitations imposed on the area by the massive indurated layer. The pasture here could be improved if tiles or plastic drains were placed above the $C_x$, but it is often so close to the surface, that mole drains or sheep drains might be preferable. For forestry or woodland, the $C_x$ would require ripping.

### Darleith series (brown forest soil of low base status).

The Darleith series on Drumboy is shallow and free from boulder clay. The rock outcrops close to the surface and none of the pits dug were deeper than fifteen inches. The soil is an excellent mull crumb of sandy clay loam, high in organic matter and carrying a wide variety of herbs and grasses.

Profile description

| | |
|---|---|
| Slope | gentle |
| Aspect | south s/west |
| Altitude | 825 feet |
| Vegetation | Agrostis tenuis (brown bent), Festuca ovina (sheep's fescue), Anthoxanthum odoratum (sweet vernal), Trifolium repens (white clover), Achillea millefolium (yarrow), Bellis perennis (daisy), Juncus conglomeratus (rush). |

Drainage class free

| Horizon | Depth ins | pH | NaF reaction | Description |
|---|---|---|---|---|
| A | 0-7 | 5.4 | nil | Brown loam, crumb structured, moderate organic matter. Roots. Worms. Few stones. No mottling. Sharp change to |
| B | 7-15 | 6.0 | high | Brown sandy clay loam. Very fine to subangular blocky. Some roots. Worms. Many stones. |
| C/R | 15- | 5.8 | high | Shattered rock of trachytic tuff. Matts of grass roots impeded by stones. |

## Agriculture.

This is potentially good pasture but is over grazed by sheep and cattle and subject to fairly severe poaching, as can be seen from the rush encroachment on this 'freely drained' soil. Shelter is provided by a small spinney of decayed Scots pine and sycamore. Many of the trees are dead, probably because they are in a pocket of poor drainage. The ground was ploughed during the war and rape was taken off it; but it was too rocky for the plough and has been under grass since 1947.

## Dunlop Series. (brown forest soil of low base status).

The Dunlop series here is developed on loam till. It differs from the Darleith in its depth, slightly heavier texture, higher base status due to the basalt rock below, and in the presence of an indurated layer which slightly impedes drainage.

### Profile description.

| | |
|---|---|
| Slope | gentle |
| Aspect | south |
| Altitude | 775 feet |
| Vegetation | Poa trivialis (rough stalked meadow grass), Lolium perenne (perennial rye), Cynosurus |

cristatus (crested dog's tail), Bellis perennis (daisy), Trifolium repens (white clover), Ranunculus spp (buttercup).

Drainage class imperfect.

| Horizon | depth ins | pH | NaF reaction | Description |
|---|---|---|---|---|
| $A_o$ | 1-0 | n.d. | | Greasy, layered humus |
| $A_1$ | 0-5 | 5·5 | slight | Organic rich clay loam diffuse to |
| $A_2$ | 5-11 | 5·5 | slight | Dark brown loamy mull. Crumb structure. Many roots. Few stones. Worms. Sharp change into |
| $B_{2g}$ | 11-14 | 5·7 | strong | Reddish brown loam, friable, subangular blocky. A few ochreous mottles. Roots. Some stones. Distinct textural change to |
| $B_{3gx}$ | 14-18 | 5·8 | v. strong | Indurated, yellowish brown loam. Platy or forced into angular blocky structure by stones. Shiny faces to peds, clay skins. Biscuity. Very difficult to dig and requires pick, but induration is less noticeable on a profile face. |

| Horizon | depth ins. | pH | NaF reaction | Description |
|---|---|---|---|---|
| | | | | Mottling. Some pitting visible. Large trachyte stones. Merging to |
| $C_g$ | 18-34 | 4.9 | strong | Brown clay loam, coarsely angular blocky with some platiness, but easier to dig. Clay skins. Mottling becoming purplish and thought due more to weathering than moist conditions. Few minute roots between peds. Many small stones of basalt material. |
| R | 34- | | | Basalt rock. |

Agriculture. The Darleith and Dunlop soils stand out as a green sward wedged between the wavy hair grass rough pasture on the hill and the rush-infested bottom land. Between them they represent the farmer's living. A second spinney of Scots pine provides cover and shelter. The Dunlop was last ploughed in 1956. It is fertilised with a composite fertiliser every year. Liming at 30 cwt/acre was done in the summer 1970 after a nine year interval. The greasy layered humus comprising the $A_o$ was not noted in 1967 and may have developed in response to the developing acidity. Such a turf is resistant to treading and liming while improving the sward, may make it more fragile and less resistant to poaching (Pohlen 1968). This should be borne in mind if it is proposed to intensify. The limitation of this soil is the indurated $B_{3gx}$ horizon which impedes drainage. It is variable both in depth and degree of induration. The drainage system appears to be working adequately for there is no rush invasion on the Dunlop sward.

### Amlaird Series. (surface water humic gley).

The Amlaird series has clay textured subsoils and is associated with the gentle slopes and valley bottoms of these volcanic uplands.

### Profile description.

| | |
|---|---|
| Slope | gentle |
| Aspect | south east |
| Altitude | 750 feet |
| Vegetation | Deschampsia caespitosa (tufted hair grass), Agrostis tenuis (brown bent), Festuca ovina (sheep's fescue), Anthoxanthum odoratum (sweet vernal), Holcus lanatus (Yorkshire fog), Juncus conglomeratus (rush). |

Drainage class poor.

| Horizon | Depth ins | pH | NaF reaction | Description |
|---|---|---|---|---|
| $A_0$ | 3-0 | | nil | Dark brown greasy humus of matted grass and grass root remains. |
| $A_1$ | 0-8 | 5.6 | nil | Dark brown clay loam. Organic matter high. A few rusty mottles along root channels. Few worms. Sharp change to |
| $A_{eg}$ | 8-14 | 5.7 | nil | Grey clay loam till, with yellow mottling. No change on exposure to air, indicating that iron has been leached out. Coarsely blocky. Many flat sandstones, similar to those in the Baidland (grass phase) $C_x$. Sharp but variable to |
| $B_{2g}$ | 14-25 | 5.8 | nil | Intensely mottled clay to clay loam, red, brown, purplish and grey patches. Very coarse blocky structure with some platiness. Many roots and root channels. Merging to |
| $B_{3g}$ | 25-36 | 6.2 | nil | Intensely mottled clay to clay loam as above, but more purplish and grey. Many 'iron drainpipes' and iron oxide-stained channels. Blue-green fragments of weathering basalt. Merging to |
| $C_1G$ | 36-48 | 6.2 | nil | Blue green clay to clay loam, very heavy. |

| Horizon | Depth ins | pH | NaF reaction | Description |
|---|---|---|---|---|
| | | | | Oxidises quickly in air to red brown colour. Coarsely prismatic. Many 'iron drain pipes' and preserved roots of birch? and alder? Horizon fills rapidly with water except after very dry spells. |
| $C_2$ | 48- | 6.3 | nil | Red brown coarse gravelly clay loam, obtainable with auger. Free draining oxidised horizon. |

Note on aggregation: one collection of this profile was allowed to dry out several weeks before sieving, and the properties of the dry aggregates differed markedly between one horizon and another,

Thus:-

$A_1$ Soil remained moist, due to the organic matter and could easily be crumbled by hand.

$A_{eg}$ Clods very hard and resistant, and required gentle pounding before sieving was possible. In water, however they slaked easily.

$B_{2g}$ Clods, although dry, broke to a friable consistency and could be crumbled by hand.

$C_1G$ Dried clods harder and less easy to crumble than $B_{2g}$.

Agriculture. The Amlaird on South Drumboy is the typical "Juncus meadow" associated with this type of soil. A drain was encountered at about 3 foot depth ie. just above or in the $C_1G$ horizon. Since the clay pan is as high as the $A_{eg}$, this is too deep to be effective. It is now thought that the drains in surface water gleys in Scotland were conventionally placed too low, and that attempts to correct their inefficiency by spacing them more closely served little purpose. The recommendation today is to place them as close to the surface as would be possible without subjecting them to damage ie. at about 2 feet; and to space them at one chain intervals, providing the gradient was adequate (J.M. Ragg pers. comm. 1971). The Amlaird series also shows remnants of the old 'ridge and furrow' drainage system, running perpendicularly down slope, suggesting it was once cultivated. There appears to be much scope for improving this soil and for extending the 'arable' acreage of the farm, if the land was drained, limed, fertilised and reseeded. Such a policy should also reduce the incidence of liver fluke associated with wet land.

Dunwan series. (ground water humic gley).

This series is located in depressions and water courses. It is developed on clay till and sometimes water sorted.

Profile description.

| | |
|---|---|
| Slope | very gentle |
| Aspect | south |
| Altitude | 735 feet |
| Vegetation | Deschampsia caespitosa (tufted hair grass), Juncus conglomeratus (conglomerate rush), Juncus effusus (soft rush), Sphagnum spp., Knautia arvensis (scabious) Viola spp. (pansy and violet). |

Drainage class very poor .

| Horizon | Depth ins. | pH | NaF reaction | Description |
|---|---|---|---|---|
| $A_0$ | 10-0 | 3.5 | nil | Thick black grass matt. No worms, or throughout profile. |
| $A_1$ | 0-5 | 4.2 | nil | Dark brown friable humified loam. Many roots. Blocky structure |
| $A_{eg}$ | 5-11 | 4.2 | nil | Uniform grey sandy clay loam. Prismatic structure. Sand grains bleached. No iron tubes. Parallel streaks of deposited organic matter. |
| BG | 11-19 | 4.3 | nil | Massive to prismatic clay loam with many iron tubes which pour with water. Many rotting birch? and alder? fragments, which have probably been a long time in the profile. A few orange mottles.<br>In some pits there is a lens of sand in this horizon, which may have been due to an influx of the fluvio-glacial material from the neighbouring Darvel series. |
| $C_1G$ | 19-30 | 5.6 | nil | Blue cheese-like clay. Much decomposing rock and stone, mainly blue, some with red-brown mottling. Spots of white sand. Massive to prismatic structure. Many 'iron drainpipes'. |

| Horizon | Depth ins. | pH | NaF reaction | Description |
|---|---|---|---|---|
| $C_2G$ | 30- | n.d. | nil | Coarse sand, obtainable on augering, single grained and structureless, probably water sorted. Blue grey colour. The ground water level is above this horizon. |

### 4. South Drumboy farm.

South Drumboy is a typical farm in the area. It takes in the greater part of Drumboy hill and is comprised of 322 acres : 64 acres of 'arable' and 258 acres of rough pasture. In 1970/71 it was supporting 84 cattle including a dairy herd of about 40, and 125 sheep. This was about the same stock as was carried in 1967, although stocking is intensifying because in the last two years the hoggs have been wintered at home instead of being sold off in the autumn. In common with other farms in the area, liming is done less often now than in the nineteen fifties. As mentioned earlier the Dunlop area was nine years without lime application. "When things get tight, that is the first to go." Mr. Young commented. Basic slag application

## Plate 1

## South Drumboy pastures

Foreground: pasture with rushes - Darleith series

Mid-distance: green pasture - Dunlop series, merging

downslope to rushes with: - Amlaird series

Mid-distance: rushes, line of Soame burn - Dunwan series

Mid-distance rising to Kingswells Farm: pasture on fluvio-

-gla-glaciald (Darvel series)

has also been discontinued not from choice but because it is now difficult to obtain. A compound fertiliser is applied to Dunlop and Darleith every spring. This means that potassium is put on in the growing season which probably increases the danger of hypomagnesaemia.

## 5. The allophane test on soils in other localities.

Scottish soils in various localities which have given a strong reaction to the sodium fluoride test are (a) basalt soils and (b) C horizons of podzols.

Campsie basalt profiles invariably reacted in the B and C horizons, but not in the A horizon. In this they appeared to show a 'cryptic podzol' property which Ragg (p.21) described for the eastern Darleith soils, and resembled also the Darleith series on Drumboy. However it could be said that the Campsie soils examined were themselves all Darleith series, and that no soils comparable to the Dunlop on South Drumboy, have yet been examined on the tertiary basalt. Analogues to the Dunlop soil which react in all horizons may yet be found there.

Podzols, in the writer's experience, with the single exception of the Baidland 'grassland phase' podzol, reacted only in the C horizon. This was the case for a number of geological types. Podzols developed on glacial moraine, old red sandstone, quartz-mica schist, and a brown podzolic soil developed on greywacke all gave no reaction in the B horizon and strong reaction in the C. The writer believes this finding to be general, but on the other hand one notes that Bracewell et al. (1970) obtained much stronger reaction from the $B_2$ horizon of a Blackhope podzol and brown forest soil derived from greywacke than from the $B_3$, and the C response was slight.

## 6. Tirau silt loam allophane soil, New Zealand.

In 1968 the writer joined the I.S.S.S. excursion to North Island, New Zealand. Tirau silt loam, an allophane soil was among those demonstrated (plate 2 ). Small

Plate 2

Road cutting soil profile of Tirau silt loam

samples were taken from the A horizon and from 12 to 20" depth of the B horizon. A shortened profile description is given below. A full description of this same profile together with the analysis can be found in "Soils of New Zealand" (1968 3 p.80).

Profile description (moderately leached yellow brown loam, Brown Ando soil).

| | |
|---|---|
| Slope | 2° near crest of rolling ridge |
| Aspect | East |
| Vegetation | Pteridium esculentum (bracken fern), Dactylis glomerata (cocksfoot), Anthoxanthum odoratum (sweet vernal) |
| Natural vegetation | Broadleaf-podocarp forest |
| Parent material | Tirau ash |
| Rainfall | 55 in. |
| Altitude | 400 ft. |
| Location | G.R. N66 273 253 Hetherington Rd. Tirau. |

| Horizon | Depth ins. | NaF react. | Description |
|---|---|---|---|
| A | 0-12 | strong | very dark brown silt loam to sandy loam; friable; mod. developed very fine crumb to granular structure; abundant roots. |
| B | 12-20 | v.str. | yellowish brown sandy loam; firm to friable;mod. developed medium nutty structure, |
| C | 20-36 | slight | yellow brown sandy loam to loamy sand; firm and generally massive. |

# CHAPTER X: MINERAL EXAMINATION OF THE SOUTH DRUMBOY SOILS.

## 1. Identification of parent rock minerals in thin section and by X-ray powder diffractometry.

### (i) Preparation.

Thin sections were made from hand specimens of rock outcrops. These included basalt from rock on the east side of Soame burn at ~735 ft. and which underlies Dunlop, Amlaird and Dunwan soils; and three types of trachyte which outcropped near the Darleith and Baidland pits at 825 and 876 ft. respectively (fig. 35 p.391). No thin sections was made of porphyry, which did not appear to outcrop at all, although it is the major formation underlying the hill top peat. Specimens were cut with a Cutrock Mark II Unicutta, mounted on glass slides with Lakeside 70 cement, partially ground with the Unicutta, and finally ground to 0.03 mm thickness with 200 and then 600 carborundum powder. The sections were covered with glass slips fixed by canada balsam.

Since the specimens were much weathered, they were also examined by X-ray powder diffractometry.. The rock was ground in an agate mortar and the powder rolled into spindles with durofix. X-ray diffraction patterns were obtained with a Philips Debije-Scherrer 114.83 mm camera, using cobalt (1.7902Å) radiation and iron filter. Lattice spacings of these and other minerals were correlated with those given in the ASTM index (1960, 1967); or with the powder data of Brown (1961), and are listed in Appendix A p.762.

### (ii) Basalt rock.

The rock in hand specimen was dark, fine grained with phenocrysts, and contained amygdales and unfilled vescicles. In this section, the groundmass was of felspar and pyroxene and the phenocrysts were olivine. This established it as Dalmeny basalt. Specimens were much weathered, with a great deal of magnetite present and the olivines altered to antigorite. There was a little anatase, and also a number of large pale green non-pleochroic crystals, of low relief and isotropic, which often contained feathery cores of low birefringency. These were not identified, but were thought to be amygdale mineral. Powder pattern data (Appendix A1 p.762 ) identified the felspar as labradorite and the pyroxene as augite. Spacings for magnetite and antigorite were also obtained. The absence of olivine spacings suggested it had altered to antigorite.

### (iii) Trachyte rock.

The rocks in hand specimen were pinkish and fine grained. One variety (a) had large rectangular phenocrysts surrounded by a brown rim, but most commonly the rocks were distinctive for red-brown 'serpentinous' veins (b). In thin section the ground mass crystals flowed in one direction, establishing the rocks as trachyte, and were mainly laths of clouded felspar, interspersed with quartz. (a) contained much magnetite, some amorphous greenish material and a few flakes of hornblende. Most distinctive were the large rectangular phenocrysts of fairly high refractive index and low birefringence, clouded and brownish with alteration and surrounded by thick rims. Some of these phenocrysts appeared not to be single grains, but to be like shards stuffed with small crystals including quartz. X-ray diffraction data (Appendix A 11 p.773) showed that the phenocrysts and the whole rock were composed of oligoclase, quartz, hematite and kaolinite. Some lines were not identified. The veined specimens (b) contained the same clouded euhedral crystals, but they were mainly confined to the groundmass among the laths of felspar, and the phenocrysts were felspars that showed carlsbad twinning. Rivulets of brilliant red and dark brown splayed over them and accompanied trains of smaller crystals that comprised the veining seen with the naked eye. Under reflected light the red mineral was orange and was concluded to be hematite, for although this normally reflects steel grey with metallic lustre, it can occur 'red and translucent' (Kerr 1959). X-ray diffraction data (Appendix A 12 p.775) showed that the veined trachyte differed from trachyte (a) in its felspar, which appeared to be orthoclase, but similarly contained hematite, quartz and kaolinite, together with unidentified mineral.

## 2. Identification of minerals in the sand fractions of Dunlop and Amlaird soils.

Sand fractions were normally recovered after soil dispersion as > 100 mesh coarse sand and > 300 mesh fine sand. They were examined under the stereoscopic microscope and grains were picked out and powdered for X-ray diffraction identification.

The Dunlop horizons were very ferruginous. The coarse sand fraction consisted in grains of quartz and labradorite felspar together with a large number of 'conglomerates' resembling pudding stones, of varying stability to disruption by biological weathering, mechanical energy (sonic vibration or shaking in water) and peroxidation. The fine sand and coarse silt fractions contained large amounts of pyroxene-magnetite aggregates and hematite. Their proportions in relation to quartz and felspar could be guaged from a quantitative electromagnetic separation that was done on the $< 100 > 200$ mesh fraction of $B_{2g}$, shown as follows:-

| | |
|---|---|
| pyroxene-magnetite + hematite aggregates | 32% |
| hematite | 30% |
| 'amorphous' minerals, mainly yellow and brown | 8% |
| clear glassy and white or stained minerals | 30% |

The ferro-minerals reached a maximum in the $C_g$, while the $B_{3gx}$ contained less pyroxene-magnetite than the other two subsoils, and many pale yellow conglomerates in the coarse sand.

The Amlaird horizons, with the exception of $C_2$ which

Table 53 Identification of sand particles in Dunlop and Amlaird soils.

| Description | Minerals | Relative abundance | Appendix A |
|---|---|---|---|
| brown tablet or flake | hematite, with goethite | abundant in fine sand | 4 |
| blackish-brown magnetic aggregate | augite, with magnetite, hematite and labradorite | fairly abundant | 3 |
| clear glassy | quartz | abundant | n.d. |
| opaque white | labradorite and quartz | abundant | 2 |
| conglomerate pudding stone | labradorite, hematite and augite | abundant in coarse sand | n.d. |
| pale to bottle-green or black glassy crystal, conchoidal fracture | augite | frequent | 5 |
| clear flake | muscovite | frequent | n.d. |
| clear green flake | chlorite | rare | n.d. |
| amorphous yellow | anatase, (with talc?) | not known | 7 |
| bright orange | heulandite | rare | 6 |
| yellow orange, clear to translucent | calcite | not known | 8 |

resembled Dunlop $C_g$, were composed mainly of white minerals quartz and felspar, reflecting the contribution of the sedimentary component in the parent till. The felspars were not examined and would be expected to be mixed. Amlaird also contained proportionately more muscovite and more bottle green crystals of augite. Pyroxene-magnetites were scarce. There were fewer conglomerates and these were strongly weathered. In the A horizons of both soils the conglomerates were powdery with weathering and there was negligible magnetic material. Thus, as the soil developed, stable quartz and relatively stable felspar and muscovite remained in the sand and silt fractions, while clay was formed from augite and felspar, and hematite from magnetite. Hematite was all-pervasive as coarse tablets, fine flakes and material 'amorphous' to the naked eye. Goethite was associated with it. In addition, there were small amounts of anatase, chlorite, calcite and heulandite. The heulandite in particular was a vivid and useful 'marker mineral', since together with calcite, it is associated with basalt, in whose fissures and cavities it was crystallised out from low temperature solutions. Hence it was an indicator of basic material in the parent till.

## 3. Identification of minerals in the clay fraction of Dunlop and Amlaird soils.

### (i) X-ray diffraction analysis.

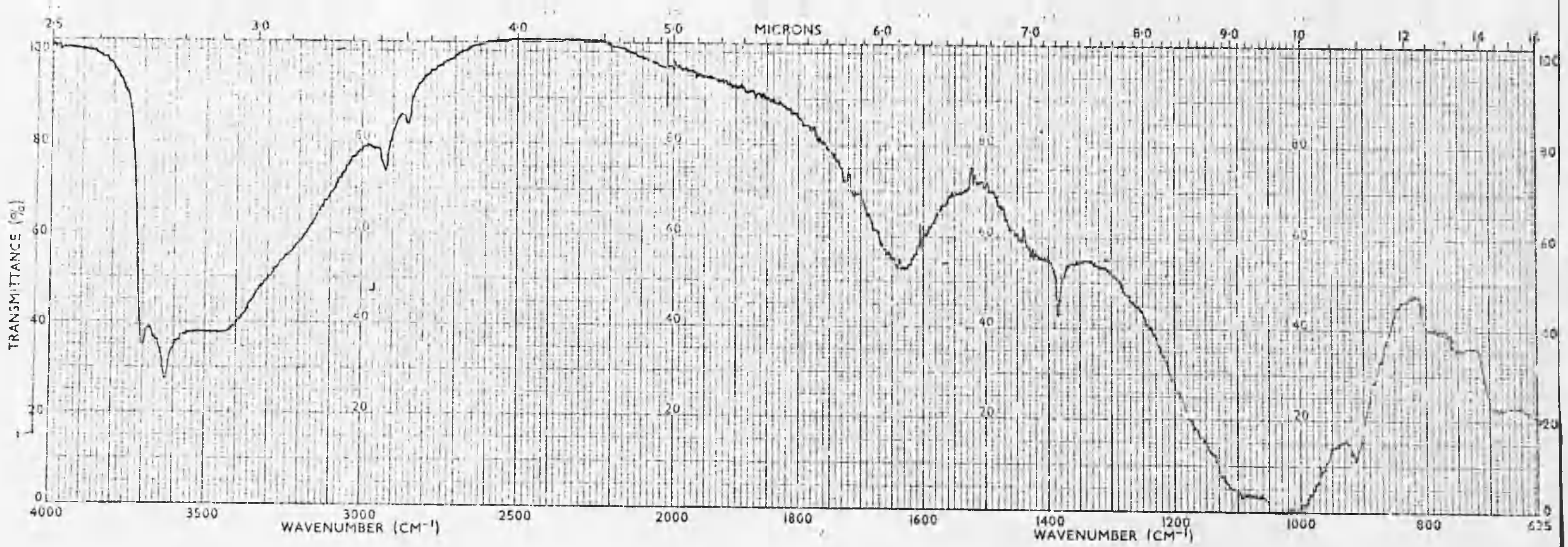
X-ray diffraction analysis of the clay fractions showed that all the soils contained kaolinite and a 14 Å clay mineral together with accessory quartz, anatase and hematite. There was a 10 Å line in the silt + clay fractions but this must have been due to muscovite, because illite appeared to be either absent in the $< 1.4\ \mu$ fractions, or only detectable as a barely perceptible diffuse 10 Å line in a few of the Dunlop samples. Typical lattice spacings for the clays in all horizons are shown in the set for Dunlop $B_{2g}$ given in Appendix A 9 p. 771. Further tests included the following:-

(a) Test for expanding mineral. A Dunlop $C_g$ clay flake was impregnated with glycerol. The 14 Å spacing expanded to 17.4 Å. This might have indicated montmorillonite but conflicts with the findings of the Kilmarnock Soil Survey Memoir (Mitchell and Jarvis 1956) which only identified vermiculite, chlorite and mixed layer 14 Å minerals in the Darleith soils. Since no other tests were made, it is simply designated an expanding 14 Å clay mineral.

(b) Tests for kaolinite. The 7.15 Å line disappeared and the 14 Å spacing collapsed to 9.15 Å when a Dunlop $C_g$ sample was heated to 560°C. These two results suggested that kaolinite was present and chlorite was absent. Kaolinite was also unequivocably established from the 3698 $cm^{-1}$ peak on the infra-red spectrum of all horizons (fig.37).

(c) Search for crandallite. There were three unidentified lines in the X-ray pattern for the bottle green augite crystals (Appendix A1), and two unidentified lines for the sol obtained after sodium fluoride extractions which might conceivably have been due to crandallite, and it was decided to see whether this phosphate mineral which Norrish (1968) had found of widespread but indeterminate occurrence was in the Darleith soils. Norrish's work was referred to in Chapter VIII p.326 and the method used was that recommended by him. Clay suspensions containing ~ 0.6 g of $< 1.4\mu$ clay were evaporated down to 40 ml in plastic beakers and 40 ml HF was added. The suspensions were swirled for 2 minutes and then transferred to a plastic vessel containing 420 ml water. They were centrifuged, washed and centrifuged in N NaOH, N HCl and twice in water. No trace of crandallite was found in any of the samples tested ie. Dunlop $A_1$, $B_{2g}$, $B_{3gx}$, Amlaird $C_1G$.

Fig. 37 Infra-red absorption spectrogram of Dunlop $B_{3gx}$ $<1.4\mu$ clay fraction (showing kaolinite 3698 $cm^{-1}$ peak).



(d) Effect of 2 minute HF treatment. The above treatment left a residue in which anatase and hematite were concentrated. Kaolinite content was reduced. The most interesting result was the disappearance of the 14 Å line and its replacement in the Dunlop samples by the 10 Å illite line, together with other illite spacings (Appendix A10 p.772). This suggests that some kind of interstratifying material was removed. It was not allophane however, because sodium fluoride treatment did not collapse the spacing.

### (ii) Differential thermal analysis.

#### Method.

Differential thermal analyses were made on a Bureau de Liason M3 micro differential thermal analyser using 6 µl semi-micro thermocouple platinum cups in which the platinum sample vials were placed. Signals were recorded on a Smith's Servoscribe 2-pen recorder. The clays were stored in vacuum desiccators over saturated magnesium nitrate solution (relative humidity ∼56%) and at least 4 days before use. They were prepared for analysis by mixing with calcined kaolinite and quartz, normally in the weight ratio 30 : 30 : 10. Quartz was included in order to calibrate the temperature curve with its $\alpha \rightarrow \beta$ phase transition at 573°C. The sample mixture was poured into a semi-micro platinum crucible and tamped lightly, so that it was about three-quarter full. Calcined kaolinite was similarly prepared for the reference thermo couple. Unperoxidised samples were heated in a nitrogen atmosphere and peroxidised samples in air. A heating rate of 20°C/minute was used, since lower heating rates produced broad shallow peaks. The controls on amplifier and recorder were normally set at second highest sensitivity ie. 20 $\mu$V on the amplifier and 5 mV on the recorder.

## Results.

Differential thermal analyses of the Darleith Association $< 1.4 \mu$ clays were very similar in all five profiles. They showed a large water desorption peak, normally in the region 84° to 97°C. and often with a shoulder of variable position. The water desorption peak might be associated with expanding clay and/or with allophanic material, and no attempt has yet been made to identify it further. All the clays exhibited a broad endothermic peak corresponding to the dehydroxylation of crystalline clay, and occurring in the region 480 - 490°C. for the brown forest soils and 507 - 512°C. for the gleys. A high temperature exothermic peak was given by all clays except Baidland $A_{eg}$, and the A horizons of Darleith, Amlaird and Dunwan. It was very small for Dunlop A. It appeared as a broad dip whose position varied between 890°and 940°C. It was suppressed in the peroxidised clays, although it could be detected at highest sensitivity in these also. The suppression was analagous to that found for the high temperature peak of a peroxidised allophane clay by Campbell et al. (1968), discussed in Chapter II 9 p.37 and illustrated in fig.3 p.36. Further investigations into the response of this peak to various clay pretreatments and its relationship to the kaolinite and allophane content of the soil have still to be made.

A peak at 298° on the Baidland $A_{eg}$ trace was possibly due to gibbsite, although one would normally expect to find it in a lower horizon, such as the $B_3$ where it was noted by Follett et al. (1965). In other respects the DTA patterns were similar to those obtained by Mitchell and Farmer (1962) for Ayrshire soils, and Follett et al. (1965) for the Drumboy Baidland and Dunwan soils. Traces for Dunlop $B_{2g}$ and Amlaird $B_{2g}$ are in fig.38a p.428A and fig. 38b p.428B ($N_2$ atmosphere).

DTA curves were also made for the Tirau B soil. For one sample, the flocs were allowed to settle until the suspension was very dilute, and at highest sensitivity

Fig. 38a <u>DTA pattern of Dunlop</u> $B_{2g}$ <u>very fine clay</u>.

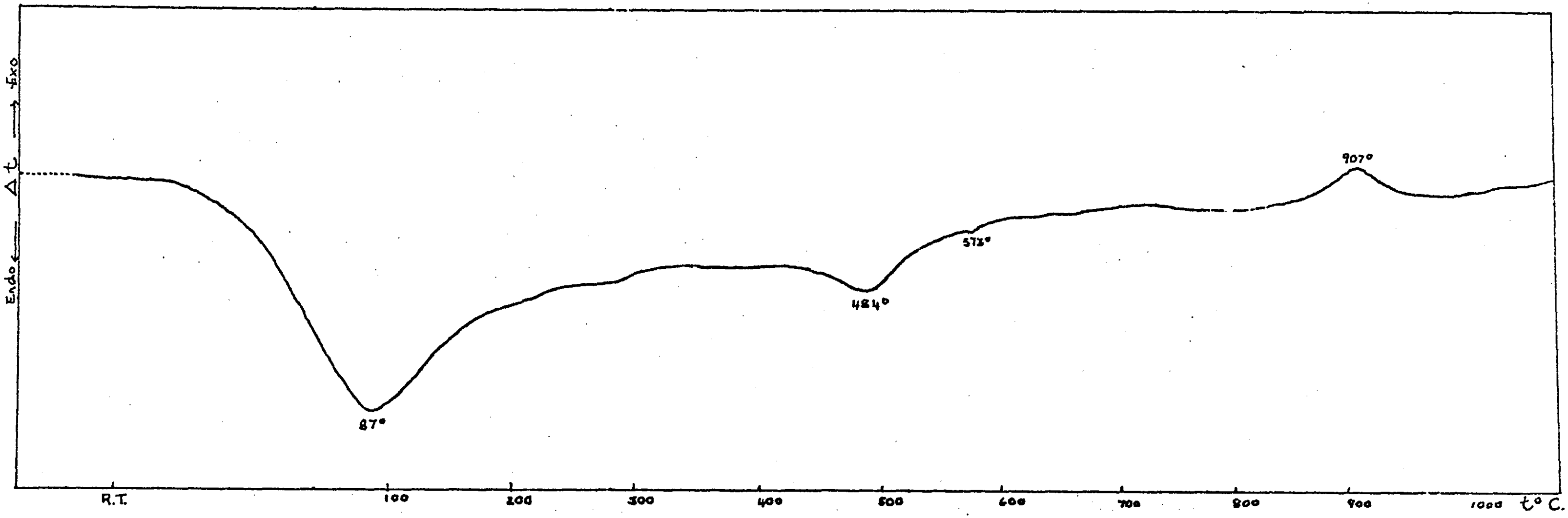
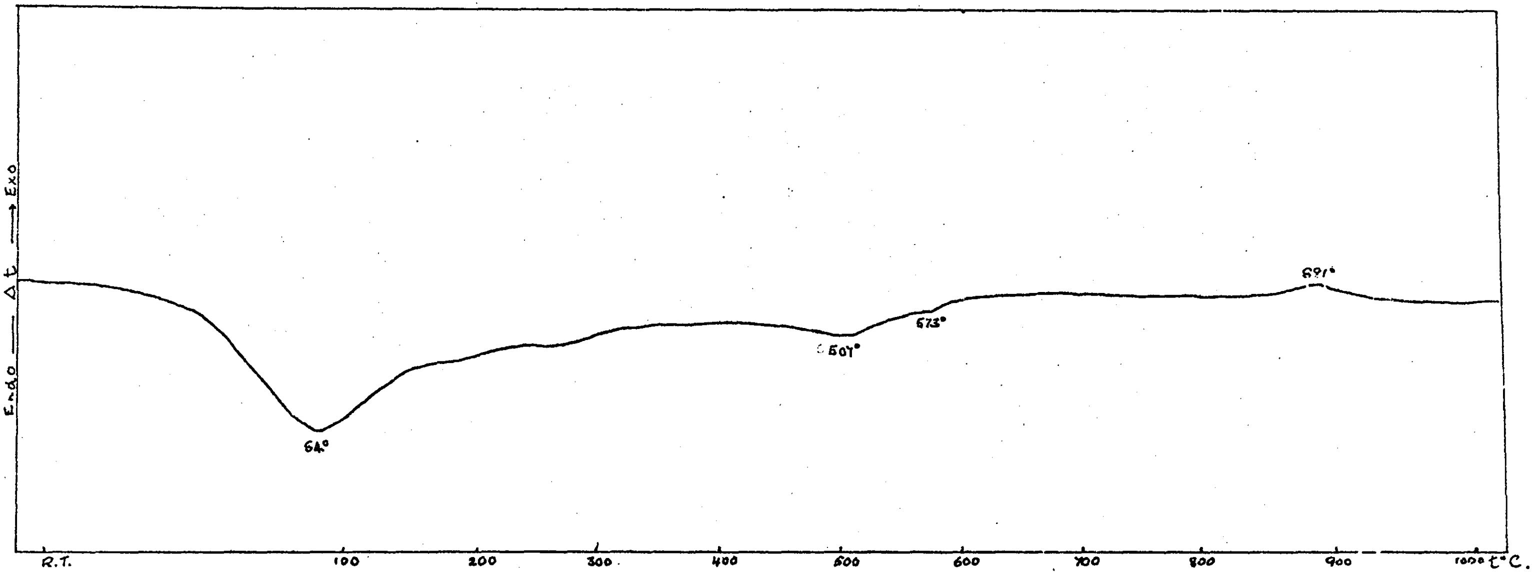


Fig. 38b DTA pattern of Amlaird $B_{2g}$ <1.4μ clay.



in $N_2$ atmosphere, a comparatively low water desorption peak was obtained at ~50°C. followed by a conspicuous endothermic peak at 304°C. which was attributed to gibbsite. The high temperature exothermic was represented by a shallow trough at ~ 891°C. In a second sample, the flocs were allowed to settle for 10 minutes before sampling, and in this case there was very sharp dehydration peak at 112°C, a shallow endotherm at 496°C. and a sharp exotherm at 922°C. The dehydration and high temperature peaks were correlated with allophane and the dehydroxylation peak with kaolinite. Kaolinite was later confirmed from an X-ray diffraction pattern of Tirau B clay which had been treated with sodium carbonate to remove allophane.

It thus appeared that gibbsite was in the very finest clay fraction, since in the first sample it escaped the flocculation which had removed most of the allophane from suspension. This is the first instance known to the writer, in which gibbsite has been found in the Tirau soil. Sample traces are shown in fig.39 p.430.

Fig. 39a DTA pattern of very dilute suspension above Tirau B flocs after 30 minutes settling.

($N_2$ atmosphere)

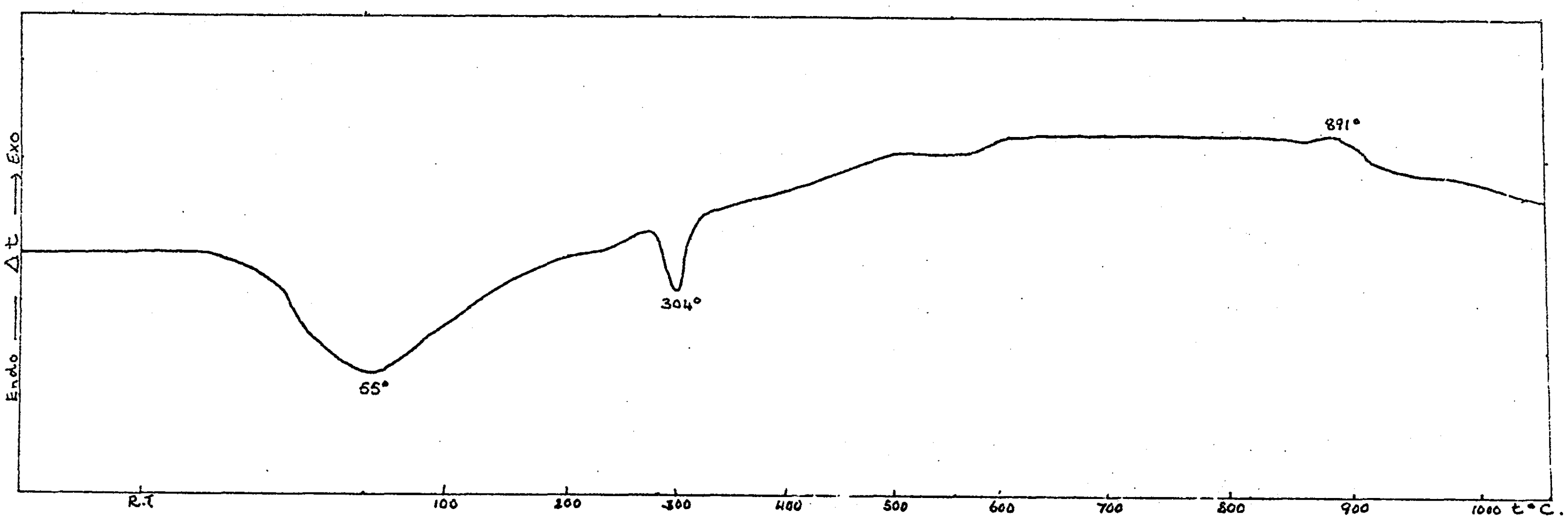
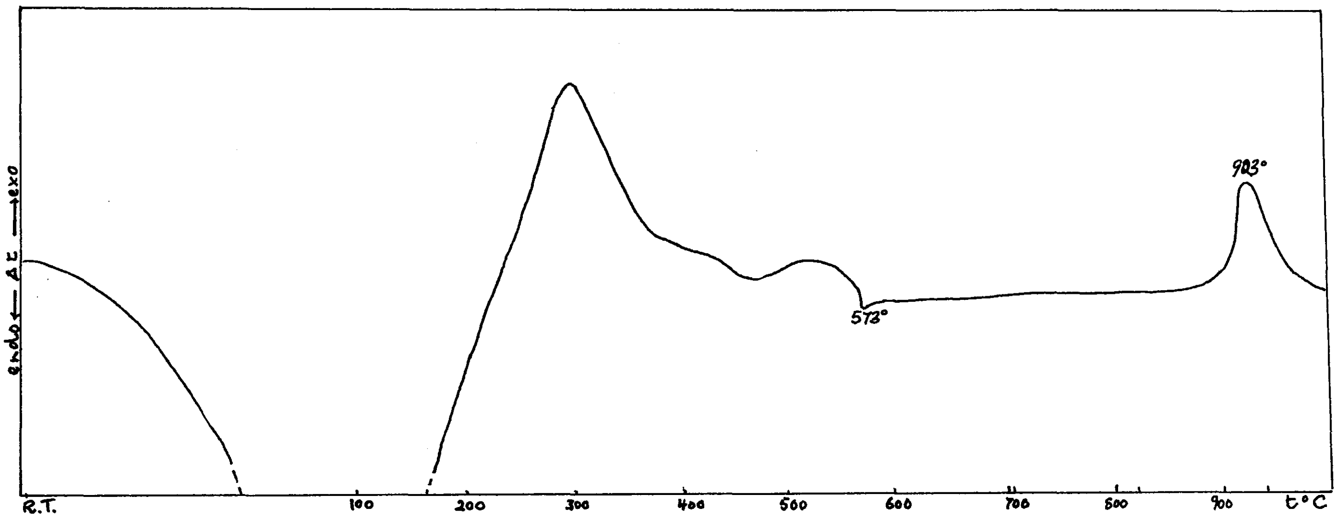


Fig. 39b DTA pattern of suspension above Tirau B flocs after 10 min. settling.

(air atmosphere)



## 4. Examination of the allophane content of Darleith and other soils.

### (i) Measurement of allophane content by NaF method.

Methods for assessing the allophane content in soils by the sodium fluoride technique were described in Chapter II 12 p.40. These methods were: noting the rise in pH in a given time (Fieldes and Perrott 1966), titration of the supernatant after centrifuging, and repeating the NaF treatments (Huang and Jackson 1965), back titration of the suspensions (Rustum and Roy 1957), and a continuous back-titration to maintain pH constant at 6.8 (Bracewell et al. 1970). In the following experiments the allophane content was assessed by noting the rise in pH in a given time.

### Exp. 1 The rise in pH for Darleith, Tirau, and mica-schist podzol soils treated with NaF solution.

50 ml saturated NaF solution was added to 1 g air-dry soil and the rise in pH with time was recorded. The pH of the NaF solution was normally 6.8 to 7.2. It was found important to make it up fresh each day, because the pH rose as it reacted with the glass. The results are shown in fig. 40 p.434 where pH values for a period of one hour are recorded, and in Table 54 pp.432 -

Table 54 pH values obtained after 30 minutes, when 1g dry soil was treated with 50 ml saturated NaF solution.

| Brown forest soils | | | | Allophane soil | |
|---|---|---|---|---|---|
| Dunlop | | Darleith | | Tirau | |
| Horizon | pH | Horizon | pH | Horizon | pH |
| $A_1$ | 9.9 | A | 8.3 | A | 10.2 |
| $A_2$ | 10.2 | B | 11.5 | B | 10.6 |
| $B_{2g}$ | 11.4 | | | | |
| $B_{3gx}$ | 11.1 | | | | |
| $C_g$ | 10.4 | | | | |

| Humic Gley soils | | | |
|---|---|---|---|
| Amlaird | | Dunwan | |
| Horizon | pH | Horizon | pH |
| $A_1$ | 8.4 | $A_1$ | 7.7 |
| $A_{eg}$ | 8.9 | $A_{eg}$ | 9.0 |
| $B_{2g}$ | 8.9 | $B_2G$ | 8.5 |
| $B_{3g}$ | 8.95 | GG | 8.3 |
| $C_1G$ | 8.9 | | |
| $C_2$ | 9.0 | | |

Contd/

Table 54 contd/

podzols

Baidland (heath phase)

| Horizon | pH |
|---|---|
| $A_{eg}$ | 9.4 |
| $B_{2g}$ | 11.2 |
| C/R | n.d. |

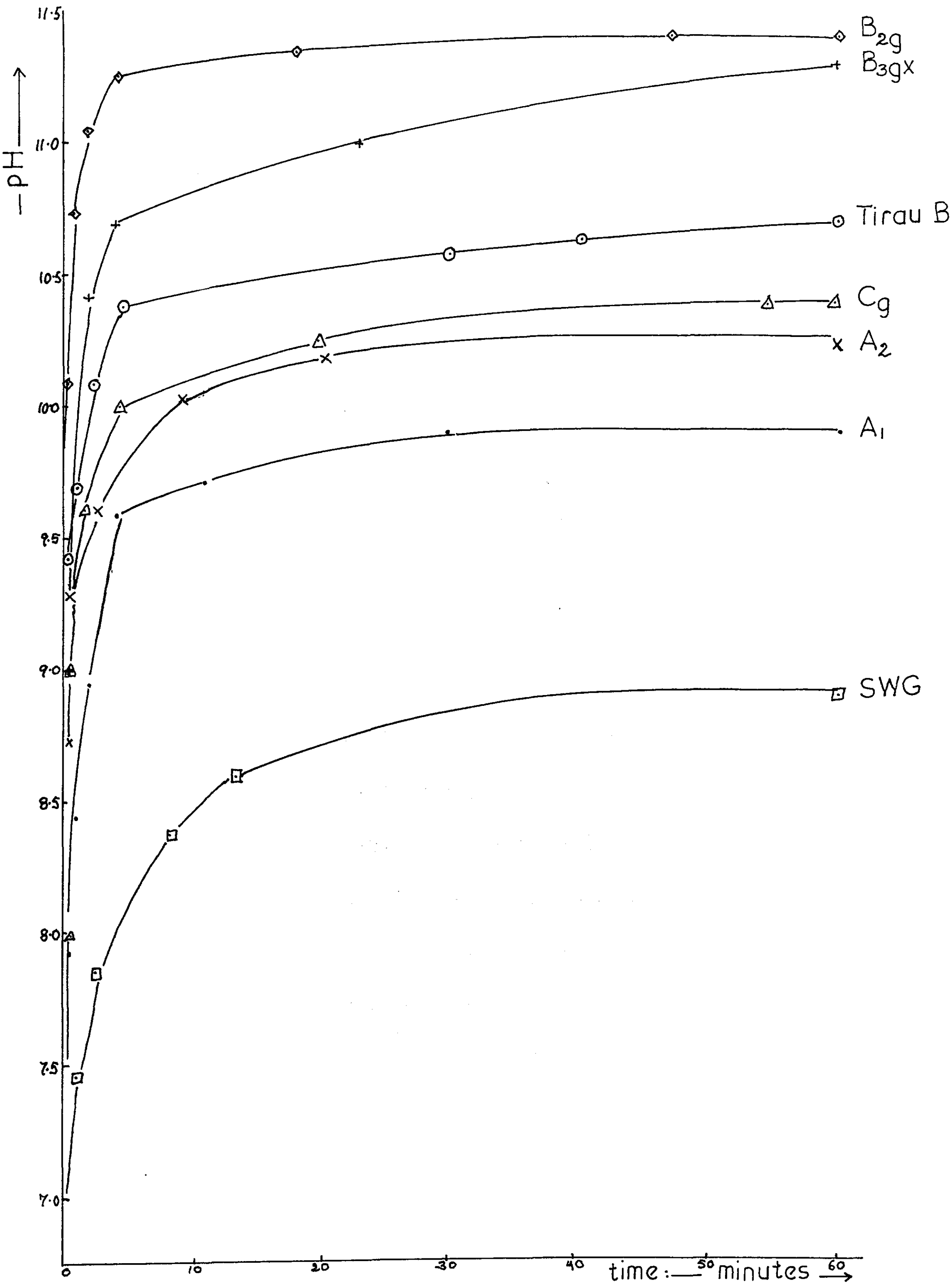
Baidland (grassland phase)

| Horizon | pH |
|---|---|
| A | n.d. |
| $B_2$ | 11.35 |
| $C_x$ | 10.2 |
| R | 8.6 |

Loch Lomond mica schist podzol.

| Horizon | pH |
|---|---|
| $A_o$ | n.d. |
| $A_e$ | n.d. |
| B | 8.4 |
| C | 10.6 |

Fig. 40 Rise in pH with time on addition of saturated NaF solution to 1g air dry soil.



433, which gives the pH after 30 minutes. Very high values were obtained for the B horizons of the Darleith association brown forest soils and podzols. The pH rose to between 11.1 and 11.5 after 30 minutes treatment. Lower values were recorded in their C horizons: 10.2 to 10.4 pH. Dunlop soil showed considerable reactivity in both its $A_1$ and $A_2$ horizons, giving pH values 9.9 and 10.2 respectively, but the Darleith series soil resembled the Campsie basalt freely drained soils examined by the writer (p. 411 ), in that the A horizon showed negligible reactivity (pH 8.3). The humic gley soils both showed low reactivity, Amlaird rising to 8.9 - 9.0 pH in all horizons except the $A_1$ which was 8.4. The Loch Lomond mica-schist podzol, in contradistinction to the Darleith podzols, only gave a pH 8.4 in the B horizon, but was 10.6 pH in the C, and in this respect followed the pattern for podzols observed by the writer (Chapter IX 5 p.411). One of the surprises perhaps, was the comparatively small rise in pH for the Tirau B soil : 10.2 and 10.6 for the A and B horizons respectively. This was also noted by Bracewell et al. (1970). Since in the Tirau profile analysis the clay fraction was estimated to be 100% allophane, the low reactivity suggests it must be rather siliceous. The $SiO_2:Al_2O_3$

ratio was reported to be 2.2 ("Soils of New Zealand" 1968 <u>3</u> p.81, for sample 8 to 12 ins. depth). One concludes that the sodium fluoride test only gives a very qualitative measurement of allophane content, but this is offset by its value as an indicator of aluminous allophane.

The Dunlop soil resembles the Tirau B soil in having allophane in all its horizons. Mitchell and Farmer (1962) noted that large amounts of alumino-silicate material were associated with the topsoils of some Ayrshire soils. Ragg however, classes the Darleith association soils as cryptic podzols (Chapter <u>II</u> <u>3</u> p.19) on the grounds that in the east of Scotland where they are subjected to less leaching, they give only weak response to flouride, while the stronger response of their western counterparts reflects more intensive leaching. This interpretation does not account for the following observations (a) the strong reactivity of Dunlop A soils (b) the strong reactivity of the Darleith podzol B horizons, distinguishing them from other podzols which, in the writer's experience, react in their C horizons (c) the discovery described later of small amounts of allophane in the Amlaird soil. The writer proposes that the high allophane activity in the Darleith soils is due to the weathering of volcanic (basalt or trachytic tuff) material and that leaching is a secondary effect. The effects of leaching can be seen in a comparison of the freely drained Darleith series on Drumboy and the Campsies, where the A horizons show negligible allophane, and the imperfectly drained Dunlop soil which retains it.

### Exp. 2 The rise in pH for a variety of soils treated with NaF solution.

An attempt was made to find a soil that would have no allophanic material ie. that would remain inert to sodium fluoride treatment, in order to provide a control for some experiments. The search proved more difficult than was anticipated. Table 55 p. 438 shows the rise in pH for a variety of soils and clays after a five minute treatment. It is seen that most of them contained materials that responded to the sodium fluoride test. Amlaird soils were found later to have more allophane than the test would suggest, but further investigation of the other soils in the table has not been made.

Table 55 pH values obtained after 5 minutes for a variety of soils, when 1 g was treated with saturated NaF solution.

| Soil or clay | pH after 5 min. |
|---|---|
| Buchlyvie clay | 7.8 |
| Larbert soil | 8.4 |
| Strathven soil | 8.6 |
| B horizon of cultivated brown forest soil on old red sandstone | 9.3 |
| Carse acid clay | 7.7 |
| Topsoil of red shale bing | 9.2 |
| Fuller's earth | 9.2 |
| Fithian illite | 9.5 |
| Amlaird $B_{2g}$ | 8.25 |
| Amlaird $C_1G$ | 8.5 |
| Amlaird $C_2$ | 8.75 |
| Keuper marl* | 8.1 |

*after 45 mins. pH = 9.95

### (iii) The effect of the heat of wetting on the sodium fluoride reaction with soils.

Various minor observations were made from time to time on the reactivity of allophane, and have been collected together in this and the following sections. They include some effects of the heat of wetting and of peroxidation, a study of reaction products, and notes on buffering and pH properties.

### Exp. 3 The reduced rise in pH when sodium fluoride was added to vibrated soils.

It was thought that if the soils were sonically dispersed before sodium fluoride treatment, the dispersion would improve the accessibility of the sites to fluoride attack and that this would be reflected in higher pH values than with aggregated soil.

1 g soil was vibrated for 30 minutes and to the final suspension volume 100 ml, 50 ml saturated NaF solution was added. The results, and those found for dry soil are shown in Table 56 p.440. It is seen that the pH values were considerably lower for the vibrated soils than for the dry soils. This could not have been due to the greater dilution, because addition of spatulas of solid sodium fluoride thereafter made no

Table 56 Comparison of the rise in pH when sodium fluoride was added to dry and to vibrated soils.

| Soil | pH after 30 minutes | |
|---|---|---|
| | dry soil | vibrated soil |
| Dunlop $B_{2g}$ | 11.4 | 10.5 |
| Dunlop $C_g$ | 10.4 | 9.9 |
| Tirau B | 10.6 | 9.9 |
| Amlaird $C_1G$ | 8.9 | 8.6 |

difference to the rise in pH.

The only explanation appears to be that addition of water to dry soil released sufficient energy by heat of wetting to activate the breaking of bonds which were not disrupted by fluoride attack alone. It will be recalled from Chapter V 3 p.224 that Storgaard Jørgensen and Mitchell (1970) pointed out that raising the temperature of $Na_2CO_3$ suspensions had the same effect as disrupting the alumina structures by ball-milling. These authors also observed that "ultrasonic treatment of Suriname and British Guiana gibbsites reduces the amount of alumina removed by the first and second extractions at all temperatures compared with that removed from the untreated samples" and suggested ultrasonic treatment might have an inhibiting effect, perhaps by altering the surface configuration. The following experiment indicates another possibility.

Exp. 4 To test whether the heat of wetting increases the reactivity of soils with sodium fluoride.

Three 1 g samples of $B_{3gx}$ soil were subjected to the following treatments:

(a) soil vibrated for 10 min. in 30 ml water, 50 ml saturated NaF solution added.

(b) soil vibrated for 10 min. in 30 ml water, heated to 80°C. and 50 ml NaF at 80°C. added.

(c) 50 ml saturated NaF diluted to 80 ml and added at 80°C. to 1 g dry soil.

(d) cold NaF added to dry soil from result in Table 56.

The rise in pH after 30 minutes was as follows:-

| | | |
|---|---|---|
| (a) | sonic + cold NaF | 10.9 |
| (b) | sonic + heated + hot NaF | 11.1 |
| (c) | dry soil + hot NaF | 11.1 |
| (d) | dry soil + cold NaF | 11.1 |

The disparity between the dry soil and vibrated soil was unfortunately not so great for the $B_{3gx}$ sample as for the others, and the experiment requires repeating with different horizons and with soils that have been in equilibrium with water for longer periods, as was the case with most of the soils in Table 56. There is a strong indication however that the heat of wetting provided sufficient activation energy to allow more OH groups to be displaced by fluoride from dry soil than from wet soil. Mattson (1931 b) discussed the heat of wetting and quoted figures from the work of Anderson (1924) and Anderson and Mattson (1926), in which the heat of wetting for Sharkey and Norfolk soils was 16.3 and 7.6 cal/g respectively.

From an experimental point of view, these results indicate that maximum displacement of hydroxyl, organic matter, phosphate and so on from allophane, will be achieved by starting with dry soils. This effect may have importance in the field also. For example if allophane undergoes changes such as taking up organic matter to a less extent in permenantly moist ie. gley soils, it will be more readily crystallised, and this may help to explain why gley soils do not contain allophane, at least in so far as they fail to respond to the fluoride test.

### (iv) The inhibiting effect of peroxide pretreatment on the sodium fluoride reaction with soils.

It was thought that removal of organic matter would unmask aluminium sites in the allophane clay and that this would be reflected in an increase in the reactivity of the soil with fluoride.

### Exp. 5 The rise in pH on sodium fluoride treatment of peroxidised and unperoxidised soils.

1 g Dunlop $B_{2g}$ soil was vibrated and made to 100 ml (pH 5.55). A further 1 g sample was peroxidised, vibtated and made to 100 ml. Its pH of 4.85 was adjusted to 5.85 with NaOH. Amlaird $C_1G$ samples were

Table 57 Comparison of the rise in pH of unperoxidised and peroxidised soils on NaF treatment.

| Soil | pH | | |
|---|---|---|---|
| | initial | after 10 min. | after 1 day |
| Dunlop $B_{2g}$ unperoxidised | 5.55 | 10.25 | 10.50 |
| Dunlop $B_{2g}$ peroxidised | 5.85 | 9.8 | 10.05 |
| Amlaird $C_1G$ unperoxidised | 6.9 | 8.45 | 8.9 |
| Amlaird $C_1G$ peroxidised | 6.9 | 8.25 | 8.62 |

similarly prepared. The samples were treated with 50 ml saturated NaF solution and their rise in pH is recorded in Table 57 p.444. It is seen that hydroxyl release was depressed by peroxidation, reflecting an inhibition of fluoride reactivity. Farmer and Mitchell (1963) have shown that peroxide treatment produces large amounts of aluminium oxalate, and an explanation for this unexpected result may be that oxalate partially protects aluminium against fluoride attack.

### (v) Observations on the buffering of allophane.

### Exp. 6 Buffering in the region pH 6 to 7 in suspensions treated with sodium fluoride.

Strong buffering was noted in the region pH 6 to 7 when soils were back-titrated with N10 HCl in order to maintain near neutral pH. This is shown by the following values for the addition of N10 HCl, when 10g Dunlop $C_g$ was treated with 100 ml aliquots of saturated sodium fluoride.

| Treatment no. | pH after 10 mins. | ml HCl to maintain pH 6.65 added during ~2 hrs. |
|---|---|---|
| 1. | 10.7 | 20 |
| 2. | 10.75 | 35 |
| 3. | 9.4 | 25 |

### Exp. 7 Development of proton releasing groups on clay after sodium fluoride treatment.

When Dunlop soils were treated with sodium fluoride to extract organic matter, as described in Chapter XIV, it was found that washing of the soils to remove the sodium fluoride and chloride salts produced a lowering of pH of the order 6.5 to 5.2, or when the suspension was made to 8.3, it fell repeatedly overnight ~~ot~~ 6.8 - 6.0. Huang and Jackson, who did not control their pH, noted a drop in pH from 9.5 to 5.5 and the development of a buffer range in clays following KF treatment. As described in Chapter II 12 p.48 and illustrated in fig.5 p.49 they correlated this buffering with the 3rd buffer range of Schwertmann and Jackson (1963,1964) and attributed it to the formation of proton donor groups hydrolysed on the freshly exposed clay surface. These were of the form $XAl - OH_2^{0.5+}$ where X is the alumino-silicate. An electronmicrograph of a KF treated mica crystal showed an etching of the surface. It is not known however, how far the acidity in the Dunlop soils was due to disruption of crystal surfaces or to the effects of unextracted allophane.

Exp. 8 Buffer range in the region 9 to 10.

Large quantities of ammonia solution were required to raise the pH of 10 g soil suspensions in the region pH 9 to 10, but these varied with (a) the clay (b) the clay's pretreatment. Dunlop $B_{2g}$ required twice as much ammonia as Dunlop $C_g$, unless the $C_g$ soil was peroxidised, when the amounts required were about the same. This was a qualitative observation only, and was attributed to the relative amounts of exposed alumina on the clay surface. In Chapter XIII it is shown that the silica : alumina ratio for extractable amorphous material was higher in the $B_{2g}$ than the $C_g$ horizon. Removal of organic matter would unmask aluminium sites.

### (vi) Identification of products of the reaction of sodium fluoride with allophane.

During the extraction of organic matter, described in Chapter XIV, it was important to examine the products of the reaction in order both to identify artefacts and also to establish the optimum conditions for the extraction, particularly optimum pH. In general 10 g of soil was stirred or shaken with 100 ml aliquots of saturated NaF solution over a period of days. The pH was either allowed to rise or it was controlled by addition of HCl. The organic matter was removed progressively in the supernatant. The residue was then washed free of salts by shaking in water and centrifuging at 10,000 rpm for 30 minutes, with repetition of this process until the chloride and/or sodium in the supernatant was negligible. Centrifuging at a lower speed, such as 3000 rpm produced a golden, slightly fluorescent sol containing fine clay. Hence this low speed was only useful after the final washing when a sol was required for examination of the fluoride reaction products. Also examined was the dialysate of organic matter extract, which contained the salts and soluble material.

### Exp. 9 Products found in the sol suspension.

The products of the fluoride reaction depended very much on the pH at which it took place. Table58 p.449 illustrates this. When the pH was controlled between 6 and 7, electrophoresis of the salt-free Dunlop $B_{2g}$ sol (pH 5.2) produced dark brown flocs at the negative electrode and a turbidity at the positive electrode. The isoelectric point was in the region 7.9. The sol at pH 5.2 was found to contain cryolite ($Na_3 AlF_6$) and a material whose powder pattern best matched $\kappa$-$Al_2O_3$. Appendix A 13 gives the spacings. Cryolite was also identified on a DTA trace by an endothermic

Table. 58 Products of the reaction of fluoride with allophane recovered from the fine clay sol.

| Soil | pH of reaction | positive colloids | negative colloids | whole sol. |
|---|---|---|---|---|
| Dunlop $B_{2g}$ | 6 - 7 | cryolite<br>K - $Al_2O_3$ | | expanding clay<br>kaolinite<br>cryolite<br>K - $Al_2O_3$<br>crandallite? |
| | 11.0 | | | Na $AlO_2$? |
| Dunlop $C_g$ | 8.8 max. | K - $Al_2O_3$<br>kaolinite tr.<br>hematite tr.<br>quartz tr. | expanding clay<br>kaolinite<br>hematite<br>anatase | |
| | 10.7 | | | expanding clay<br>kaolinite<br>hematite<br>anatase<br>illite tr. |
| Amlaird $B_{2g}$ | 8.9 | | | kaolinite<br>hematite<br>anatase<br>K - $Al_2O_3$ |

phase change at 563°C. It has not yet been checked whether cryolite was also present in the negative fraction, or whether it too carried a positive charge. Nor is it known whether the cryolite was itself colloidal, or if was kept in suspension by association with organic matter. It dissolved at some pH below 8.8. This was shown for example by raising the pH of the positive fraction to 8.87, collecting it as negative. There was no cryolite in the product. In addition, a Dunlop $C_g$ whose pH was not allowed to rise above 8.8 and an Amlaird $B_{2g}$ whose pH rose only to 8.9 both yielded sols containing $\kappa$ - $Al_2O_3$ but no cryolite. Their X-ray diffraction patterns are indexed in Appendices A 14 and 15 respectively. $\kappa$-$Al_2O_3$ dissolved in more alkaline suspension. A Dunlop $B_{2g}$ sample whose pH rose $> 11.0$, showed no alumina species in the sol, but some of the lines may be due to $NaAlO_2$ (Appendix A 16). Since this sol contained no clay it must have been very dilute. A Dunlop $C_g$ sample whose pH rose to $\sim 10.7$ showed only soil clays present in the sol (Appendix A 17). These included expanding clay, kaolinite, hematite, anatase and a trace of illite.

It is of interest to note that sols containing both negative and positive material were extremely stable. This further illustrates an experiment of Mattson (1922) who observed that negative humus particles and quartz particles made positive by adsorption of ferric hydrolysis products, merely sped past each other when in dilute suspension, and did not aggregate even on collision.

Exp. 10 Products found in the organic matter extracts.

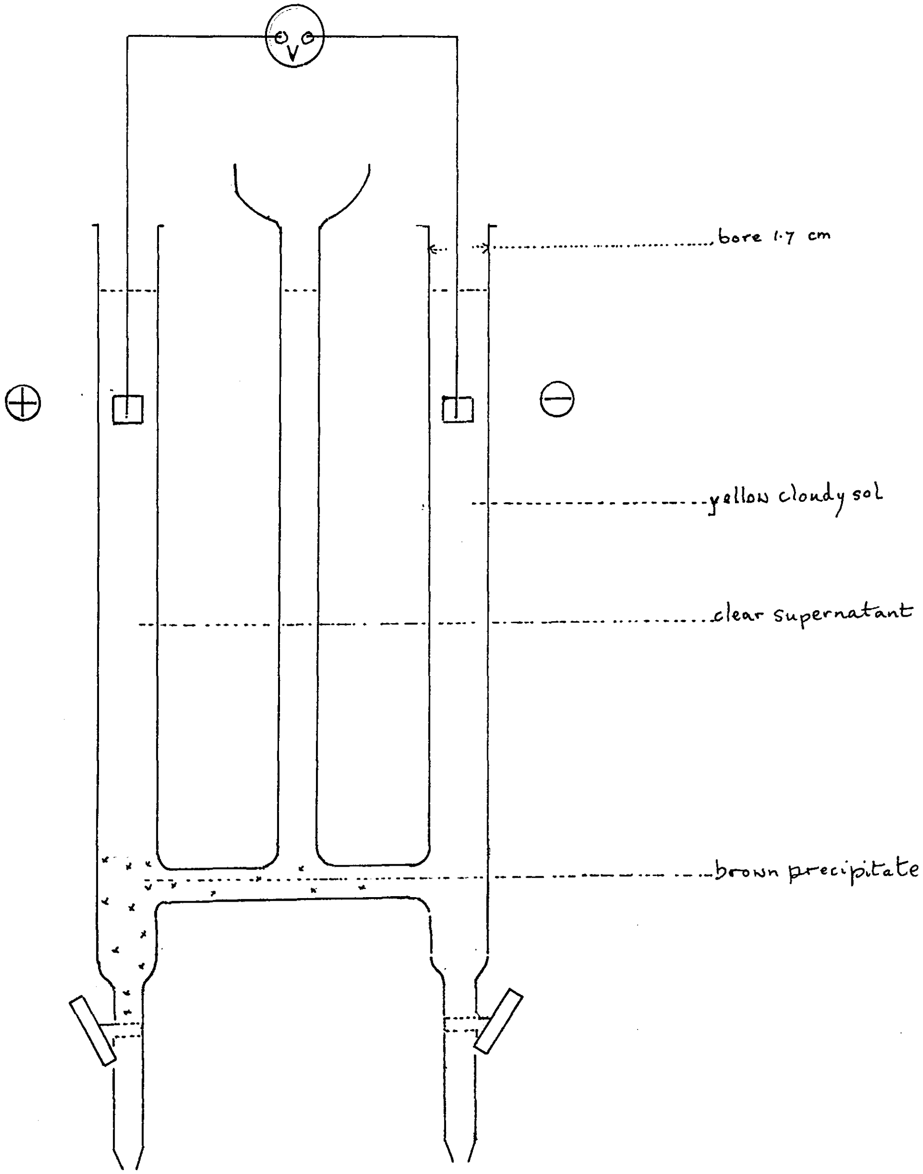
Appendix A 18 shows that the water extracts contained NaF and possibly $NaAlO_2.3H_2O$. One of the surprising observations made during attempts to remove salt from the organic matter extracts was the very small amount of $H^+$ and $OH^-$ displaced from IR 120 and IRA 400 exchange resins when leached with the extract. This suggested that non-ionic products had been formed, and at first it was supposed that most of the salt could be accounted for as cryolite. When the extract was dialysed however, and the dialysate concentrated by evaporation or by passing it through a charcoal column, large quantities of white precipitate were obtained. This was insoluble in dilute acid, alkali and organic solvents. It was soluble in $HClO_4$ and concentrated $HNO_3$ and dissolved after one day in concentrated HCl and $H_2SO_4$. It gave a poor X-ray diffraction pattern (Appendix A 17) and could not be identified.

## (vii) Attempts to separate the allophane clay from the crystalline clay fraction.

### Exp. 11 Crude separation by electrophoresis.

A strongly diluted suspension of Dunlop $C_g$ (1969) was used, in the hope that organic matter interference would be minimal. The initial pH was 5.1. There was a clear separation of material in the two limbs of the vessel as shown in the figure41 p.453. The limb with the positive electrode contained a heavy precipitate and clear supernatant. The limb with the negative electrode contained a yellow cloudy material which persisted the next day. It should be noted that Tirau B clay dispersions are yellowish and that ferric oxide is yellow when the particles are only about 50 Å diameter, so that a yellow colour is often associated with small sized particles. The positive clay could not be precipitated with sodium dodecyl sulphate ( a negatively charged detergent) but this was probably because it had acquired a negative charge at the unbuffered cathode. Addition of HCl to bring an aliquot to pH 5.2 precipitated the clay before a second test could be made. This in turn however, could have been due to allophane flocculation in the region of the isoelectric point.

Fig. 41 Electrophoresis of Dunlop $C_g$ fine clay ($pH_i$ 5.1) and separation into positive and negative fractions.



### Exp. 12 Separation of lithium saturated clays by electrophoresis.

It was wondered whether the electrophoretic separation might be improved by saturating the clays with $Li^+$, so that repulsion was enhanced by the increased water of hydration adsorbed on the clay. A sample of Dunlop $C_g$ was vibrated in 10 mmoles/l lithium chloride, and then further diluted. Positive and negative material was recovered after electrophoresis. The positive material was recycled to purify it, and its pH was controlled with HCl additions. At pH 2.65 it gave a precipitate with sodium dodecyl sulphate after five minutes, whereas cetyl ammonium bromide, a positively charged detergent, failed to precipitate it.

These rather primitive experiments suggested that allophane material could be separated, at least in some measure from the crystalline clay, even if it was present, as has been surmised (Follett et al. 1965), as a closely associated coating on the clay crystals.

### (viii) Demonstration of "exchange alkalinity" by Darleith soils.

It will be recalled from the discussion in Chapter VII p.294 that Mattson (1931 a, 1931 b) showed how the acidoid : basoid ratio of soil clays influenced soil pH, making soils with a high ratio appear acid, by dissociation of $H^+$ cations, and soils with a low ratio appear basic by dissociation of $OH^-$ anions. The pH values of the Dunlop and Amlaird soils are given in Table 59 p.456 but it would have been necessary to dialyse them to find the pH of their exchange neutrality. Nevertheless the influence of the allophane fraction in giving the soils an 'exchange alkalinity' was observed very simply in the 'suspension effect'.

In most soils the pH of the suspension is found more acid than the pH of the supernatant. Van Olphen (1963) ascribed this entirely to the difference in liquid junction potential between the suspension and the salt bridge. Mattson however, showed (1931 b) that the 'suspension effect' was governed by the relative dissociation of the $H^+$ and $OH^-$ ions, and that an alkaline suspension effect was given by soils with low $SiO_2:R_2O_3$ ratio, as illustrated in Table 47 p.315.

Table 59 pH values of Dunlop and Amlaird soils. (soil : water ratio 1 : 2.5)

| Horizon | pH | Horizon | pH |
|---|---|---|---|
| Dunlop $A_1$ | 5.8 | Amlaird $A_1$ | 4.98 |
| $B_{2g}$ | 4.85 | $A_{eg}$ | 5.35 |
| $B_{3gx}$ | 5.35 | $B_{2g}$ | 5.75 |
| $C_g$ | 5.05 | $C_1G$ | 7.25 |
|  |  | $C_2$ | 7.62 |

### Exp. 13 The alkalinity of Darleith soil suspensions with respect to their supernatants.

The pH of the clear or slightly turbid supernatant was taken, and then that of the stirred suspension. Peroxidised soils were most easily examined because they were flocculated; moreover the removal of organic matter from allophane probably enhanced the effects. The pH measurements are given in Table 60 p.458. The Dunlop $B_{2g}$ and $C_g$ peroxidised soils were more alkaline in their suspension by about 0.2 units. The peroxidised Amlaird $B_{2g}$ showed only very slight difference or none at all, but this in itself was significant since most soils show exchange acidity. The Amlaird $C_1G$ results suggest that the anion exchange $Cl^-$ resin unmasked more allophane than the peroxide. One must also bear in mind the effects of the removal of strongly bound anions on the adsorption and dissociation of $OH^-$ ions. This may account for the spectacular difference, observed on one occasion, between pH 4.95 for the supernatant and 5.58 in the suspension. It was indeed this difference which first drew attention to the phenomenon. Further investigations are required on the effects of anion exchange resins on the Dunlop and Amlaird soils both in this connection, and in connection with the flocculation effects described in the next Chapter.

Table 60 <u>The pH of the suspension and supernatant of some Dunlop and Amlaird soils</u>.

| Soil | pre-treatment | pH supernatant | pH suspension |
|---|---|---|---|
| Dunlop $B_{2g}$ | unperoxidised | 5.4 | 5.45 |
| Dunlop $B_{2g}$ | peroxidised | 4.35 | 4.55 |
| Dunlop $B_{2g}$ | peroxidised | 4.15 | 4.35 |
| Dunlop $C_g$ | peroxidised | 4.05 | 4.25 |
| Dunlop $C_g$ | peroxidised | 4.25 | 4.5 |
| Amlaird $B_{2g}$ | peroxidised | 5.12 | 5.2 |
| Amlaird $B_{2g}$ | peroxidised | 5.15 | 5.15 |
| Amlaird $C_1G$ | shaken with anion exchange resin ($Cl^-$) | 5.45 | 5.67..unstirred flocs<br>5.6 ...suspension |
| Amlaird $C_1G$ | shaken with anion exchange resin ($Cl^-$) | 4.95 (after 15 minutes equilibriation) | 5.58 |

# CHAPTER XI : PRELIMINARY STUDIES IN MECHANICAL ANALYSIS: SOME ANOMALIES FOUND FOR THE DARLEITH SOILS.

## 1. Methods of mechanical analysis.

### (i) Choice of method.

The method chosen for the routine dispersion of soils prior to mechanical analysis was that of ultra sonic disintegration, or 'sonic treatment' as it is referred to in this work. The procedure recommended by Edwards and Bremner (1967) was normally followed. It appeared to give good results. The dispersions were very stable and occasional failures were at first attributed to inefficient stirring. Certain anomalies came to light, however, and the discovery of these is described in this Chapter, while their systematic investigation is the subject of Chapter XIII. The origin of the anomalies was thought to be the allophane content of the Darleith soils.

### (ii) Ultra-sonic dispersion.

An M.S.E. 100 watt Ultrasonic Disintegrator (18-20 Kc) with 19 mm titanium probe was used to disperse the soils. 10 g air dry soil was suspended in 25 ml deionised water contained in a water-cooled vessel. The probe was lowered a few millimetres below the surface of the liquid and the suspension was stirred by magnetic stirrer. Sonic treatment was usually half an hour. Soils very high in clay became viscous and soils high in organic matter were difficult to stir, so that in these cases 5 g soil was used. When dispersing agents were employed, they were best added prior to sonic treatment.

### (iii) Separation of the size fractions.

The dispersed soil was sieved through 100 and 300 mesh sieves, separating coarse from fine sand respectively, and the $< 50\ \mu$ fraction was passed into a litre cylinder. This was made to volume, stoppered and shaken for pipette analysis by the method of Kilmer and Alexander (1949). The fine silt + clay fraction was pipetted from a 10 cm depth after sedimenting a period of time appropriate for the temperature of the suspension, in accordance with the Stoke's Law Equation, and the clay fraction $< 1.4\ \mu$ esd (equivalent settling diameter) was recovered in a similar manner after sedimenting for 16 hours at 20°C. Occasionally the $< 2\ \mu$ esd clay was pipetted after sedimenting 8 hours at 20°C.

The clay + silt and clay fractions were peroxidised with 2 to 6 ml analar 30% $H_2O_2$, evaporated and weighed after overnight drying in an oven at 110°C. Sands were dried and weighed in the same way. Topsoil sands often contained much organic matter, and this was removed by vibrating them in $CHCl_3$ for a few seconds and decanting the floating debris. Where sand aggregates were bound with organic matter this was sometimes peroxidised. The organic matter content of the soil was found by the Walkely - Black method (1947) and the percent weight of each size fraction was calculated from the oven dry weight of mineral soil. Coarse silt % was found by subtraction, except on a few occasions when it was recovered by decanting and weighed.

The size of the particles in the soil separates as determined by sieve mesh number and equivalent settling diameter was as follows:-

| soil fraction | mesh no. | particle diameter μ |
|---|---|---|
| coarse sand | 100 | 2000 - 150 |
| fine sand | 300 | 150 - 50 |
| coarse silt | - | 50 - 20 |
| fine silt | - | 20 - 1.4 |
| clay | - | < 1.4 |

The constant temperature oven varied between 19°C. in winter and 22°C. in summer, and the appropriate corrections for the time of sampling of clay calculated from Stokes' Law are given in the appendix on p.485. The calculations also showed that for a sixteen hour, 20°C settling time the clays are correctly $< 1.41\ \mu$ esd.

It was found essential to use analar $H_2O_2$. General purpose $H_2O_2$ evaporated to leave impurities which both interfered with the clay weights and produced artefacts in the sand fractions.

### (iv) Peroxidation.

When soils were peroxidised for some specific purpose, they were suspended in about 50 ml water, heated and stirred on a magnetic hotplate at ~90°C., and 5 ml aliquots of analar 30% $H_2O_2$ were added until peroxidation was thought as complete as possible. 1 to 2 days treatment with 10 to 25 ml $H_2O_2$, depending on the organic matter content of the horizon, was usually given. Sonic treatment of peroxidised soils produced highly viscous suspensions, and it was found best to divide the suspension in half and vibrate each one separately.

### (v) Dispersion in alkali, calgon and NaCl.

For sonic dispersion in alkali, 20 drops of 1:1 ammonia solution were added to the sonic vessel and

~ 20 drops were added subsequently so that the pH of a litre of suspension was in the region 9.6 to 10.2. The same total quantity of alkali was added to the shaking vessel when an overnight shaking method was used. Calgon dispersing agent was made up as 3.7 g sodium hexametaphosphate and 0.749 g $Na_2CO_3$ per 100 ml. 10 ml calgon was added to the soil suspension. The weight due to this amount was subtracted from the clay + silt and clay pipetted fractions.

On two occasions NaCl was used as dispersant, and 0.09 g NaCl was added to the sonic vessel. This was equivalent to 60 mmoles/l while disruption was in progress and 1.5 mmoles/l after dilution to 1 litre.

### (vi) Methods of shaking.

Three methods of shaking were used, (a) a 10 : 600 soil : water ratio, in which 10 g soil was shaken 16 hours in ~600 ml on a rotary shaker. (b) 10 : 60 soil : water ratio, with 16 hours shaking on a rotary shaker. (c) 10 : 60 soil : water ratio, with 16 hours shaking on a reciprocating shaker.

## 2. Disruption of the aggregates.

In estimating the efficiency of a method of mechanical analysis it is essential to distinguish between the three processes of disruption, dispersion and prevention of flocculation. The corrective treatment required to improve the results is different in each case and occasionally a treatment may be so wrong that the situation is worsened. In the Darleith soils, flocculation problems were not obvious, but flocculation could be induced as will be seen later. The most obvious problem was disruption, because of the extreme firmness of the aggregates or 'conglomerates' in the coarse sand fraction, particularly in the brown forest soils. The experiments below illustrate three methods of disruption : sonic vibration, water shaking and peroxidation. Their relative efficiency was gauged from the percent weight of sand recovered and by optical examination of the sand fraction.

### (i) Sonic disruption.

### Exp. 14 Progressive analysis of a sonic dispersion.

Table 61 records the results obtained when a Dunlop $B_{2g}$ (1969) sample was subjected first to wet sieving, and then to successive sonic treatments for

Table 61 % Soil separates of Dunlop $B_{2g}$ (1969) horizon after progressive sonic disintegration.

(Exp.14 p.464)

| Soil fraction | wet sieving | 1st sonic | 2nd sonic | 3rd sonic |
|---|---|---|---|---|
| coarse sand (100 mesh) | 23.8 | 12.7 | 11.2 | 10.6 |
| medium sand (200 mesh) | 20.0 | 9.4 | 9.9 | 8.8 |
| fine sand (300 mesh) | 8.7 | 5.6 | 3.9 | 4.0 |
| coarse silt | n.d. | 15.0 | 16.0 | 14.8 |
| fine silt | n.d. | 36.4 | 34.5 | 36.8 |
| clay < 1.4μ | n.d. | 20.9 | 24.5 | 26.0 |

10 + 10 + 10 minutes, with optical examination of the sand fractions and reconstitution of the soil after each step. In this case there was only about 5% increase in clay between the first and third sonic treatments, and a 2% decrease in coarse sand. The role of the agitation was to disperse the clay coating the water-stable aggregates and then progressively disrupt them. Ferro-alumino-silicate conglomerates, which on X-ray evidence consisted mainly in augite, labradorite and hematite, were most resistant. The fragile tablets of hematite tended to be flaked apart. Magnetite-rich pyroxene was probably protected from further disruption by collecting on the bar magnet, and thus appeared to concentrate in the fine sand and coarse silt fraction. The mineralogyhas been described in more detail in Chapter X.

Exp. 15 Effect of prolonging sonic treatment.

In the above experiment, most of the disruption was complete in the first 10 minutes. The process could be very variable however. Two Dunlop $B_{2g}$ (1971) samples were sonic dispersed in ammonia solution for 30 and 60 minutes. The prolonged treatment raised the clay percentage from 23 to 26.5% and decreased the coarse sand from 25.9 to 17.4% (Table 64 , p.525). The variability in the efficiency probably reflects differences in stirring efficiency and perhaps also depth of probe in the liquid.

### (ii) Disruption by shaking in water.

### Exp. 16 Comparison of shaking and vibration treatments in water only.

Samples of soil : water ratio 10 : 60 were shaken 16 hours on a reciprocating shaker, and the clay precentages obtained for three soils compared with those obtained by sonic $H_2O$ treatment thus:-

| | Dunlop $B_{2g}$ | Dunlop $C_g$ | Amlaird $B_{2g}$ |
|---|---|---|---|
| shaking | 18.1 | 18.0 | 26.8 |
| sonic | 19.24 | 29.6 | 43.1 |

The greater efficiency of the shaking method for Dunlop $B_{2g}$ than for the other two soils almost certainly reflects its higher sand content. Edwards and Bremner (1967) noted the abrasive effect of sand in improving the dispersion. There is no doubt that longer shaking times would have yielded clay percentages for the heavier soils similar to those achieved by sonic vibration.

### Exp. 17 Comparison of shaking methods.

It is not only a high soil : water ratio which is important in obtaining a good result. A method of agitation must be chosen which is sufficiently disruptive. Rotary shaking of a Dunlop $B_{2g}$ soil with a 10 : 60 soil : water ratio yielded less than 7% clay. Optical examination showed the coarse and fine sands to be still clay coated, so that their grains looked amorphous. Coarse sand aggregates were clearly composed of fine sand and silt particles embedded in the matrix. The inefficiency of the rotary method of shaking appears at first to be in contradiction to the finding of Bourget (1967), who reported that seven Quebec soils gave the same clay percentage when agitated in calgon by any one of 4 methods, including the rotary method, and for 2, 4 or 8 hours. Bourget concluded from this that comparable mechanical analysis results would be obtained from different laboratories regardless of differences in their methods of agitation. He attributed the consistency in his results however to the soils' pretreatment with acid leaching and peroxidation. Disruption must have been almost complete before the shaking stage, so that shaking merely improved on the dispersion. This is confirmed in the next experiment.

(iii) Disruption by peroxidation.

Exp. 18 Disruption of soil aggregates by $H_2O_2$.

5 g Dunlop $B_{2g}$ (1969) was peroxidised in 100 ml water with a total of 60 ml 30% $H_2O_2$, and stirred with a magnetic stirrer at 85 - 95°C. for two days. The yield of coarse and fine sand was 10.5 and 11.47% respectively, and can be compared with the 11.6 and 12.3% obtained from sonic dispersion in water (Table 63 p.524.) When peroxidation was followed by sonic treatment, the disruption was more pronounced : 7.8 and 9.5% of coarse and fine sand was recovered. Optical examination of the sands from the $H_2O_2$ -only treatment, showed that very few of the ferro-conglomerates remained in the coarse sand. Most of the minerals were quartz or felspar. The fine sand fraction however, contained a fair proportion of hematite and pyroxene. The $H_2O_2$/sonic treatment gave a coarse sand fraction similar to the above, but the fine sand looked white to the naked eye and was almost devoid of ferro minerals. It was as though they had been blown apart. This happened on every occasion when sonic vibration followed prolonged peroxidation. These findings explain the consistency in Bourget's results and confirm the conclusion of Edwards and Bremner that "use of calgon as a dispersing agent following prolonged treatment of soils with

6% $H_2O_2$ causes little further disruption of the aggregates." The role of calgon, after such treatment, probably lies in its ability to prevent flocculation.

Conclusions: The disruptive efficiency of the three methods, sonic vibration, reciprocator shaking and magnetic stirring in hydrogen peroxide was remarkably similar for the soils studied. The powerful effect of. hydrogen peroxide illustrates the all-important role of organic matter in soil aggregation. The resistance of the Darleith coarse sand conglomerates to disruption however, suggests there is a case for not basing reports of soil field texture on ultimate particle size analysis but on aggregates stable to a milder treatment.

## 3. Dispersion of the aggregates.

### Exp.19 Sonic dispersion in water and in dispersing agents.

Clay yields obtained from sonic dispersion in water and in ammonia solution can be compared in Tables 62-67 , and in the figures collected below:-

| | | Dunlop (1971) | | | | Amlaird |
|---|---|---|---|---|---|---|
| Treatment | | $A_1$ | $B_{2g}$ | $B_{3gx}$ | $C_g$ | $B_{2g}$ |
| Sonic | $H_2O$ | 26.9 | 19.2 | 21.8 | 25.0 | 43.1 |
| Sonic | $NH_3$ | 34.9 | 23.0 | 22.0 | 29.6 | 40.1 |

It is seen that the biggest improvement made by dispersion in alkali was for the $A_1$ horizon. Other Drumboy A horizons were also noticed to be less stable than subsoils with sonic/$H_2O$ treatment, because they often coagulated within about a week on standing. The results suggest that organic rich soils require to be peptised in order to disperse clay-organic matter aggregates. Longer sonic treatment might have achieved this, but it was decided that A horizon soils should be vibrated in ammonia solution as a matter of routine.

NaCl was also investigated as a dispersing agent, but only 17.3% clay was obtained for Dunlop $B_{2g}$ (1971). This may have been due to the fact that the $Na^+$

concentration in the sonic vessel was 60 mmoles/l, or within the threshold limit of 25 to 150 mmoles/l for a univalent ion, and after dilution to 1.5 mmole/l shaking was not prolonged enough to disperse the coagulates.

## 4. The stability of dispersed soils.

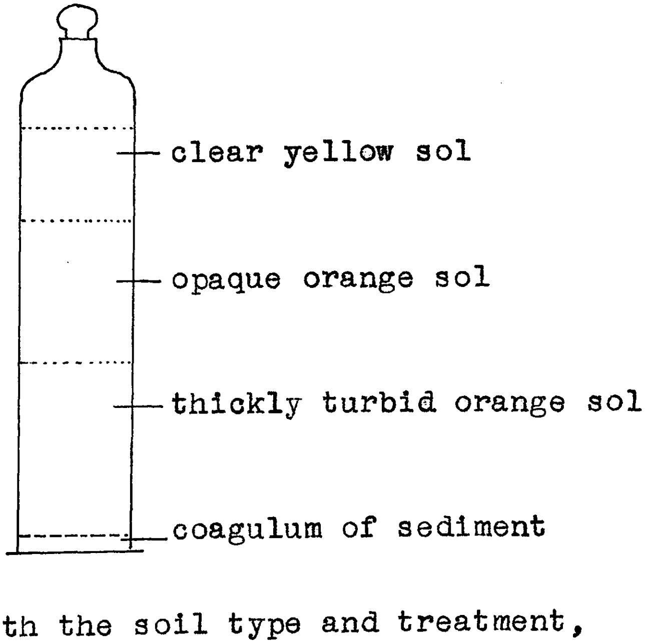
Dispersions were not normally thrown out after mechanical analysis but were kept as long as possible, both in order to observe whether they sedimented to form a coagulum or subsidsided to form flocs; and in order to determine their stability by shaking them up and resampling after days, weeks, or months after the initial dispersion. Soils that were properly dispersed were very stable.

Exp. 20 Mechanical analyses to test the stability of suspensions.

Amlaird $B_{2g}$ was sonic dispersed in water and a clay yield of 43.1% was obtained. The same result was found when the suspension was reshaken and analysed after 2½ months. Dunlop $A_1$ was similarly stable when it had been sonic dispersed in ammonia, after a period of 1½ months.

Exp. 21 The course of sedimentation.

Stable dispersions always sedimented in the same manner. After some weeks or months, the sol in the cylinder was seen to be divided into three or four zones, thus:-



The colours varied with the soil type and treatment, but the zones with their sharply defined boundaries always developed. Through time they subsided, so that after many months a clear coloured sol remained in the cylinder. The writer is puzzled by the zonation; but the subsidence would seem to indicate some form of hindered settling due to brownian motion, distinct from the hindered settling due to flocculation.

Exp. 22 Colloid mill sols.

Sonic dispersions sedimented eventually to clear golden-brown sols that were stable for years. A Dunlop $B_{2g}$ sol that had stood two years contained 5% clay. It's X-ray diffraction pattern and DTA trace were both identical to those of the $< 1.4 \mu$ clay fraction. The small size and great stability of the particles suggested that sonic vibration had acted as a 'colloid mill', but this could not be verified because samples dispersed by shaking were not kept long enough for comparison.

## 5. Flocculation of Darleith soils.

### (i) Flocculation produced by peroxidation.

### Exp. 23 Flocculation of peroxidised Dunlop $B_{2g}$.

When 10 g Dunlop $B_{2g}$ (1969) was peroxidised in ~50 ml water, the suspension (pH 5.1) became thick and swollen. It was evaporated to 30 ml for transfer to the sonic vessel, but the suspension became so viscous under vibration that the treatment had to be given to half the suspension at a time. It was made to volume (pH 6.0) and a clay percentage of 37.86% was obtained together with a sand total of 17.5%. This compared with 27.8% clay and 23.9% sand for sonic/$H_2O$ dispersion (Table 63 p.524). The higher clay yield was assumed to be the result of better disruption following peroxidation. Seven days later, the onset of a massive flocculation was observed. Coarse flocs were subsiding in the body of the vessel and at the foot there was spectacular build-up of platy flocs overlain by skeins of 'woolly' flocs that were up to 4 cm long and 1 cm thick. After eight hours the supernatant was clear except for a faint white turbidity, and the flocs were about 3 inches deep.

### Exp. 24 Filtration rates of flocculated and coagulated clays.

The above experiment was thought to provide a demonstration of the difference between the 'subsidence' of flocs and the 'sedimentation' and 'coagulation' of particles distinguished by La Mer (1967) and described in Chapter III 7 p.112. A filtration experiment was done with a view to comparing the rate of filtration through clay coagulates. 590 ml clear supernatant was separated and the flocs + liquid that remained were poured into a wide funnel fitted with a Whatman No. 1 27 cm filter paper. The liquid was allowed to percolate for 25 minutes and then the rest of the supernatant was added from a leaching tube and dripped down the side of the filter paper at a rate of 50 drops/minute. The total time taken for the liquid of an 800 ml suspension to percolate through the flocs was 4 hr. 32 min. This is of a comparable order to that achieved by Smellie and La Mer (1956) when they measured the filtration rate of a slime which had been flocculated with flocgel and $Ca(OH)_2$. This preliminary investigation was put on one side and was taken up again later when the whole question of the difference between flocculation and coagulation came under review (Chapter XIII ).

Exp. 25 <u>Flocculation of peroxidised Amlaird $B_{2g}$</u>.

It was assumed that the massive flocculation of the Dunlop $B_{2g}$ was due to the unmasking of positive allophane sites by the removal of organic matter. To test this assumption, the Amlaird $B_{2g}$ soil which NaF tests had shown contained 'no allophane', was peroxidised and vibrated. The Amlaird soil (pH 5.2) similarly swelled on sonic treatment, but this viscosity was expected from its high clay content. On dilution to one litre there was no induction period as with the Dunlop. The phenomenon of 'hindered settling' took place immediately, with streams of flocs moving up the cylinder paralleled by counter streams of flocs moving down. Subsidence was signalled by the development of a clear watery rim which widened as the mass of flocs sank down. Amlaird $B_{2g}$ flocculated almost completely overnight.

<u>Discussion</u>: This result was totally unexpected. It was assumed that in both cases, flocculation had been brought about by the unmasking of positive sites when organic matter was removed. The positive sites could be due to those in clay mineral edges or they could be due to allophane. One notes the pH for 10 g soil/25 ml water was 4.9 and 5.8 for Dunlop and Amlaird respectively. The writer assumed that flocculation after peroxidation

was not commonly observed because Edwards and Bremner (1967) had studied a wide range of soils, and peroxidation followed by sonic treatment in water gave stable suspensions (Table 9 p.130). They observed that Olmstead (1931), the first to use the sonic method, reported it was necessary to disperse in ammonia to prevent the flocculation of vibrated soils, but the inference was that his soils were unusual. Emerson (1967) classified acid soils that flocculated independently of salt concentration as class 6 in aggregate stability, (p.207). Those he examined contained kaolinite and he assumed the flocculation was due to edge-face interactions. Soils containing allophane would also be of this class.

It was thought that perhaps peroxidation had unmasked an allophane content which was not detectable in the NaF tests for Amlaird $B_{2g}$. Experiment 5 p. 443 in Chapter X showed that peroxidation inhibited the fluoride reaction, perhaps through oxalate competition for the aluminium, so that a negative response of peroxidised Amlaird $B_{2g}$ to the NaF test would be misleading. Experiment 1 p.431 showed that Amlaird $C_1G$ only rose to 7.9 pH in 30 minutes, whereas the unperoxidised sample rose to 8.8 (Tables 54 and 57). It was planned to discover whether flocculation was due to allophane in both the brown forest and gley soils by removing the amorphous material with NaF and then subjecting the soils to peroxide and sonic treatment. In the meantime it was assumed that whichever mechanism was responsible, the positive charges would disappear in alkaline suspension. To test this, mechanical analyses were made on soils that had been agitated in ammonia.

### Exp. 26 Mechanical analysis of peroxidised Amlaird $B_{2g}$ after sonic vibration and shaking in ammonia.

10 g Amlaird $B_{2g}$ was peroxidised, vibrated in water and transferred to a cylinder, where the flocs settled out immediately. 40 drops 1:1 $NH_3$ solution were added and the suspension dispersed with vigorous hand shaking. 39.1% clay was determined by pipette analysis (Table 67 p.528) which can be compared to 40.1% from sonic/$NH_3$ treatment.

### Exp. 27 Mechanical analysis of peroxidised Dunlop $B_{2g}$ after rotary shaking in ammonia.

10 g Dunlop $B_{2g}$ (1969) was peroxidised, dialysed to remove soluble salts and transferred to a litre shaking vessel (pH 5.95 in ~ 600 ml). The development of a clear rim showed that flocculation was beginning. 40 drops $NH_3$ were added and the suspension was rotary shaken for 16 hours. Pipette analysis determined 16%

clay. This compares with 27.8% by the sonic/$H_2O$ and 37.9% by the $H_2O_2$/sonic/$H_2O$ method. The high percent of the latter, originally thought the result of efficient disruption, could be spurious and due to an unobserved hindered settling. But the low percent achieved in this experiment was puzzling. It was attributed at the time to inefficient shaking.

### Exp. 28 The effects of sonic treatment followed by peroxidation.

When the sequence was reversed and 5 g Amlaird $C_1G$ was given sonic treatment and then peroxide treatment, there was no visible sign of flocculation at first, but the clay yield was only 21.6% as compared with 39.8% for the sonic-only method. Flocculation was slower and less perceptible. After five weeks the body of the suspension were still turbid, although layers of flocs had gathered at the base.

### (ii) Flocculation produced by anion exchange resins.

It was speculated that organic matter might be removed with an anion exchange resin, provided the content was fairly low. Some of the uncertainty associated with peroxide treatment, such as the production of oxalates (Farmer and Mitchell 1963), could be avoided if this was the case.

Exp. 29 Flocculation of Amlaird $C_1G$ with anion exchange resin.

10 g Amlaird $C_1G$ was ground to pass a 52 mesh sieve and 25 ml Amberlite 1RA 400 resin of $>$ 30 mesh size and in the chloride form was shaken with it in ~500 ml water on a rotary shaker for 24 hours. The pH after shaking was 6.1. It was stood under observation in the vessel, and on the second day had developed zones differing in colour and depth of turbidity. The suspension was evaporated down to small volume for sonic treatment. It flocculated during the vibration, but on dilution to 1 litre and shaking, it appeared to be dispersed. Massive flocculation occurred on the third day, and the suspension left a clear supernatant, subsiding into a mass of flaky or woolly flocs.

A variation of this experiment was done in which 5 g Amlaird $C_1G$ was sonic dispersed and sieved to remove the sands. Silt + clay was evaporated down to 100 ml and transferred to a 4 oz. jar. It was shaken on a rotary shaker with 10 ml of the Amberlite resin described above for 17 hours, and left to stand for a further 48 hours. It was fully flocculated. A duplicate gave the same result.

Discussion. It appeared that the anion exchange resin removed some subatance in whose presence the soils were able to disperse in water. This might have been organic matter, phosphate, silicate anion or any substance capable of masking positive charges on the clay. It could have been held by allophane, by clay mineral edges or by iron oxides, for each of these would be capable of flocculating with negatively charged clay mineral faces. The anion exchange resins were not analysed and this aspect of the investigation has still to be pursued.

## (iii) Experiments with cation exchange resins.

The next step was to extract the allophane or sesquioxide material in order to see whether its removal would eliminate the flocculating agent. It was proposed to try this with fluoride. Tamm's acid oxalate was also considered. At the time however, it was decided to experiment with a cation exchange resin in the $H^+$ form, on the premise that this might act in a similar manner to Tamm's oxalate, and be more efficient in taking up aluminium and perhaps also iron-hydroxy polymers than a resin in the $Na^+$ form.

### Exp. 30 Mechanical analysis of Dunlop $B_{2g}$ after dispersion with an $H^+$- exchange resin.

5 g Dunlop $B_{2g}$ (1969) was peroxidised (pH 5.1). Amberlite IRC-50 resin in the $H^+$- form was sieved to retain particles > 100 mesh for easy separation from the sand fraction, and 36 ml resin (pH 4.4) was rotary shaken with 60 ml peroxidised suspension for 24 hours in an 8 oz. bottle. The suspension (pH 5.05) was sieved and transferred to a litre cylinder. The clay yield was 23.7%, which can be compared with 27.8% for sonic/$H_2O$ dispersion (Table 63 p.524). The suspension showed no sign of flocculation over a period of three months and formed a compacted sediment. It was concluded that the exchange resin had removed metal cations whose presence normally promoted flocculation after $H_2O_2$ treatment. The resin for this experiment was not investigated. Analysis of cation exchange resins used in soil dispersions are described in Chapter XIII.

### Exp.31 Trials with $Na^+$- exchange resin.

The $Na^+$- resin dispersion method of Edwards and Bremner (1965) was tried. Amberlite IRC- 50 in the $Na^+$ form was sieved to retain particles > 100 mesh, and it was calculated that 4 ml resin of cation exchange capacity 3.5 me/ml would suffice to provide the recommended

14 me/10 g soil. Accordingly 4 ml aliquots of resin were shaken with 10 g Dunlop $B_{2g}$ and 10 g Amlaird $C_1G$ in 60 ml water on a rotary shaker for 24 hours (pH 6.9). The results were disappointing. 7.3% and 20% clay was determined for the Dunlop and Amlaird soils respectively. On optical examination, the Amlaird sands were fairly clean, but the Dunlop sands were clay coated. This can be attributed to inefficient shaking and poor disruption. The soil that was treated with the $H^+$- resin was peroxidised and therefore the resin had access.

### (iv) Natural flocculation of Dunlop $C_g$ soil.

### Exp.32 Flocculation of Dunlop $C_g$ (1969) on sonic vibration.

10 g Dunlop $C_g$ (1969) soil was vibrated in 35 ml water (pH 4.7). When the suspension was transferred to a litre cylinder and diluted (pH 5.6), it was seen to be flocculating. Vigorous shaking failed to disperse the flocs which settled some 200 ml deep at the base of the cylinder. Although this behaviour was unexpected, it was assumed that the flocculation was brought about by positive charges which in the $C_g$ horizon, were not masked by organic matter. The percent organic matter content for the three subsoils $C_g$, $B_{3gx}$ and $B_{2g}$ were 0.4, 3 and 6 respectively. Thus stable suspensions were

achieved by those horizons which contained sufficient organic matter to mask the positive sites from interaction with the negatively charged clay minerals. When this was removed with $H_2O_2$ or an anion exchange resin, flocculation occurred in the same manner as with the $C_g$ horizon.

### (v) The removal of allophane with NaF and the effect on the soils' flocculating properties.

In order to prove that the flocculation of both the brown forest soils and the gley soils was due to allophane and not to edge-face flocculation of clay minerals, allophane was selectively extracted with sodium fluoride, and the soils' behaviour observed after peroxidation.

### Exp. 33 Removal of allophane from Dunlop $B_{2g}$ with NaF solution.

10 g Dunlop $B_{2g}$ was stirred for 5 days with 100 ml saturated NaF and the released OH- was titrated with 120 ml N10 HCl to maintain pH 6.5. The soil was washed till free of salt and an aliquot was peroxidised. It flocculated. A further 100 ml aliquot of unperoxidised suspension was tested with 50 ml NaF solution and rose to 8.35 pH in twelve minutes. This rise, although

small, was of the same order as that shown by the Amlaird horizons, and it was considered that the sodium fluoride treatment might have been insufficient.

Exp. 34 Removal of allophane from Amlaird $B_{2g}$ with NaF solution.

10 g Amlaird $B_{2g}$ was suspended in 100 ml saturated NaF solution (pH 6.8) and rose to 7.6 pH in 3 minutes. It was shaken on a reciprocating shaker for 24 hours, centrifuged at 10,000 rpm and washed once in water. The supernatants were strongly coloured by organic matter. 100 ml NaF solution (pH 7.3) was again added. To the writer's surprise the pH rose to 9.35 in 15 minutes and 35 ml HCl was required to lower the pH to 6.5. Buffering was very strong in the pH 7 - 8 region. It was stood two days and then centrifuged and washed. A third aliquot of 100 ml NaF solution was added (pH 7.35) and centrifuged and washed four times in water. The washings were still strongly yellow with extracted organic matter. The residue was peroxidised overnight in 10 ml 30% analar $H_2O_2$ and then vibrated for 30 minutes. There was no sign of flocculation. The clay yield (Table 67 p.528) was 41%, despite some loss of clay in the supernatant while centrifuging. Optical examination of the sand fractions showed they were mainly composed

of quartz and felspar; the ferro-minerals, particularly the pyroxene-magnetite,having been 'blown apart' on removal of their binding material of clay-organic matter.

It was concluded that the Amlaird soil contained a small amount of allophane. The reason why the response to fluoride should have been so much stronger on the second application than the first was not clear. One could argue that the first NaF treatment removed organic matter and unmasked aluminium which was only free to be complexed by fluoride when the competing organic matter had been centrifuged off. It has already been mentioned that reactive aluminium could not be detected by sodium fluoride after peroxide treatment, and that fluoride inhibition might be due to oxalate competition (Exp. 5 p.443). It appeared that only a very small number of allophane sites was required to initiate flocculation with the clay minerals. This explained why the Dunlop $B_{2g}$ in Exp. 33 continued to flocculate on peroxidation, even though a sodium fluoride test indicated there was virtually no allophane left.

### Exp. 35 Removal of allophane from Dunlop $C_g$ with NaF solution.

10 g Dunlop $C_g$ was suspended in 100 ml saturated NaF solution (pH 6.8). The pH rose to 10.7 in 12 minutes

and thereafter it was maintained at ~6.5 with N10 HCl. The soil was shaken on a reciprocating shaker for 24 hours, centrifuged at 10,000 rpm and washed once in water. The supernatants were strongly coloured by organic matter. In all, a total of six 100 ml aliquots of NaF were added, and the soil was shaken, centrifuged and washed as above in each case. The pH rise in 12 minutes and the mls N10 HCl added to maintain pH at 6.5 are shown below:-

| No. | pH rise | ml N10 HCl |
|---|---|---|
| 1 | 10.7 | 16 |
| 2 | 10.75 | 35 |
| 3 | 9.4 | 25 |
| 4 | 8.5 | 6 |
| 5 | 8.6 | 7 |
| 6 | 8.4 | 6 |

The residue was centrifuged and washed several times in water, peroxidised in 10 ml 30% $H_2O_2$ and vibrated for 30 minutes. The yield of clay was 41.4%, or 10% more clay than by any other method despite some loss in centrifuging. This illustrates the binding role which allophane and its associated organic matter must have played, although the long hours of shaking may also have contributed to the high clay percentage. There was no sign of flocculation. (But see experiment p.658).

One notes the intense buffering produced in the region pH 6.5 to 8 after the soil had been equilibriated with sodium fluoride. It might be argued that this was due to an attack on the clay minerals, as found by Huang and Jackson (1965), who correlated the buffering of clays after NaF treatment with the etching of muscovite revealed by electron micrographs (Chapter II 12 p.48). There can be no doubt however, that in this case most of the buffering was brought about by the reactivity of the unextracted allophane.

### (vi) Further observations on the behaviour of Dunlop $C_g$

### Exp. 36 Sonic dispersion of Dunlop $C_g$ (1970, 1971).

The flocculation of the Dunlop $C_g$ horizon was discovered by chance. Neither of the samples collected in 1970 and 1971 showed this behaviour until they were peroxidised. $C_g$ (1971) yielded 25% clay on immediate pipette analysis and the same amount was obtained two weeks later (Table 67 p.528). In the writer's experience, flocs once formed would not have permitted this stability. Once again the effect was attributed to organic matter and it was supposed that the small increase from 0.3% for the 1969 soil to 0.7% for the 1971 soil was sufficient to inhibit allophane-mineral clay interaction. The influence of other factors could not of course, be ruled out.

Exp. 37 Sonic dispersion of Dunlop $C_g$ (1969) in ammonia solution.

It was assumed that the positive charges would disappear in alkaline suspension and allow the soils to disperse. This proved to be the case. When 10 g Dunlop $C_g$ (1969) was vibrated in ammonia solution the clay percentage yield was 31.8% (Table 65 p.526).

Exp. 38 Failure of classical analysis method for Dunlop $C_g$ (1969).

10g Dunlop $C_g$ (1969) was peroxidised and shaken overnight in 600 ml ammonia solution on a rotary shaker. Table 65 shows that the clay yield was only 6.8%. The reason for this was not understood at the time.

## Conclusions.

The work described in this Chapter was exploratory. Its prime aim was to learn how far the sonic dispersion technique could be relied on in mechanical analysis. The discovery of the flocculating behaviour of the peroxidised soils and of the Dunlop $C_g$ soil justified this precaution. It emphasised the importance of distinguishing between dispersion following efficient disruption and for which no chemical aids one required, providing that lime, gypsum and soluble salts are absent, and the dispersion of flocs formed under certain conditions and for which chemical aids are required. The experiments of Edwards and Bremner (1967) might have led one to believe that only rather rare soils were resistant to sonic dispersion in water, but flocculation here has been ascribed to allophane and soils with allophane are widespread. Since however, the sonic method normally disperses with peroxidation, only deep subsoils high in allophane and low in organic matter might be expected to give trouble. Bourget (1968) reported that five Quebec soils failed to disperse properly when vibrated in water, although not enough is known about these to speculate on the reason. Emerson's work (1971) has already been described in Chapter IV A p. 134. He concluded that most soils could be sonic dispersed in water, except "acid soils which contain a suite of minerals which normally form flocculated suspensions in water (class 6 soils), gypseous soils, and carbonate soils with a clay fraction of low organic matter content."

In view of the results so far established, the writer recommends that the best routine method for the mechanical analysis of soils is sonic vibration in ammonia eg. pH 9.5-10. This would take care of soils that flocculated due to positive-negative charge interactions and organic soils that disperse better in alkali. Calcareous soils and soils high in soluble salts are easily identified as needing special treatment.

The discovery of small amounts of allophane in the Amlaird soil suggests that it may be preserved ie. prevented from crystallising or from being removed, by an association with organic matter. It also suggests that it developed from a volcanic parent material rather than in a leaching process. One must reserve judgement however, because non-volcanic gley soils may show the same behaviour on peroxidation and on renewed NaF treatment as the surface water gley. Exp. 2 Table 55 p.438 showed how common in soil is a small response to sodium fluoride.

At this stage it appeared that the very minor problem of the flocculation of the soils had been solved. Two anomalous results of low clay yield for Dunlop $B_{2g}$ and $C_g$ (Exp. 27 and 38) following peroxide/shaking in ammonia treatment were overlooked. Their significance only became clear after work described in Chapter XIII on the flocculation of New Zealand allophane.

# CHAPTER XII: DISPERSION OF SOILS BY CHARGE REVERSING AGENTS.

## 1. The allophane problem.

In the months before returning to the flocculation experiments, the writer learned of the resistance of allophane soils to dispersion, especially at high pH, as described in Chapter IV A 3 p.140 where an account was given of the work of Davies (1933) and Birrell and Fieldes (1952). It was not realised at first that almost all allophane soils behave in this way. It was thought that the difficult soils were those containing both allophane and sesquioxides, as suggested at that time by Birrell and Fieldes. By good fortune the writer had brought back a small sample of Tirau silt loam from New Zealand. It appeared that no headway had been made with its dispersion, because the ISSS Excursion Handbook (1968) noted in the profile description that "clay content as given by mechanical analysis is believed to be much below the true figure." Gibbsite was marked as absent. DTA traces (fig. 39 p.430) however, showed that on the contrary it was present in the extremely fine clay fraction, and this finding gave support to the "sesquioxide hypothesis" of Birrell and Fieldes.

The only advance in the situation of 1952 when Birrell and Fieldes had concluded "There is no practical method in sight for completely dispersing soils containing all but traces of oxides of iron and aluminium as well as allophane" appeared to be the discovery by Ahmad and Prashad (1970) that such soils could be dispersed in zirconium nitrate. An investigation of this discovery is the concern of this Chapter.

It will be recalled from Chapter IV A p. 155 that Ahmad and Prashad successfully dispersed some allophane-containing Caribbean soils by adding zirconium nitrate to the suspensions. The method was fairly fierce, since the pH was lowered to 2.9 - 3.0 and a large quantity of aluminium was dissolved, but nevertheless it succeeded where all others, including shaking in acid alone, had failed. The authors attributed the result to a charge reversal brought about by the exchange of $Zr^{4+}$ for $Al^{3+}$ on the exchange complex and in the clay lattice. The writer disagreed with this interpretation on the grounds that the zirconium ion would be hydrolysed, but was unaware at that time of the work of Matijević et al. (1960 - 1967), discussed in Chapters III 5 (iv) p. 101 and IV A p. 160 which would have illuminated the problem from the beginning.

On the other hand, preconceived ideas of the mechanism of the zirconium ion's dispersive ability might have allowed various aspects to be missed.

## 2. Reagents and materials for the charge-reversal experiments.

### (i) Preparation of zirconium nitrate solution.

16.75 g of technical grade zirconium nitrate was dissolved in 500 ml deionised water. It formed a thick cloudy suspension which was probably a mixture of zirconium hydroxide and zirconium nitrate (Mellor 1941). It was centrifuged at 3000 rpm and the supernatant was used in all subsequent experiments. Duplicate gravimetric determinations of the zirconium as zirconium phosphate found the solution was 0.112M. Powder X-ray diffractometry showed that an evaporated sample contained a substance which most closely matched Zr $(NO_3)_4$ $5H_2O$ (Appendix A 21).

Matijević et al. (1962b) noted that zirconium nitrate solutions were stable over a period of several months. Hence, after 8 months it was thought advisable to make up a fresh solution. For Exp.58 p.520 this second solution was used. Its molarity has not yet been determined but was estimated to be ~0.07M.

Properties of the zirconium nitrate solution.

The pH of the solution was 1.35. When dilute NaOH was added dropwise, the substance became turbid at ~ pH 2.4 and precipitated out at 3.05. This behaviour would be expected to vary because of the colloidal nature of the hydroxide. The existence of a positively charged hydrolysis product was confirmed by the appearance of a white precipitate at the negative electrode when the solution was electrophoreted. Similarly, a precipitate was obtained when a drop of 1% sodium dodecyl sulphate, a negatively charged detergent, was added to the solution.

(ii) Preparation of thorium nitrate solution.

8.3009 g analar thorium nitrate (Th $(NO_3)_4$ $5H_2O$) was dissolved in 500 ml deionised water to give a

0.02912 M solution. Thorium nitrate is very soluble in water, so that in this case there are no precipitation problems as with zirconium nitrate. The pH was 2.5.

(iii) Ferric hydroxide sols.

A positive sol was made by pouring a 2% solution of ferric chloride into a litre of boiling water and stirring vigorously. The dark red colloidal solution obtained is stable for a very long time. A sample made in Nov. 1967 for instance, was still stable in Nov. 1971. The pH was 1.9.

A negative sol was made by adding 1:1 $NH_3$ solution at great speed to the positive sol. In this way the isoelectric point was passed without precipitation. The method was only sporadically successful and the suspensions were not very stable.

(iv) 1% Sodium dodecyl sulphate (SDS) : 1g was wetted with alcohol and made into a paste. Water was added gradually and made to 100 ml. This detergent is negatively charged.

(v) 1% Cetyl ammonium bromide (Cetab) : 1g was prepared in a similar manner to SDS. This detergent is positively charged.

(vi) 1% Salmine sulphate : 1 g was wetted with alcohol, dissolved in water, filtered and made to 100 ml. Its pH was 2.7. Salmine sulphate is a positively charged protein with an isoelectric point at about pH 8.0.

(vii) Organic matter extract : organic matter extracted from Dunlop A horizon with NaF solution, was dialysed free of salts. It was negatively charged.

(viii) Clay suspensions : suspensions of very fine clay were pipetted at regular depth from cylinders of dispersions which had been standing some months. These were clear golden sols in which changes in turbidity and the onset of precipitation was readily followed. Dunlop and Amlaird suspensions were deemed a source of clay with and without allophane respectively. Tirau B dispersed in HCl was a source of allophane clay. When flocs were used, these were silt + clay fractions from the various soils, and the silt was removed where necessary, by decanting.

(ix) Tirau silt loam : one small sample was taken from the A horizon of the profile described in "Soils of New Zealand" (1968 3 p.80) and three small samples from the B horizon at a depth of 12 to 20 inches. Unfortunately, the B samples were not mixed together before use and there might be some slight disparity between them. In the mechanical analyses that follow, the soil separates for the A horizon are given as percent oven dry mineral soil, using the profile data of 10.6% carbon (Table 16 p.150). The B horizon soil separates are given as percent oven dry soil since the carbon data varied from 7.2 to 2.3%. The neglect of organic matter in the calculation gives clay percentages which are too low by 2 to $<1\%$.

## 3. Dispersion and flocculation of soils with HCl.

### Exp. 39 Dispersion of Tirau B in HCl.

5 ml Tirau B flocs (pH 7.3) were brought to pH 4.3 with HCl. The silt sized material sedimented and the clay dispersed. The acid dispersion remained stable 'indefinitely' ie. clay sedimentation followed Stokes' Law. A second aliquot was stable at least to pH 3.0.

### Exp.40 Flocculation of Dunlop $B_{2g}$ in HCl.

25 ml very dilute Dunlop $B_{2g}$ sol was titrated with N/100 HCl, and precipitation was reproducible at pH 3.62 on addition of 1 ml acid.

### Exp.41 Flocculation of Amlaird $B_{2g}$ in HCl.

5 ml Amlaird $B_{2g}$ sol was titrated with N/10 HCl added dropwise. It was still clear at pH 3.45 and thereafter appeared very very slightly turbid. The pH was lowered to 2.7 and precipitation followed after the sol had stood for two hours.

### Exp.42 The flocculation of Tirau B acid dispersion on addition of clay minerals.

5 ml Tirau B flocs were dispersed in HCl at pH 3.35. 5 ml Amlaird $B_{2g}$ sol was added and there was an immediate precipitation at pH 3.6.

Conclusions: Tirau B suspensions can be stabilised in dilute acid. This may be due to protonation of the hydroxy groups or the mere absence of mechanisms which flocculate the allophane in other pH ranges ie. in the neutral range, isoelectric flocculation; in the high pH range, mechanism unknown. The small amount of kaolinite present is insufficient to initiate mutual flocculation.

Dunlop $B_{2g}$ flocculates in HCl at a higher pH than Amlaird $B_{2g}$. This could be due to the development of an increased positive charge on the allophane component until it is sufficient for isoelectric precipitation with the clay minerals. With Amlaird $B_{2g}$, positive charges require much stronger acidity in order to build up on the clay mineral edges or on the small amount of allophane later found to be present. One notes (a) that flocculation would be inhibited in both soils by organic matter masking the positive sites and (b) in the Dunlop case, the $H^+$ concentration was 0.4 mmoles/l, so there was no electrolyte coagulation effect. This might have occurred in the Amlaird case where the $H^+$ concentration was 10 mmole/l.

The flocculation of the Tirau B positively charged dispersion on addition of a negatively charged clay mineral sol illustrates the impossibility of dispersing soils in dilute acid unless they are almost entirely allophane in the clay fraction, and explains why the HCl dispersions of Ahmad and Prashad (1970) gave such variable results. These depended on the proportions of layered clay to allophane, or more specifically, on the proportions of negative to positive charge present in the sol. (Chapter IV A Table 18 p.157).

## 4. Dispersion of soils with zirconium nitrate.

### Exp. 43 Dispersion of Tirau B with zirconium ion.

Zirconium nitrate solution was added dropwise to 50 ml Tirau B flocs until 0.25 ml had been given. The pH fell from 7 to 3.65 and the flocs dispersed. After 4 days the pH had risen to 4.3. It rose no higher than this, and the dispersion was stable 'indefinitely'.

### Exp. 44 Dispersion of Dunlop $C_g$ with Zr ion.

Zirconium nitrate solution was added dropwise to 25 ml containing 1g Dunlop $C_g$ (1969) flocculated soil (pH 4.9). The flocs dispersed when the pH was lowered to 3.55 and reappeared as the pH rose fairly rapidly to 3.8. Dispersion and a stable pH was finally established at pH 3.65 after 0.5 ml Zr solution had been added. Aliquots were tested with drops of cetab, SDS and salmine sulphate, and proved stable to cetab and salmine sulphate but were precipitated by SDS ie. the suspension was positive. After 4 days the pH of the dispersion had risen to 4.2 and it was flocculated. It was redispersed at pH 3.6.

### Exp. 45 Dispersion of Amlaird $B_{2g}$ with Zr ion.

10 ml Amlaird $B_{2g}$ sol at pH 6.4 was brought to pH 3.1 with 0.1 ml Zr and there was an immediate

precipitate. However, when only 5 ml Amlaird $B_{2g}$ was used, and the pH brought to 3.2 with 0.05 ml Zr, the dispersion remained stable and addition of 1 drop cetab failed to precipitate it.

Exp. 46 Dispersion of a mixture of Tirau B and Amlaird $B_{2g}$ with Zr ion.

5 ml Tirau B flocs were dispersed in HCl at pH 3.35, and reprecipitated with 5 ml Amlaird $B_{2g}$ as in Exp. 42 On addition of 0.05 ml Zr solution the pH fell to 3.35 and the flocs dispersed.

Exp. 47 The displacement of cetab from a clay mineral / cetab precipitate by Zr ion.

2 drops cetab were added to 10 ml Dunlop $C_g$ sol and the clay precipitated. The suspension was divided in half and 5 drops Zr was added to one 5 ml aliquot, lowering the pH to 3.0. The suspension became turbid and the displacement of the cetab was seen in the appearance of soap bubbles on the surface of the liquid.

Exp. 48 The effect of adding organic matter to Tirau B acid and Zr dispersions.

Two 5 ml aliquots of Tirau B flocs were dispersed at pH 3.15 with Zr and HCl solutions respectively. 2 ml Dunlop $A_1$ organic matter extract was added to each and the pH rose to 3.3. The Zr dispersion remained stable but the HCl dispersion flocculated.

Exp.49 Dispersion of organic matter and $Fe(OH)_3$ mixed sols by Zr ion.

5 ml $Fe(OH)_3$ sol was mixed with 2 ml Dunlop A organic extract and formed a turbid suspension (pH 3.65).

5 ml $Fe(OH)_3$ sol + 0.05 ml Zr solution was mixed with 2 ml Dunlop A organic extract and a very clear sol was obtained (pH 3.75).

Exp.50 Dispersion of Amlaird and $Fe(OH)_3$ mixed sols by Zr ion.

5 ml $Fe(OH)_3$ sol was mixed with 10 ml Amlaird $B_{2g}$ sol and there was an immediate precipitate.

5 ml $Fe(OH)_3$ sol + 0.15 ml Zr solution was added to 10 ml Amlaird $B_{2g}$ sol and the dispersion was clearer than the slightly turbid Amlaird sol on its own.

## Conclusions.

The positively charged zirconium polycation, formed from the hydrolysis product of $Zr^{4+}$ as described in Chapter IV A p.160, stabilised the suspensions by adsorbing on negative colloids and reversing their charge. Evidence that the sols became positively charged was shown by their stability to cetab and salmine sulphate, and by the ability of SDS to precipitate them. Each clay appeared to have a threshold pH above which it flocculated and below which it dispersed. These threshold pH's were 4.3, 3.65, 3.2 for Tirau B, Dunlop $C_g$, Amlaird $B_{2g}$ respectively under the conditions described and were presumably related not only to the concentration of Zr added but to the amount of negative charge present which required to be reversed. This was very small for Tirau B, moderate for Dunlop $C_g$ and greatest for Amlaird $B_{2g}$ with only very minor allophane component.

## 5. The stabilising of $Fe(OH)_3$ sols with Zr ion.

### Exp. 51 Redispersion of $Fe(OH)_3$ precipitate with Zr ion.

The ferric hydroxide sol was precipitated at pH 10 with NaOH and the pH of the suspension was then lowered to 6.5 with HCl. Addition of 0.15 ml Zr solution and vigorous shaking dispersed the precipitate to a turbid but stable suspension (pH 3.15). This was remarkable in view of the great insolubility of ferric hydroxide precipitates.

### Exp. 52 Stability of $Fe(OH)_3$ sols at raised pH in the presence of Zr ion.

Two sets of 5 ml ferric hydroxide sol were pipetted into test tubes and 0.1 ml Zr solution was added to each tube of one set. A series of pH values was obtained by adding varying amounts of dilute NaOH. The $Fe(OH)_3$ control precipitated overnight from sols whose pH was more than 4.0 and gave clear supernatants. The $Fe(OH)_3$/Zr sols showed a slight precipitate at pH 4.42, but continued to hold a clear golden supernatant in all sols at pH less than 4.65 even after standing for eight days.

These experiments showed that the zirconium hydrolysis product was capable of redispersing a highly insoluble positive hydroxide, and of inhibiting the precipitation of a positively charged colloid. The mechanism could be either (a) the reversal of negative charges developed by the colloid as the isoelectric pH was approached or (b) a steric effect, in which the introduction of further positive charge to the sol increased the repulsion between groups; or it could be a combination of both.

## 6. Dispersion of soils with $Fe(OH)_3$ sol.

When some variations to exp.51 were tried, in which negative colloids were protected from co-precipitation with $Fe(OH)_3$ by zirconium, the results suggested that the ability of the Zr agent to reverse the charge was improved by the presence of the positive colloid. It was thought that perhaps the introduction of positive repelling groups might help the 'stretch' the zirconium polymer and increase its surface coverage, and the following experiment was done to test the proposition.

### Exp. 53 Dispersion of Dunlop $B_{2g}$ flocs with $Fe(OH)_3$ sol.

Dunlop $B_{2g}$ peroxidised flocs were used in 10 ml aliquots.

5 ml $Fe(OH)_3$ at pH 1.9 + 0.05 ml Zr was added to 10 ml Dunlop $B_{2g}$ flocs and the initial pH of 2.6 was raised to 4.2 with drops of NaOH. The dispersion was stable 'indefinitely', and an aliquot precipitated with SDS.

5 ml $Fe(OH)_3$ at pH 1.9 was added to 10 ml $B_{2g}$ flocs and the initial pH of 2.65 was raised to pH 4.15 with drops of NaOH. This dispersion was also stable 'indefinitely', and an aliquot precipitated with SDS.

Hence, the $Fe(OH)_3$ sol itself was able to stabilise the Dunlop $B_{2g}$ flocs by reversing their charge. The same results were obtained at lower pH. With Amlaird $B_{2g}$ sol however, a precipitate was always obtained when ferric hydroxide was added, even if 10 ml $Fe(OH)_3$ was added to 5 ml Amlaird and the pH was 2.0, although no doubt there would be some proportion in which stability would be achieved. It was concluded that the $Fe(OH)_3$ sol was in equilibrium with its hydrolysis products, which were present either in solution or on the surface of the particle. Their concentration was sufficient to reverse the charge on Dunlop $B_{2g}$ clay, which was probably already coated with considerable amounts of positive allophane, but insufficient to reverse the charge on the Amlaird.

Exp.54 Dispersion of Tirau B in the presence of $Fe(OH)_3$.

5 ml Tirau B suspension which had been dispersed in HCl and was at pH 4.3 was added to 5 ml $Fe(OH)_3$ sol at pH 1.9. The pH of the mixture was 3.45. The dispersion remained stable 'indefinitely'.

## Conclusions.

The discovery of the ability of the $Fe(OH)_3$ sol to disperse soils suggests that ferric oxide is not likely to be a factor responsible for the flocculation of allophane, as proposed by Birrell and Fieldes (1952, 1968). Ferric oxide in soil is likely to be either highly crystalline and inert, or negatively charged due to adsorption of organic matter and anions, or if positively charged, tending to promote dispersion rather than flocculation, by virtue of its charge reversing properties.

## 7. The dispersion of soils with thorium nitrate.

Parallel sets of experiments were made to those with zirconium nitrate, using thorium nitrate solution. The results with Dunlop flocs and sols and with Amlaird sols were similar, and the same pH range of stability was obtained.

## Conclusions.

Many of these results illustrate the findings of Matijević et al. (1960-1967) in their experiments on the charge reversal of halide sols by the hydrolysis products of metal cations such as Fe, Al, Zr, Th and Zn. The variability in the clay systems follows from their variable contributions of negative and positive charge. A quanitiative assessment of the ability of HCl and Zr ion to disperse the Tirau B soil, and of Zr ion to disperse the Darleith soils, follows in the next section which deals with their mechanical analysis.

## 8. Mechanical analysis of zirconium nitrate dispersions and Tirau B HCl dispersion.

### Method.

The zirconium nitrate solution was normally pipetted dropwise into 25 ml of soil suspension in the sonic vessel, until the pH stabilised at 4.0. Sonic treatment was given for 30 minutes and the suspensions were sieved to separate the sands, and made to ~990 ml in the cylinder. The pH was checked and Zr solution added until the suspension remained stable for an overnight period at the pH required. The experiments in section 3 suggested that this was pH 4.3 for the Tirau soil and 3.6 to 3.7 for the Dunlop soils. The suspensions were made to 1 litre. The weight of 5 ml oven dried zirconium nitrate was obtained, and the appropriate weights due to Zr addition were subtracted from the pipetted samples.

### Exp. 55 Dispersion of Tirau B in HCl.

Dispersion of the Tirau B soil in hydrochloric acid was effected after sonic treatment and sand separation by adding dilute HCl to ~990 ml of suspended flocs and shaking, until dispersion was perceived. It might have been better to have added acid prior to sonic treatment, in order to avoid the very high viscosity which developed and prevent the formation of flocs. The dispersion pH was 4.3 to 4.4, and the HCl was added from time to time until the pH and the dispersion remained stable for an overnight period. It was then made to 1 litre.

Results and discussion.

The results for the Tirau B mechanical analyses are collected in Table 68 p.529 . It is seen that the HCl dispersion yielded 23.7% clay at suspension pH of 4.4, and the zirconium nitrate dispersion yielded 23.6 and 24.2% clay of $< 1.4\mu$ and $< 2.0\mu$ respectively. The final pH was 4.3, although it had been lower than this when Zr additions were being made. Both dispersions sedimented slowly to a compact coagulum. After 5 months the Zr suspension was shaken and the silt + clay and clay percentages analysed again. They remained exactly the same.

These results can be compared to the figures given in the profile analysis ("Soils of New Zealand" 1968 3 p.80). Samples taken at 8 to 12 and 13 to 20 inches depth showed that 5% and 7% $< 2\mu$ clay was obtained by the calgon method and 24% and 33% by the dissolution method for the two horizons respectively. If it is assumed that the writer's sample, taken from 12 to 20 inches depth, came from the base of their 8 to 12 inch horizon, then there is close agreement between the dissolution method and the dispersions in both HCl and zirconium nitrate.

A further sample of Tirau B was peroxidised prior to sonic treatment and dispersed with 2 ml Zr solution at pH 4.2. The yield of clay was 20.3%, and this appeared to be the maximum obtainable because additions totalling 3.2 and 4.7 ml Zr, producing a suspension pH of 4.05 and 3.72 respectively, brought no change in the result. It is not clear why the yield was lower than that of the unperoxidised soil. There may have been sampling differences.

It can be concluded from these results that efficient dispersion of Tirau B was achieved by protonation alone, and the charge reversal mechanism was superfluous. It is of interest that the kaolinite, whose content was perhaps of the order of the 2 to 5% found by Birrell and Fieldes (1952), was not isoelectrically flocculated, since it was found in the stable HCl suspension. (Appendix A 22 ). Its stability may have been due to hydrolysed alumina on the allophane surface being present in sufficient quantity to reverse the kaolinite negative charge.

Neither the HCl nor the Zr method caused damage by dissolving aluminium. The Zr dispersion was examined after six months and 6.4 μg Al/ml or $2.5 \times 10^{-4}$ moles/l was found in the solution. The HCl dispersion was not analysed, but fig.24 p.228shows that at pH 4.4 and 4.3, amorphous $Al(OH)_3$ would be in equilibrium with $3 \times 10^{-4}$ and $6 \times 10^{-4}$ moles Al/l respectively. While both dispersing agents were equally mild and efficient, HCl would be preferred for this soil for the sake of simplicity and because it allows the clays to be examined afterwards without the interference of an artefact. For soils however, containing some unspecified amount of clay mineral, like those investigated by Ahmad and Prashad, or the Dunlop soils under conditions to be described, dispersion in zirconium nitrate offers a solution.

## 9. Exp.56 Mechanical analysis of zirconium nitrate dispersions of Dunlop soils at pH 3.7 and below.

The tests in section 4 showed that the pH at which the zirconium polycation dispersed a suspension varied with each soil. The critical pH could be awkward to obtain because there was a rise in pH with time after each Zr addition and equilibrium was not established for several days. For example, zirconium nitrate might be added to give an initial pH 3.0. It would rise rapidly to 3.5 and then slowly over the period of a day to 3.8. In the $B_{2g}$ case, the quantity of added zirconium was doubled from 8 to 16 ml, but the improvement in clay percentage was negligible because the pH remained at 3.7 after equilibriating. One did not want to counteract this trend by acidifying too much. However, with the peroxidised samples that were well-flocculated, it was easy to see that pH 3.4 was the critical pH, because dispersion did not take place until then.

The mechanical analysis results can be compared with those of other methods in Tables 64, 66, 68 on p525 ,527 ,529 , respectively. In Table 71 p.532 the clay percentages for the Zr dispersions are compared with those for the standard sonic/$NH_3$ dispersions. It is seen that at pH 3.4 the Zr dispersions yielded similar clay values to the standard dispersions, but at pH 3.7 the yield was down by 3 to 7 percent. This was undoubtedly due to the pH being too high. It was at first assumed that the peroxidised soils would require more zirconium ion than the unperoxidised soils, but this argument is not valid because the removal of organic matter from the Dunlop soils unmasks both negative and positive sites and their relative proportions are variable.

The method suffers from a major disadvantage in that the higher the clay mineral content, the lower the pH of efficient dispersion and the greater the attack on the aluminium, particularly the non-crystalline allophane aluminium. Fig. 24 p.228 shows that at pH 3.7 and pH 3.4, the dissolved aluminium in equilibrium with $Al(OH)_3$ is 0.05 and 0.4 moles/l respectively. Ahmad and Prashad's samples were dispersed at lower pH still, 3.0 and 2.9, dissolving $>$ 1 mole/l. This may not matter very much when mechanical analysis is the only end in view, but if the properties of the clay fraction are to be examined, these could be strongly altered by damage to the allophane fraction. However, it is not necessary to disperse coils with zirconium nitrate at this low pH, as is demonstrated in the next section.

## 10. Mechanical analysis of zirconium and thorium nitrate dispersions at controlled pH.

If the graphs of Matijević et al. (1960-67) for the stabilisation of halide sols by the hydrolysis products of Zr and similar cations are examined, it is seen (a) that stabilisation was achieved up to fairly high pH values (fig. 20 p.162), the stability being governed by the concentration of the polycation and the charge on the species at any particular pH; (b) that in general, the higher the pH, the greater the concentration of the stabilising polycation for a given molarity of dispersing agent (fig. 17 p.103). Hence, when in the last experiments the pH was lowered, the concentration of Zr polycation/mole zirconium nitrate was actually being reduced, and the increased efficiency of the dispersion was undoubtedly achieved by the production of positive charge on clay edges and on allophane rather than by the increase in Zr concentration, for by this means the amount of negative charge required to be reversed was decreased. If Amlaird soil had been used, the pH of dispersion would have been much lower.

A number of test tube trials were made with Amlaird and Dunlop sols and flocs in order to guage the quantities of zirconium and also of thorium reagent required to bring about reversal of charge and dispersion at a more elevated pH. These indicated that the behaviour of clay suspensions differed considerably from that of the 'model' halide sols worked on by Matijević and his colleagues, because as the pH was raised, so the negative charge required to be reversed increased. The mechanical analyses that follow show that much larger quantities of reversing ion were required even for a quite modest rise in pH.

Exp. 57 Mechanical analysis of peroxidised Dunlop $C_g$ with thorium nitrate at pH 4.3.

10 g Dunlop $C_g$ (1971) soil was peroxidised with 9 ml $H_2O_2$, vibrated, sieved and made to ~ 950 ml. Weak flocculation occurred. The pH was brought to 6.8

with NaOH with the idea of trying to achieve charge reversal in this range. The suspension dispersed however, due to the fact that the allophane became negatively charged at this pH. The clay percent was found by pipette analysis to be 24.8. The pH was then lowered with thorium nitrate and on addition of 5 ml (pH 6.65) massive flocculation occurred. After 21 ml (pH 4.1) flocculation became weaker and turbidity developed, until at pH 3.6 after 40 ml Th had been added, the charge was found to be reversed. Thereafter the pH was alternately raised to 4.3-4.8 and depressed as a result of adding further thorium nitrate. This was continued until flocs no longer appeared when the suspension was left to stand and until it maintained a steady positive charge. Three clay analyses were made on successive days. The pH for each at the start of sedimentation was 4.5 and fell to 4.3 by morning. This regular fall in pH contrasts with the rise noted on p.515 when thorium or zirconium were added without NaOH.

The sediment appeared to be a coagulum and 1 ml aliquots of suspension with SDS gave percipitates confirming positive charge. The clay yields were 23.1, 23.1, 23.4% for additions of 80, 90 and 100 ml thorium nitrate respectively, and were comparable to the 24.8% obtained for the same soil sample when its positive charge due to allophane was neutralised at pH 6.8. Tables 66 and 71B on p.527, and 532, indicate that the yield was a few percent below the amount analysed by most other methods, and that for some reason, the fine silt was high.

NOTE. Small additions of Th or Zr solution inhibited the action of cetab, so that suspensions which were still negatively charged failed to produce a precipitate in the cetab test. It was necessary to confirm the presence of negative charge by electrophoresis of an aliquot.

### Exp. 58 Mechanical analysis of peroxidised Dunlop $B_{2g}$ with zirconium nitrate at pH 4.3.

10 g Dunlop $B_{2g}$ (1971) soil was peroxidised with 28 ml $H_2O_2$, vibrated, sieved and made to ~980 ml. It flocculated. The same procedure was followed as with the $C_g$/Th dispersion. Zirconium nitrate was added alternately with NaOH in order to obtain dispersion in the range pH 4.3 to 4.8. The $B_{2g}$ appeared to form a flocculant precipitate more readily than the $C_g$ suspension and to be less stable, even though the charge was reversed. Two successive pipette analyses gave clay yields of 22.7 and 23.8% after 113 and 123 ml zirconium nitrate had been added. Table 64 p.525 shows

that this result compares well with other dispersion techniques. The standard sonic/$NH_3$ method gave 23% clay.

## 11. Conclusions.

Table 71B p.532 summarises the data on the zirconium and thorium dispersions achieved at pH 4.5 - 4.3, and gives the volumes and oven dry weights of the reagents and the molarities of their solutions. The thorium nitrate was weak (0.029 M) and could have been made a more convenient concentration. Hence in future experiments it would be preferred to zirconium nitrate whose insolubility precluded solutions stronger than $\sim$0.1 M.

Comparison with similar data for the acid dispersions (Table 71A p.532) shows that the rise in dispersion pH from 3.4 - 4.3 increased the amount of reagent required to disperse peroxidised Dunlop $B_{2g}$ (1971) from 2.37 to 8.25 mmoles/l. This should be further compared with the 0.03 mmoles/l that was sufficient to disperse the silver bromide sol studied by Matijević et al. (1962) and illustrated in fig. 20 p. 162.

It has thus been found unnecessary to disperse allophane-containing soils under the very acid conditions used by Ahmad and Prashad (1970), who quoted pH 2.9 and 3.0 for maximum dispersion of two Caribbean soils (Table 19 p. 159). The milder conditions that prevail at pH 4.3 - 4.5 make this dispersion method more attractive. It still suffers from some disadvantage in that detailed studies of the chemical and mineralogical properties of the clay fraction may be interfered with by the presence of the hydrolysis products of the metal ions. Anion and cation exchange properties, phosphate retention and infra red spectra studies would be particularly affected. It is possible however, that these polycations can be readily displaced by dialysis or by shaking with cation exchange resin. This has yet to be attempted.

It will be seen later that allophane-containing soils are most simply dispersed by the cation exchange resin method of Edwards and Bremner (1965), but it would be a pity if for that reason further investigation of the properties of reversed-charge clays were overlooked. They may be interesting and important in their own right, particularly since the exotic species used in these experiments are matched in soil by the polycations of aluminium and iron whose mode of action is the same.

Table 62 <u>% Soil separates for Dunlop $A_1$ horizon obtained from different soil dispersion treatments</u>.

| Treatment (5 g soil) | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $< 1.4\mu$ |
|---|---|---|---|---|---|
| Sonic \| NaCl | 16.0 | 9.6 | 9.7 | 41.1 | 19.8 |
| Sonic \| $H_2O$ | 16.3 | 10.5 | 8.9 | 37.5 | 26.8 |
| Na-resin 25 ml \| recip. shake \| 60 ml $H_2O$ | 15.6 | 8.6 | 14.8 | 38.9 | 27.1 + $NH_3$ → 32.1 |
| Sonic \| $NH_3$ | 14.2 | 9.6 | 8.9 | 32.4 | 34.9 |
| $H_2O_2$ \| Sonic \| $H_2O$ | 14.0 | 8.9 | 7.3 | 30.4 | 39.4 + $NH_3$ → 39.4 |

Table 63 % Soil separates for Dunlop $B_{2g}$ (1969) horizon obtained from different soil dispersion treatments.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $< 1.4\mu$ |
|---|---|---|---|---|---|
| $H_2O_2$ | 10.5 | 11.4 | Flocculated . . . | | |
| Na-resin 4 ml ∣ rotary shake ∣ 60 ml $H_2O$ | 46.3 | 16.6 | 8.0 | 19.8 | 7.3 |
| $H_2O_2$ ‖ dialysis ‖ rotary shake ∣ 600 ml $NH_3$ | 10.9 | 12.0 | 7.6 | 42.5 | 16.0 |
| $H_2O_2$ ‖ H-resin 36 ml ∣ rotary shake ∣ 60 ml $H_2O$ | n.d. | n.d. | n.d. | 33.1 | 23.7 |
| progressive sonic ∣ $H_2O$ | 10.6 | 12.8 | 14.1 | 36.5 | 26.0 |
| sonic ∣ $H_2O$ | 11.6 | 12.3 | 15.7 | 32.6 | 27.8 |
| $H_2O_2$ ‖ sonic ∣ Zr pH 3.4 | 5.6 | 11.8 | 14.7 | 37.8 | 30.1 |
| $H_2O_2$ ‖ sonic ∣ calgon | 8.2 | 10.4 | 15.5 | 33.4 | 32.5 |
| $H_2O_2$ ‖ sonic ∣ $H_2O$ | 7.8 | 9.5 | 7.9 | 36.9 | 37.9 → flocculated |

Table 64 % Soil separates for Dunlop $B_{2g}$ (1971) obtained from different dispersion treatments.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay < 1.4μ |
|---|---|---|---|---|---|
| $H_2O_2$ ‖ recip shake \| 60 ml $H_2O$ | 15.4 | 23.5 | Flocculation . . . | | |
| $H_2O_2$ ‖ sonic \| $NH_3$ | 15.2 | 13.4 | Flocculation . . . | | |
| $H_2O_2$ ‖ sonic \| NaOH pH 12 | n.d. | n.d. | Flocculation . . . | | |
| $H_2O_2$ ‖ recip shake \| Calgon | 24.7 | 15.5 | 11.2 | 31.9 | 16.7 |
| Sonic \| Zr pH 3.7 | 21.3 | 14.9 | 11.4 | 35.1 | 17.3 |
| Sonic \| NaCl | 23.0 | 15.0 | 10.9 | 33.5 | 17.6 |
| Recip shake \| 60 ml $H_2O$ | 29.5 | 11.6 | 9.7 | 31.1 | 18.1 |
| Sonic \| $H_2O$ | 23.9 | 11.9 | 13.9 | 31.1 | 19.2 |
| $H_2O_2$ ‖ sonic \| Zr pH 3.4 | 18.6 | 13.4 | 11.4 | 35.1 | 21.5 |
| Recip shake \| 60 ml + $NH_3$ $H_2O$ | 14.5 | 22.7 | 10.7 | 31.3 | 21.8 |

Contd/

Table 64 Contd.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay < 1.4µ |
|---|---|---|---|---|---|
| $H_2O_2$ ‖ $SiO_2$ $NH_3$ ∣ recip shake ∣ resin 15 ml ∣ 60 ml $H_2O$ | 20.0 | 16.4 | 12.0 | 29.6 | 23.0 |
| Sonic ∣ $NH_3$ | 25.5 | 11.7 | 11.0 | 28.8 | 23.0 |
| $H_2O_2$ ‖ sonic ∣ Zr pH 4.3 | 17.3 | 16.0 | 10.0 | 34.9 | 23.8 |
| NaF ∣ sonic ∣ $H_2O$ | 19.8 | 12.4 | 17.9 | 25.7 | 24.2 |
| Recip shake ∣ resin 20 ml ∣ 60 ml $H_2O$ | 30.8 | 11.0 | 8.3 | 25.5 | 24.4 |
| $H_2O_2$ ‖ recip shake ∣ resin 15 ml ∣ 60ml $H_2O$ ∣ $NH_3$ | 24.5 | 15.6 | 6.8 | 29.1 | 25.0 |
| Sonic ∣ $NH_3$ 1 hour | 17.4 | 13.0 | 11.9 | 31.2 | 26.5 |
| $H_2O_2$ ‖ sonic ∣ $NH_3$ $SiO_2$ | 14.5 | 13.4 | 11.8 | 33.0 | 27.3 |

Table 65 <u>% Soil separates for Dunlop $C_g$ (1969) horizon obtained from different dispersion treatments</u>.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $<1.4\mu$ |
|---|---|---|---|---|---|
| Sonic \| $H_2O$ | 11.2 | 14.0 | Flocculation . . | . . . . . | |
| $H_2O_2$ ‖ rotary shake \| $NH_3$ 600 ml | 22.7 | 18.1 | 13.8 | 35.5 | 6.8 |
| Sonic \| Zr pH 3.65 | 11.3 | 16.2 | 17.3 | 30.4 | 24.8 |
| Sonic \| $NH_3$ | 8.5 | 15.0 | 13.3 | 31.4 | 31.8 |

Table 66 % soil separates for Dunlop $C_g$ (1971) obtained from different dispersion treatments.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay <1.4µ |
|---|---|---|---|---|---|
| $H_2O_2 \parallel$ sonic $\mid H_2O$ | n.d. | n.d. | Flocculation . . . . | | |
| Recip shake $\mid$ 60 ml $H_2O$ $\mid NH_3$ | 17.7 | 15.2 | 15.1 | 33.0 | 19.0 |
| Recip shake $\mid$ 60 ml $H_2O$ | 19.4 | 13.0 | 15.0 | 33.3 | 19.3 |
| $H_2O_2 \parallel$ resin 15 ml $\parallel NH_3$ | 18.3 | 13.3 | 10.2 | 35.3 | 22.9 |
| $H_2O_2 \parallel$ sonic $\mid$ Th pH 4.3 | 9.5 | 12.3 | 14.0 | 40.8 | 23.4 |
| $H_2O_2 \parallel$ sonic $\mid$ NaOH pH 6.8 | 9.5 | 12.3 | 15.9 | 37.5 | 24.8 |
| Sonic $\mid$ Zr pH 3.7 | 10.9 | 15.8 | 14.7 | 32.6 | 26.2 |
| Sonic $\mid H_2O$ | 10.9 | 15.3 | 15.3 | 33.5 | 25.0 |
| $H_2O_2 \parallel$ sonic $\mid NH_3$ | 10.4 | 14.1 | 13.6 | 34.9 | 27.0 |

Contd/

Table 66 Contd/

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $<1.4\mu$ |
|---|---|---|---|---|---|
| Sonic $\mid$ $SiO_2$ $NH_3$ | 13.8 | 12.8 | 12.9 | 31.5 | 29.0 |
| $H_2O_2$ $\parallel$ Sonic $\mid$ $SiO_2$ $NH_3$ | 9.6 | 13.3 | 13.6 | 34.2 | 29.3 |
| Sonic $\mid$ $NH_3$ | 13.7 | 13.5 | 11.4 | 31.9 | 29.5 |
| Recip shake $\mid$ resin 17 ml $\mid$ 60 ml $H_2O$ | 20.1 | 11.7 | 10.9 | 27.4 | 29.9 |
| NaF $\parallel$ $H_2O_2$ $\parallel$ Sonic $\mid$ $H_2O$ | 12.5 | 10.2 | 9.9 | 26.0 | 41.4 |

Table 67 % Soil separates for Amlaird $B_{2g}$ horizon obtained from different soil dispersion treatments.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $<1.4\mu$ |
|---|---|---|---|---|---|
| $H_2O_2 \parallel$ sonic $\mid H_2O$ | | | Flocculation . . . . . | | |
| $H_2O_2 \parallel$ sonic ┌ $NH_3$ pH 10. . .<br>excess └ NaOH pH 12 . . . | | | Flocculation . . . . . | | |
| Recip. shake $\mid$ 60 ml $H_2O$ | 9.7 | 12.3 | 10.8 | 40.4 | 26.8 + NaCl → 26.8 |
| NaF $\parallel$ sonic $\mid H_2O$ | 8.3 | 10.5 | 10.0 | 32.8 | 38.4 $\xrightarrow[\text{months}]{2}$ 40.3 |
| $H_2O_2 \parallel$ sonic $\mid NH_3$ | 6.4 | 10.7 | 10.1 | 33.7 | 39.1 |
| Sonic $\mid NH_3$ | 7.6 | 11.5 | 10.5 | 30.3 | 40.1 |
| NaF $\parallel H_2O_2 \parallel$ sonic $\mid H_2O$ | 7.1 | 8.9 | 14.1 | 28.9 | 41.0 |
| Sonic $\parallel H_2O$ | 7.5 | 9.8 | 10.5 | 30.1 | 43.1 |
| Na-resin 20 ml $\mid$ recip. shake $\mid$ 60 ml $H_2O$ | 9.0 | 11.6 | 10.9 | 24.9 | 43.6 $\xrightarrow[\text{months}]{2}$ 45.5 |

Table 68 % Soil separates for Tirau B horizon obtained from different soil dispersion treatments.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $\leq 1.4$ μ |
|---|---|---|---|---|---|
| Sonic \| $H_2O$ or $NH_3$ | n.d. | n.d. | Flocculated . . . | | |
| $H_2O_2$ ‖ recip. shake \| Na-resin 15 ml \| 60 ml $H_2O$ | 7.8 | 16.5 | Flocculated . . . | | |
| $H_2O_2$ ‖ sonic \| $SiO_2$ + $NH_3$ | 5.3 | 21.0 | 25.8 | 36.0 | 11.9 |
| $H_2O_2$ ‖ sonic \| Zr | 7.7 | 16.1 | 23.6 | 33.1 | 19.5 |
| Sonic \| Zr pH 4.3 | 5.3 | 23.8 | 12.3 | 36.0 | 22.6 |
| Sonic \| HCl pH 4.4 | 5.2 | 23.0 | 20.7 | 27.4 | 23.7 |
| Recip. shake \| Na-resin 12 ml \| 60 ml $H_2O$ ‖ $NH_3$ | 9.8 | 17.1 | 25.6 | 27.1 | 20.4-$NH_3$→24.9 |
| Sonic \| $SiO_2$ + $NH_3$ | 4.2 | 15.8 | 29.7 | 24.6 | 25.7 |
| $H_2O_2$ ‖ recip. shake \| Na-resin 15 ml \| 60 ml $H_2O$ ‖ $NH_3$ | 7.5 | 14.5 | 29.2 | 18.0 | 26.8 |

Table 69 <u>% Soil separates for Loch Lomond mica-schist podzol C horizon obtained from different dispersion treatments</u>.

| Treatment | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay <1.4 µ |
|---|---|---|---|---|---|
| Sonic $\mid$ $H_2O$ | | | Flocculation . . . . . . | | |
| $H_2O_2$ excess $\parallel$ sonic ┐ NaOH pH 12 . . . | | | | | |
| └ $NH_3$ pH 10 . . . | | | Flocculation . . . . . . | | |
| Sonic $\mid$ $NH_3$ | 2.0 | 10.1 | 20.9 | 57.4 | 9.6 |
| $H_2O_2$ $\parallel$ sonic $\mid$ $NH_3$ | 2.9 | 11.0 | 19.1 | 53.7 | 13.3 + $SiO_2$ → 13.3 |

(% organic matter = 6.75.)

Table 70 % Soil separates for Dunlop (1971) soils and Amlaird soils after standard treatment of sonic dispersion in ammonia solution, or *in water only.

| Soil | Horizon | Coarse sand | Fine sand | Coarse silt | Fine silt | Clay $<1.4\mu$ | Organic matter % |
|---|---|---|---|---|---|---|---|
| Dunlop | $A_1$ | 14.2 | 9.6 | 8.9 | 32.4 | 34.9 | 15.94 |
| Brown | $B_{2g}$ | 25.5 | 11.7 | 10.9 | 28.9 | 23.0 | 4.51 |
| forest | $B_{3gx}$ | 17.5 | 15.1 | 12.0 | 34.0 | 22.0 | 2.18 |
| soil | $C_g$ | 13.7 | 13.5 | 11.3 | 31.9 | 29.6 | 0.69 |
| Amlaird | $A_o$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| surface | $A_1$ | 8.4 | 11.3 | 23.6 | 21.7 | 35.0 | 12.46 |
| water | $A_{eg}$ | 8.7 | 10.9 | 12.2 | 31.2 | 37.0 | 2.97 |
| gley | $B_{2g}$ | 7.6 | 11.5 | 10.5 | 30.3 | 40.1 | 1.70 |
|  | * $C_1G$ | 8.9 | 11.5 | 16.0 | 23.8 | 39.8 | 0.79 |
|  | * $C_2$ | 9.9 | 14.6 | 13.7 | 26.3 | 35.5 | 0.46 |

Table 71A Clay percentages obtained from zirconium nitrate dispersion of Dunlop soils at pH 3.7 - 3.4.

| Soil | zirconium used | | | dispersion | clay % OD mineral soil | |
|---|---|---|---|---|---|---|
| | ml/l | mM/l | g/l | pH | sonic/Zr | sonic $NH_3$ |
| $C_g$(1969) | 6.7 | 0.73 | 0.19 | 3.7 | 24.8 | 31.8 |
| $C_g$(1971) | 8.5 | 0.93 | 0.23 | 3.7 | 26.6 | 29.6 |
| $B_{2g}$(1971) | 8.0 | 0.88 | 0.22 | 3.7 | 17.3 | 23.0 |
| (repeat) | 16.0 | 1.76 | 0.44 | 3.7 | 17.3 | 23.0 |
| $B_{2g}$(1969)\|$H_2O_2$ | 14.4 | 1.58 | 0.39 | 3.4 | 30.1 | 27.8 |
| $B_{2g}$(1971)\|$H_2O_2$ | 21.5 | 2.37 | 0.59 | 3.4 | 21.5 | 23.0 |

Table 71B Clay percentages from zirconium and thorium nitrate dispersions pH 4.5 - 4.3.

| | | | | | | |
|---|---|---|---|---|---|---|
| | zirconium used | | | | | |
| $B_{2g}$(1971)\|$H_2O_2$ | 130 | ~8.25 | 2.43 | 4.3 | 23.8 | 23.0 |
| | thorium used | | | | | |
| $C_g$(1971)\|$H_2O_2$ | 100 | 2.9 | 1.49 | 4.3 | 23.4 | 29.6 |

# CHAPTER XIII: INVESTIGATIONS INTO THE COURSE AND MECHANISM OF THE FLOCCULATION OF SOILS CONTAINING ALLOPHANE.

## 1. The allophane problem at high pH.

The work in this Chapter was inspired by the hope that it would be possible to discover the mechanism of the flocculation of allophane at high pH, and to devise milder methods for its successful dispersion than the acid zirconium nitrate method, which at that time was the only one known to the writer. The Darleith soils, although they contained allophane, had not been found to behave in the same way. The flocculation of the Dunlop $C_g$ (1969) soil was readily understood as due to the isoelectric precipitation of allophane and clay minerals, and the flocs dispersed in ammonia solution in the expected manner. The two pieces of evidence which suggested conditions under which this did not occur had been overlooked. It will be seen later in this Chapter that the Dunlop soils, and even the Amlaird soils behaved in exactly the same way as New Zealand allophane under those conditions.

At this stage it might be helpful to summarise what was known about the flocculation of allophane soils from the work of Davies (1933) and Birrell and Fieldes (1952), described in detail in Chapter IV A p.140 since it was their evidence and their theories which initially influenced the writer's train of thought and scheme of experiments.

(a) Flocculation occurred at neutral pH, but was increased by alkali, by motor dispersion and by sieving.
(b) Dispersion was best achieved in N/200 HCl, in some cases.
(c) It could be achieved by the removal of sesquioxides as in a deferration procedure.
(d) It could be achieved at high pH by boiling in NaOH, centrifuging off and redispersing in NaOH. Addition of acid then led to reflocculation at pH 9.6 which persisted at least to pH 2.5. The soil was again redispersed by centrifuging off and dispersing in N/200 HCl.
(e) Addition of an allophane soil containing gibbsite to an alkali dispersion of a 95% allophane soil derived from "water-sorted ash", containing no gibbsite, led to their mutual flocculation.
(f) It was concluded that such soils consisted in "two colloidal systems of different isoelectric points capable of mutual coagulation under the appropriate pH conditions, these being allophane on the one hand and

aluminium or ferric hydroxide on the other . . . dispersion should be possible in a weakly acid medium (provided the anion concentration is sufficiently low), or in a strongly alkaline medium (provided the cation concentration is low enough). There seems also some critical concentration of iron or aluminium in the soil, above which neither acid nor alkaline media are effective." (Birrell and Fieldes 1952).

At the time, the writer was unaware of the fact that almost all allophane soils flocculated at high pH, irrespective of their sesquioxide content ("Soils of New Zealand" 1968 2 p.40), and that the 'water-sorted ash' which yielded 64% clay in alkaline dispersion was an outstanding exception (Table 12 p. 142). Hence it was proposed to test the sesquioxide theory. The ferruginous nature of the Darleith soils indicated that iron oxide did not, for them, constitute a 'disturbing factor', although possibly it was too crystalline to act in this way. The only Darleith soil shown from DTA traces to contain gibbsite was Baidland $A_{eg}$ but this did not contain allophane. It was planned to add gibbsite to the Dunlop soils and see what happened. The experiments described in the last Chapter in which ferric hydroxide sol was added to Dunlop suspensions were also envisaged.

At the same time, the Birrell and Fieldes explanation that the isoelectric points of allophane, gibbsite and ferric oxide, believed to be in the region 6.6, 8.0 and 7.0 respectively, were such that they caused flocculation throughout the pH range did not seem credible. Two other ideas suggested themselves, and since these also initiated some of the experiments which follow, they are described below. The first was the 'polyelectrolyte hypothesis', and the second the 'silica hypothesis'.

In the polyelectrolyte hypothesis, the writer proposed that instead of viewing allophane primarily as a clay with a pH dependent charge, it should be imagined as a polyelectrolyte, a hydrophilic colloid, whose flocculating properties or dispersive behaviour could be understood in terms of the non-specific but chemical interactions of its hydroxy groups with the surface groups of clay minerals, sesquioxides or allophane itself. The analogy between allophane and polyelectrolytes like starch and krilium was suggested by the known disarray of its silica and alumina groups, the large and possibly indented surface of allophane, and the high concentration of hydroxyls thought to be present. This picture of its flocculating powers followed La Mer's opinion (1967) discussed in Chapter III 7 p.112, that in the interaction between polyelectrolytes and clay, the primary forces were the non-specific van der Waals forces, and electrostatic forces were secondary. If allophane was a polyelectrolyte, then like other polyelectrolytes its behaviour would be unpredictable, dependent on a range of unknown non-specific interactions; influenced by steric factors and the composition of the electrolyte solution. It might also, in common with some other polyelectrolytes, show 'sensitising activity' or 'protective activity' at different levels of allophane and electrolyte concentration. Moreover, the properties of allophane could perhaps be modified, as those of clay minerals were modified but with greater effect, by the introduction of anionic groups to the aluminous sites.

The silica hypothesis was suggested by Birrell and Fieldes' experiment outlined in (d) p.534, in which they removed some flocculating material by boiling the soil in NaOH and centrifuging it off, and also by centrifuging it off at pH 2.5. They seem to have concluded that excess electrolyte was removed ie. that a flocculating concentration of cations was centrifuged off at high pH and a flocculating concentration of anions at low pH, but the argument was carried no further than this. The writer however, wondered whether dissolved alumina or in particular, silica could be the "disturbing factor." Flocculation was reported to be strong at pH 6.6, and one could assume the electrostatic mechanism operated from ~4.5 to 7.0 or throughout the acid range when clay minerals were present. Alumina was still insoluble at pH 7 but silica would steadily dissolve. This fact, and the discovery that water purification chemists used silica as a catalytic flocculating agent in the precipitation of river colloids, and in concentrations as low as 3 ppm, suggested the idea that perhaps silica was the flocculator of allophane soils, dissolving from the amorphous allophane surface, particularly as the pH was raised, removable after boiling in alkali by centrifuging, and again dissolving from the fresh surface as time passed. Thus it was postulated, the flocculation which reappeared for Birrell and Fieldes after HCl had been added to pH 9.6, was due to redissolved silica, and it persisted regardless of pH, because the soil could only be redispersed by centrifuging the silica off. It so happened this was done at pH 2.5.

A series of experiments were envisaged in which it was hoped (a) to determine the isoelectric point and allophane content of the Dunlop soils, with a view to studying the influence of allophane on their CEC and phosphate retention. (b) to test out the sesquioxide, polyelectrolyte and silica hypotheses, or any others which might explain the flocculating properties of allophane soils.

## 2. Reagents and analytical methods.

### (i) Baylis sol of colloidal silica.

Colloidal silica was prepared as a Baylis sol (Baylis 1936, Wheaton and Walker 1950). An estimated 1.5% solution of silica was made by diluting 5 ml sodium silicate solution (water glass) to 95 ml with deionised water. It was assumed that the water glass contained 28.7% $SiO_2$ and that the 1.5% solution had an alkalinity of 7330 ppm $CaCO_3$. It was required to neutralise this solution to 1100 to 1300 ppm $CaCO_3$ alkalinity, since greater acidity would lead to gel formation and greater alkalinity would inhibit the rapid formation of colloidal silica. 12 to 13 ml N $H_2SO_4$ was added for this purpose. The solution was allowed to age 2 hours and then made to 240 ml to give a 0.67% solution. The recommended dilution was 0.6% so that the volume should correctly have been made to 270 ml. The solution was not analysed for $SiO_2$ concentration. It was only stable for about two days and flocculated slowly thereafter. The pH of the 0.67% solution was 11.0. The negative charge on the colloid was confirmed by procipitation with a drop of 1% cetab.

### (ii) Gibbsite sol.

A gibbsite sample was donated from La Porte Industries, Wirral. Its particle size was given as 40 $\mu$ diameter, and it produced an X-ray diffraction pattern identical with gibbsite, except for a few unidentified lines (Appendix A20 p. 782). An initial difficulty was encountered in that when the gibbsite was ground and sonically dispersed, it could not be made to flocculate with any charged species over any range of pH, nor did it have electrophoretic mobility. It remained dispersed, and could only be precipitated in hot water. It was surmised that a dispersing agent had been incorporated.

This was confirmed by a molybdate test which showed the gibbsite held a large quantity of phosphate. The phosphate was removed by suspending the silt sized material in hot 60% $HClO_4$ for five minutes and decanting into 2 litres of water. In this way the perchloric acid dissolved the phosphated surface and prevented re-adsorption by hydrolysing the phosphate polymers. When the gibbsite silt was ground to clay size in a Wig-L-bug tests with molybdate reagent showed it to be free of phosphate. Aliquots were dispersed in HCl at ~ pH 3.9 and in NaOH at ~ pH 10.0. Electrophoresis of sols adjusted to a series of pH values showed the gibbsite had a very small mobility and an isoelectric point in the region pH 8.0. Neither of the sols were particularly stable. Addition of silica sol however to the alkaline gibbsite and of zirconium nitrate to the acidic gibbsite produced sols which were stable for many months.

### (iii) Silica analysis. Molybdenum blue method.
(Shapiro and Brannock 1952).

### Reagents

Ammonium molybdate solution: 7.5 g ammonium molybdate was dissolved in 75 ml $H_2O$ and 25 ml 20% $H_2SO_4$ was added. The solution was mixed, stored 24 hours before use in a pyrex bottle and filtered. It was prepared fresh weekly.

Tartaric acid solution: 8g tartaric acid was dissolved in 100 ml $H_2O$ and stored in a plastic bottle.

Reducing solution: (a) 0.7g sodium sulphite was dissolved in 10 ml $H_2O$. 0.15g 1-amino 2-naphthol 4-sulphonic acid was added and the solution mixed. (b) 10g sodium metabisulphite was dissolved in 90 ml $H_2O$. Solutions (a) and (b) were mixed and stored in an amber bottle. They were rejected after three days.

Standard silica solution (50$\mu$g /ml): spec. pure silica was ignited in a vitreosil crucible over a meker burner for 20 min., cooled in a desiccator and 0.05g was weighed into a silver crucible together with 1.5g NaOH pellets. The covered crucible was heated for 5 min. at 750 - 800°C, cooled and $\sim$ 20 ml $H_2O$ added. It was heated on a steam bath and then poured into a litre beaker containing 20 ml 2.5 N $H_2SO_4$ and 600 ml $H_2O$. It was mixed on a magnetic stirrer and made to 1 litre, the resulting solution containing 50 $\mu$g $SiO_2$/1. A blank of sodium hydroxide solution was similarly prepared. Both solutions were stored in plastic bottles in a frig.

Procedure.

100 ml volumetric flasks were cleaned by steeping them overnight in a 50:50 mixture of conc. $H_2SO_4$ : $HNO_3$. They were rinsed thoroughly in water and filled with water until ready for use.

Standard curve: Standard solutions were prepared in duplicate by pipetting $x$ ml standard $SiO_2$ solution into a 100 ml flask, where $x$ = 0 to 10 ml, followed by 10 - $x$ ml fusion blank and making to 72 ml with water. The pH of this solution was 1.7. The reagents were added with the help of a stop-clock. 2 ml molybdate was added with mixing, giving the pale yellow colour of silico-12-molybdate. After exactly 10 mins. 5 ml tartaric acid was added with mixing. After exactly 4 mins. 2 ml reducing solution was added. The solutions were made to 100 ml, shaken and allowed to stand at least 30 minutes. Optical densities of the blue solutions were read in 1 cm cells on a Unicam SP 500 spectrophotometer at 610 mμ vs. the reagent blank, and a standard curve was constructed for 0 - 5 μg $SiO_2$/ml.

Sample solutions require to contain monomeric silicic acid and to be free of organic or other reducing agents. In the presence of sulphuric acid, maximum values for the colour development of yellow silico - 12 - molybdate are obtained between pH 1 and 2.5 (Govett 1961). The writer however, found it best to maintain sample pH at the same pH as the standard solutions ie. 1.6 - 1.7 before molybdate addition. Conditions are also critical in other respects, such as in the degree of polymerisation of the molybdate (Govett 1961); hence the need to renew it weekly. Interferences from iron and phosphate were removed by the addition of tartaric acid.

Aliquots of sample were pipetted into a beaker and made to ~ 70 ml with water, and the amount of 2.5 N $H_2SO_4$ or 5 N NaOH required to bring them to pH 1.6 - 1.7 was noted, these amounts being used to prepare the solutions for reagent addition. For some reason it was found essential that samples containing sodium carbonate should be diluted in this way prior to addition of acid, or low results were obtained. This observation correlates with that of Govett (1961) who found that for alkali fusions, sodium hydroxide was preferred, because sodium carbonate gave low silica results.

(iv) Alumina analysis. Oxine-chloroform method (Riley 1958)

Reagents.

Complexing solution:

(a) 25% W/V hydroxylamine hydrochloride: 25 g $NH_2OH.HCl$ was dissolved in 100 ml water.

(b) sodium acetate (0.5 N): 17.0 g hydrated NaOAc was dissolved in water and diluted to 250 ml.

(c) bipyridyl solution: 0.2 g 2,2' - bipyridyl was dissolved in 100 ml 0.2N HCl.

4 ml hydroxylamine hydrochloride, 50 ml 0.5N sodium acetate, and 20 ml bipyridyl solution were mixed and made to 100 ml. The solution was stable for at least one month.

8-hydroxy quinoline reagent (oxine). 1.25 8-hydroxyquinoline was dissolved in 250 ml B.P. chloroform. It was filtered and stored in an amber glass bottle in a frig, and rejected if it became coloured.

Standard alumina solution (20 $\mu$g/ml): 0.9303 g $AlK(SO_4)_2.12\ H_2O$ was dissolved in water and made to 500 ml in a volumetric flask as standard <u>I</u>, containing 200 $\mu$g $Al_2O_3$/ml. 10 ml of this was diluted to 100 ml for working use as standard <u>II</u>, containing 20 $\mu$g $Al_2O_3$/ml.

<u>Procedure</u>.

Standard curve: $x$ ml standard <u>II</u> solution was pipetted into a stoppered 50 ml separating funnel and $10-x$ ml $H_2O$ was added, where $x =$ 0 - 10 ml. 10 ml complexing reagent was added, taking care to keep the stem of the funnel dry. The pH was checked and found to be 5.0. After 5 minutes 20 ml 8-hydroxyquinoline was added. The funnel was stoppered and shaken by hand, the stopper being loosened to allow $CHCl_3$ vapour to escape after the first two or three shakes. After 2 minutes shaking, the yellow chloroform layer was run through a small plug of filter paper, held in the stem of a 2.5 cm funnel, into a perfectly dry 25 ml volumetric flask. 2-3 ml $CHCl_3$ were added to the separating funnel which was rinsed by rotating it gently and the chloroform washings were passed into the flask. The solutions were made to 25 ml with $CHCl_3$ and stored in a cupboard until ready to be measured, because aluminium-oxinate solutions are somewhat light sensitive. Optical densities were read on a Hitachi Perkin Elmer 139 spectrophotometer at 410 mμ in a 1 cm cell vs. a chloroform blank, and the value of the reagent blank was subtracted. A standard curve was constructed for 0 - 8 μg $Al_2O_3$/ml.

<u>Sample solutions</u> require to be buffered by the complexing reagent within the narrow limits 4.9 - 5.0 in order to remove iron interference. Aliquots of sample solution containing 10 ml complexing reagent were brought to pH 4.9 - 5.0 with 30% acetic acid or solid hydrated

sodium acetate as required. It was found that sample aliquots of up to 25 ml were often required to obtain a convenient concentration, thus bringing the $H_2O$: $CHCl_3$ ratio to at least 35:20, but this did not appear to affect the extraction. Smaller $H_2O$: $CHCl_3$ ratios than 1:1 however inhibited the extraction by forming an emulsion on shaking. The larger volumes, and the effervescence of solutions containing carbonate made a 100 ml separating funnel more convenient than a 50 ml funnel.

(v) Iron oxide analysis. Bipyridyl method (Riley 1958).

Complexing solution: as for alumina.

Standard iron oxide solution (100 μg/ml): 0.0699 g specpure iron sponge was suspended in 2N HCl, heated to dissolve it and made to 1 litre. The resultant solution contained 100 μg $Fe_2O_3$/1.

Procedure.

Standard curve: 1 - 5 ml aliquots of standard $Fe_2O_3$ solution were pipetted into 100 ml volumetric flasks. 20 ml complexing reagent was added, such that the pH was 4.8 to 5.0 and the solutions were diluted to 100 ml. The optical densities were read in a 1 cm cell at 522 mμ on a Hitachi Perkin Elmer 139 spectrophotometer vs. a reagent blank. The red colour was stable for up to 30 hours. A standard curve was constructed for 0 - 5 μg $Fe_2O_3$/ml.

Sample solutions were brought to pH 4.8 to 5.0 after addition of the complexing reagent by addition of 30% acetic acid or solid hydrated sodium acetate.

### (vi) Analysis of calcium, magnesium, sodium and potassium.

Calcium and magnesium concentrations were measured on a Unicam SP 90 atomic absorption spectrophotometer at wavelengths 422.7 and 285.2 mμ respectively. Potassium and sodium were measured on the same instrument at wavelengths 766.5 and 589.0 mμ respectively, using the emission mode. Standard solutions were made in the following concentrations: calcium 0 - 15 μg Ca/ml, magnesium 0 - 2 μg Mg/ml, sodium 0 - 10 μg Na/ml, potassium 0 - 10 μg K/ml.

N.B. Water. Deionised water was used in all experiments in this thesis.

## 3. Further studies on the normal flocculation and dispersion of allophane in Scottish soils.

### (i) Flocculation of allophane in Dunlop and Podzol C horizons.

At this stage the writer assumed there were only a few ends to tie up on the flocculation of allophane in the Dunlop soils. The classical dispersion of peroxidised $C_g$ had for some reason proved a failure and it was proposed to vibrate a peroxidised sample in ammonia on the premise that sonic treatment would be more efficient. At the same time it was predicted that podzol C horizons, which field tests had shown to contain allophane, might flocculate in the same fashion as Dunlop $C_g$ (1969) on sonic treatment. The Loch Lomond mica-schist podzol C had given a strong response to fluoride treatment (pH 10.4 in 15 minutes). On the other hand, its organic matter content was high (6.75%) for a C horizon, so that it might be necessary to peroxidise it first, as with Dunlop $C_g$ (1971), before the positive sites could exert an influence.

## Exp. 59 Mechanical analysis of peroxidised Dunlop $C_g$ (1971) soil in alkaline suspension.

10 g Dunlop $C_g$ (1971) was peroxidised in 5 ml $H_2O_2$ and then vibrated in ammonia solution. A stable dispersion was achieved and the clay yield was 27% (Table 66 p.527). This compares with 25% and 29% for sonic /$H_2O$ and sonic /$NH_3$ dispersions respectively.

## Exp. 60 Mechanical analysis of podzol C horizon by sonic vibration.

10 g Loch Lomond mica schist podzol C soil was vibrated in water and made to 900 ml (pH 5.45). It showed strong hindered settling and next day a few ml of flocs had piled up in the base of the cylinder. These were dispersed when drops of ammonia were added to bring the suspension pH to 10. The clay yield (Table 69 p.530) was 9.6% and corresponded with its estimated silt loam texture. This experiment confirmed the importance of using sonic /$NH_3$ rather than sonic /$H_2O$ as a routine method in mechanical analysis. It also suggested that if 6.75% organic matter had failed to inhibit the flocculation of 9.6% clay, the organic matter must be present in a more inert form than in Dunlop $C_g$, where 0.7% organic matter prevented

flocculation of a suspension containing 25% clay.

### Exp.61 Mechanical analysis of the peroxidised podzol C in alkaline suspension.

10 g podzol C was peroxidised with 9.0 ml 30% analar $H_2O_2$ (pH 4.3) and vibrated in ammonia (pH 9.9). The suspension was made to 1 litre (pH 9.85) and pipette analysis yielded 13.3% clay, as compared with 9.6% for the unperoxidised sonic/$NH_3$ dispersion.

### (ii) Exp.62 The effect of dilution on flocculation.

It was wondered how far flocculation could be forestalled by making up more dilute suspensions.

1 g Dunlop $C_g$ (1971) soil was given sonic treatment and then peroxidised in order to produce flocs. There was immediate flocculation when a 1% suspension was made by diluting to 100 ml (pH 4.7), but on further dilution to 250 ml (pH 4.95) the flocs were eliminated. They did not return when the pH was lowered to 4.6 with dilute HCl. However, the suspension was allowed to stand and flocculation occurred after about a week.

Conclusion. The tendency to flocculate was always present in peroxidised Dunlop soils when the pH was below the isoelectric point of allophane. It could be delayed by diluting or encouraged by concentrating suspensions, as also by shaking, sonic treatment and sieving ie. flocculation was promoted by increasing the chance of effective collisions. It was not advisable to suppose that one could take advantage of this delay by doing mechanical analysis on dilute suspensions, because erroneously high results might be obtained if sampling were done at the stage of hindered settling, as well as erroneously low results if sampling were done after subsidence had set in. The anomalous 37.9% clay of the $H_2O_2$/sonic Dunlop $B_{2g}$ (1969) (Table 63 p.524) was almost certainly an example of the former case, and the 6.8% clay from $H_2O_2$/sonic Dunlop $C_g$ (1969) (Table 65 p.526) was an example of the latter.

### (iii) Investigation of the isoelectric point of the Dünlop flocs.

### Exp.63 Search for the isoelectric point of Dunlop $C_g$.

Aliquots of Dunlop $C_g$ (1969) flocs were transferred to 100 ml beakers and their pH was adjusted with drops of dilute NaOH. A preliminary search for the region of the isoelectric point was made by following the onset of flocculation in the development of a clear band of water at the top of the suspension after vigorous stirring.

| pH | Observation. |
|---|---|
| 5.1 | Flocculation in $<$ 1 minute |
| 5.4 | Flocculation in 1 minute |
| 5.8 | Slight flocculation after 7 minutes |
| 6.0 | No flocculation after 7 minutes. Next day, slight clear rim. Hindered settling may be taking place, however. |

Exp. 64 1 g Dunlop $C_g$ (1971) was given sonic treatment, and peroxidised in order to produce flocs for the experiment. A 2% suspension of silt + clay was made (pH 4.9) and 10 ml aliquots were examined over a range of pH values with the following results:-

| drops NaOH added | pH | flocculation in 2 minutes | supernatant turbidity after 3 hours. |
|---|---|---|---|
| 0 | 4.9 | immediate | v. slightly turbid |
| 2 | 5.25 | immediate | v. slightly turbid |
| 3 | 5.4 | uncertain | medium turbid |
| 4 | 5.6 | none | turbid |
| 8 | 5.92 | none | strongly turbid |

The pH 5.92 sample remained strongly turbid for several days. It was weakly turbid after 8 days and precipitated as compacted flocs.

These results suggested that at this dilution, and in the absence of strong electrolyte under which such experiments are normally done, allophane became negatively charged in the region of pH 6.0. Further evidence was provided from an experiment described in Chapter XII p.519 in which the flocs of a 1% soil suspension were dispersed and mechanical analysis done successfully at pH 6.8 (Table 66 p. 527).

Next it was proposed to compare the flocculation pH of the three Dunlop subsoils. Flocculated suspensions of $B_{2g}$ and $B_{3gx}$ were prepared by peroxidising 5 g of each, giving them sonic treatment, separating the sands and making up the suspensions to 500 ml with water. It was also proposed to use these stock suspensions for flocculation experiments with gibbsite and silica sol at high pH.

### Exp. 65 Search for the isoelectric point of Dunlop $B_{3gx}$.

20 ml aliquots of Dunlop $B_{3gx}$ flocs (pH 5.25) were pipetted into test tubes. They were adjusted to a range of values up to pH 6.45 with drops of dilute NaOH, shaken on a wrist shaker, and left to stand. Observations were made as follows:-

| pH | supernatant turbidity after 90 minutes | supernatant turbidity next day |
|---|---|---|
| 5.25 | clear | ↕ clear. complete flocculation |
| 5.9 | pale turbid | |
| 6.0 | pale turbid | |
| 6.15 | pale turbid | |
| 6.25 | pale turbid | |
| 6.35 | strongly turbid | |
| 6.45 | strongly turbid | |

Discussion. The $C_g$ pH 5.92 sample was still strongly turbid after 3 days, while the more dilute and less clay-rich $B_{3gx}$ suspension had completely flocculated even at pH 6.45. There might be two reasons for the difference in behaviour: (a) the $B_{3gx}$ was known to contain more allophane than the $C_g$ (Table 54 p.432), and (b) it might be expected to be more aluminous and thus to have a higher isoelectric point. It was intended to further investigate the isoelectric points of both soils, by extending the pH range on the alkaline side, but this experiment was abandoned because on the same day an observation was made which disrupted the whole argument.

## 4. Discovery of the flocculation of peroxidised Dunlop soils in alkaline suspension.

### Exp. 66 Flocculation of Dunlop $B_{3gx}$ in NaOH at pH 10.0.

Two samples containing 20 ml peroxidised Dunlop $B_{3gx}$ silt + clay flocs were made to pH 10 with NaOH, with the intention of then adding gibbsite to one of them. Next day the samples were found heavily flocculated. Their pH had fallen to 9.0 and 8.75. Further NaOH was added to each to bring their pH to ~ 10 and 0.5 ml gibbsite was added to one of them. They were given sonic treatment. The gibbsite suspension flocculated over a period of one day, just as the sesquioxide theory would have predicted. Its alkaline control was even more heavily flocculated. This result was so unexpected it was immediately repeated.

### Exp. 67 Flocculation of Dunlop $B_{2g}$ and $B_{3gx}$ in $NH_4OH$ at pH 10.

Two 20 ml aliquots each of $B_{2g}$ and $B_{3gx}$ peroxidised flocs were made alkaline to pH 10 with $NH_3$ solution. 1 ml 0.26% alkaline gibbsite sol was added to one of each pair, and all four samples were vibrated for 15 minutes and stood for observation. $B_{2g}$-gibbsite sample (pH 9.65) and the $B_{2g}$ control (pH 10.0) had both flocculated. $B_{3gx}$ gibbsite sample (pH 9.7) and $B_{3gx}$ control (pH 9.85) appeared stable. When the $B_{2g}$ samples were given further sonic treatment they both flocculated vigorously to give flocs 2 ml deep in 20 min.

The experiments were repeated and gave the same results, $B_{2g}$ flocculating more rapidly than $B_{3gx}$ which took up to 6 days in ammonia. At the same time there was to hand, a cylinder of Dunlop $A_1$ which had been peroxidised, vibrated and shaken in ammonia solution. It had appeared stable for the purpose of mechanical analysis, but now 4 weeks later, it was seen to contain ½ an inch of flocs at the base of the cylinder instead of the normal compacted sediment. Peroxidised Dunlop $C_g$ on the other hand gave no subsequent sign of flocculation. After three months, the suspension developed the zones of varying turbidity and the compacted sediment that were normally observed for clays that settled in accordance with Stokes' Law. Similarly, podzol C showed no sign of flocculation.

## Discussion.

The peroxidised Dunlop soils, with the apparent exception of $C_g$, were behaving in the same way as the 'difficult' allophane soils described by Birrell and

Fieldes (1952). The experiments were repeated three times and the rate of flocculation seemed to depend mainly on the degree of agitation to which the samples were subjected. Suspensions remained turbid longer, it seemed, when vibrated briefly or only shaken. This was in agreement with Davies' finding (1933) that motor dispersion assisted the flocculation of allophane. Time for flocculation varied from 3 to 6 days for the $B_{3gx}$ when it was dispersed in ammonia and for the $B_{2g}$, given commensurate treatment, it varied from immediate flocculation to six hours. For some reason when $B_{3gx}$ was dispersed in NaOH at pH 10 flocculation was much more rapid than when it was dispersed in ammonia at pH 10. This result was not understood at the time and its importance was not realised until much later. It will be returned to again at the end of this Chapter.

There seemed to be a marked difference between the behaviour of peroxidised Dunlop $C_g$, Podzol C and Amlaird $B_{2g}$ soils on the one hand, and peroxidised Dunlop $B_{3gx}$, $B_{2g}$ and $A_1$ soils on the other. The former group flocculated when below neutral pH, often without peroxidation pretreatment, and was dispersible in ammonia ie. when the positive clay component was made negative in alkali. The latter group remained flocculated at high pH in the manner of Tirau allophane.

The mechanism for this flocculation was now seriously considered. The 'sesquioxide hypothesis' that gibbsite and limonite promote the flocculation of soils containing allophane appeared no longer tenable. Addition of ferric oxide sol to Dunlop $B_{2g}$ flocs had actually dispersed them (Chapter XII 6 p.507) and gibbsite appeared to have inhibited the flocculation of $B_{3gx}$ (p.556). The original argument of Birrell and Fieldes (1952) was indeed based on very slender evidence: a stable alkaline sol of 'water-sorted ash' soil containing 95% allophane and no gibbsite was flocculated on addition of a suspension of 'pre-Hamilton ash' soil which contained considerable gibbsite. The authors did not say they added gibbsite itself to the dispersion of the water-sorted ash, and when years later, they reported that "addition of gibbsite will cause gradual flocculation of an apparently stable suspension" ("Soils of New Zealand" 1968 2 p.40), one suspects they were referring to the above experiment.

It was now postulated that, whatever the mechanism, the key to the differing flocculation behaviour of the two groups of soils was in the relative aluminous content of their allophane clay. Allophane in soils low in organic matter was conjectured to be more siliceous than allophane in soils rich in organic matter. The siliceous group: Dunlop $C_g$, Amlaird $B_{2g}$, podzol C, only flocculated by the simple mechanism due to a mixed suspension of negatively charged clay minerals and positively charged allophane. Tirau B and peroxidised Dunlop $B_{2g}$ and $B_{3gx}$ whose reactive sites had been unmasked by the removal of organic matter, flocculated at high pH by some other mechanism. It was planned to test this idea by (a) a careful comparison of the flocculating behaviour of the peroxidised Dunlop, podzol C and Tirau B soils and (b) correlating this with the silica : alumina ratios of the allophane extracted from each soil.

It was also thought that if the hypothesis was correct, it provided an explanation for the association of gibbsite with flocculating soils observed by Birrell and Fieldes: gibbsite would have formed in soils that contained more aluminium than the allophane could incorporate. It was thus not the cause but the indicator of a flocculating soil ie. of aluminous allophane. This explanation was found to be superfluous when the profile analyses given in "Soils of New Zealand" came to be examined. Allophane soils that defied mechanical analysis were not exceptional, but the norm. They rarely contained gibbsite or free ferric oxide. Birrell and Fieldes still maintained that "mutual co-precipitation in the presence of hydrous oxides" was one factor that inhibited dispersion, but laid more stress on the suggestion that allophane's high isoelectric point prevented the usual agents from shifting the pH far enough from it to allow complete dispersion. Partial dispersion they said, could be obtained in both weakly acid and fairly strong ($\sim$ pH 12) alkaline media provided the electrolyte concentration was sufficiently low ("Soils of New Zealand" 1968 2 p.40).

## 5. Dispersion of soils containing allophane in the presence of colloidal silica.

The hypothesis that dissolved silica might be responsible for flocculation at high pH, put forward by the writer on p.537 was also now in doubt. It was noted that water-chemists found difficulty in using colloidal silica as a flocculating catalyst for alkaline waters because it would not precipitate negatively charged sesquioxides (Wheaton and Walker 1950). This was confirmed in the following tests:-

### Exp. 68 Dispersion of gibbsite by $SiO_2$ sol.

One drop of Baylis $SiO_2$ sol was added to an unstable alkaline gibbsite sol. The resultant sol remained stable 'indefinitely'.

### Exp. 69 Dispersion of $Fe(OH)_3$ by $SiO_2$ sol.

The acid $Fe(OH)_3$ sol was diluted and to one 20 ml aliquot (pH 2.35) two drops of $SiO_2$ sol were added (pH 2.45). Two drops of 1:1 ammonia were given to this and to the $Fe(OH)_3$ control. The pH rose to 9.7. The control ferric hydroxide precipitated, while that with silica became very slightly turbid and remained so 'indefinetely' (ie. at least five months). However, when ammonia was added to the $Fe(OH)_3$ first, and a precipitate obtained, the silica sol was not then able to peptise it.

Thus, far from causing flocculation, alkaline silica sol brought about dispersion and it was decided as part of the planned experiments to see whether the resistant flocs also could be dispersed in colloidal silica. There was nothing new in this proposal. Clays for ceramic ware are frequently deflocculated by alkaline solutions of sodium silicate (McBain 1950). Birrell and Fieldes (1952) dispersed the water-sorted ash in sodium silicate and obtained comparable results to their sodium carbonate dispersion. Unfortunately they did not say whether they tried it on the flocculating type of allophane soils. Mattson (1930a) found that alumino-silicates prepared from $AlCl_3$ and $Na_2SiO_3$ solutions were dispersed, except in the region of their isoelectric point, provided only univalent ions were present. Dispersion however, was much enhanced with the silica added in colloidal form, prepared by acidifying $Na_2SiO_3$ before mixing it with $AlCl_3$ or $FeCl_3$. The alumino-silicate sol so formed was protected from flocculation at pH values above 4.3, while the ferro-silicate sol only precipitated in a narrow range at pH 4.2. This was described in Chapter III 4 (iii) p. 74 ).

Exp.70 The relative flocculation of soils containing allophane at high pH, and their dispersion with colloidal silica.

5 g Dunlop $C_g$ (1971) soil was peroxidised, vibrated, sieved and made to 500 ml in the same manner as the $B_{2g}$ and $B_{3gx}$ soils. Each 500 ml cylinder was well shaken and 50 ml aliquots of peroxidised flocs were pipetted into 50 ml cylinders. Two drops of 1:1 $NH_3$ were added to each subsoil triplicate and the pH made 10.2. Two drops of $SiO_2$ sol were added to one set of flocs, two ml alkaline gibbsite to a second set and the third set was the control. Each suspension was vibrated for three minutes, the silt discarded, and the clay returned to the 50 ml cylinder for observation. Similar series of Tirau B (25 ml) and peroxidised Tirau B (30 ml) were prepared. Since two drops of silica sol proved an ineffective addition for the peroxidised Tirau B, 1 ml and 3 ml additions were made in that case. The course of flocculation or sedimentation for each soil treatment is shown in Tables 72 and 73 .

## Discussion.

The following facts began to emerge as a result of these experiments.

Table 72 Dispersion and flocculation behaviour of peroxidised Dunlop $C_g$ and $B_{3gx}$ flocs in alkali and with silica or gibbsite.

| | |
|---|---|
| $C_g/NH_3$: | very stable till 4th day. Zoning perceived on 6th day. On 10th day flocculated, with 3 ml flocs and nearly clear supernatant. |
| $C_g/NH_3$/Gibbsite: | very stable till 4th day. Zoning perceived on 6th day. On 10th day, supernatant turbid with 5 ml clear rim and 2 ml of precipitated flocs. |
| $C_g/NH_3/SiO_2$: | very stable till 4th day. Zoning perceived on 6th day. On 10th day, supernatant turbid yellow with 3 ml clear rim; no flocs. On 21st day, supernatant clear yellow sol, compact coagulum. |
| $B_{3gx}/NH_3$: | stable on 1st day. Almost complete flocculation on 4th day. |
| $B_{3gx}/NH_3$/Gibbsite: | very stable on 1st day. On 6th day, 5 ml clear rim and sharp interface with a column of turbid material, suggesting hindered settling. On 10th day, clear supernatant and compacted flocs. |
| $B_{3gx}/NH_3/SiO_2$: | very stable on 1st day. On 6th day, 3 ml clear rim and pale turbid supernatant. On 10th day, 4 ml clear rim, pale turbid supernatant. On 21st day, a paler turbid supernatant, but still stable. Thin coagulum. |

Table 73 Dispersion and flocculation behaviour of peroxidised Dunlop $B_{2g}$ flocs and untreated and peroxidised Tirau B flocs.

| | |
|---|---|
| $B_{2g}/NH_3$: | flocculation in a few minutes. |
| $B_{2g}/NH_3$/Gibbsite: | flocculation in a few minutes. |
| $B_{2g}/NH_3/SiO_2$: | very stable on 1st day. On 6th day 11 ml clear rim and sharp interface to thickly turbid material. Flocs uncertain. On 12th day, clear supernatant and 3 ml loosely packed flocs. |
| $B_{2g}/SiO_2$/pH 5.75: | flocculated slowly in one hour. |
| Tirau B/$NH_3$: | stable on 1st day. On 2nd day, 5 ml clear rim, strongly turbid supernatant. On 4th day, 10 ml clear rim, turbid supernatant, flocs. 5th day, flocculated. |
| Tirau B/$NH_3/SiO_2$: | very stable on 1st day. Zoning perceived on 4th day. Came down by ~ 14th day as compacted precipitate. |
| Tirau B/$H_2O_2$/ $NH_3$: | flocculated in one hour. |
| Tirau B/$H_2O_2$//$NH_3$: | flocculated 1st day. |
| Tirau B/$H_2O_2$ $NH_3/SiO_2$ (0.1 ml): | flocculation. 1 ml $SiO_2$ added and suspension stable. On 21st day supernatant strongly turbid, some flocs? After 5 months, clear supernatant and compact coagulum. |
| Tirau B/$H_2O_2$ $NH_3/SiO_2$ (3 ml): | supernatant stable for 2 months. After 5 months, pale yellow. Green supernatant and compact coagulum. |

(a) There was a spectrum of behaviour in the tendency of the soils to flocculate and not a division of behaviour into two groups. At this stage the evidence for this statement rested on the behaviour of Dunlop $C_g$; that of Loch Lomond podzol C and the Amlaird soils remained to be checked. The Dunlop $C_g$ was shown to flocculate in ammonia in the same way, although to a less extent, as the $B_{3gx}$ and $B_{2g}$. The reason for the successful mechanical analysis of peroxidised Dunlop $C_g$ (1971) described earlier (Exp.59 p.527, Table 66) and yielding 27% clay, was due to the fact that it had not been peroxidised as fully. Only 5 ml $H_2O_2$ had been used. Similarly, only 5 ml had been used to peroxidise Amlaird $B_{2g}$ and Loch Lomond podzol C. This had proved sufficient to flocculate Dunlop $C_g$ electrostatically at pH ~4.6, but insufficient to flocculate it by the unknown mechanism at pH 10. Unfortunately, up until this time, quantities of peroxide added were not meticulously recorded. It had been the practice to add ~ 5 ml for a C horizon. The 5 ml/5 g, instead of 5 ml/10g which was added to $C_g$ in Exp. 70 above, was sufficient to bring about alkali flocculation. Later experiments as will be seen, showed that 60 and 50 ml $H_2O_2$ added to Loch Lomond Podzol C and Amlaird $B_{2g}$ respectively, brought about immediate massive flocculation in the podzol on addition of $NH_3$, and a slow flocculation beginning 3 hours after $NH_3$ addition for Amlaird.

These facts now illuminate the 'anomalous' clay yields of 16% and 6.8% obtained in the classical mechanical analyses of Dunlop $B_{2g}$ (1969) and Dunlop $C_g$ (1969) respectively (Chapter XII pp.479, 490). Once attributed to inefficient shaking, these results can now be interpreted as a consequence of the soils' peroxidation and alkali treatment. The fact that the soils subsequently sedimented without visible flocculation can be explained as due to the mild rotary shaking they recieved, instead of sonic vibration which gives rise to massive flocs. Finally, the larger recovery of clay from $B_{2g}$ (16%) than $C_g$ (6.8%) was almost certainly due to the dialysis of $B_{2g}$ following peroxidation (p.479). $C_g$ was not dialysed. Support for this deduction was obtained later, in Exp. 75 p.601, where Tirau B was dialysed and partially dispersed.

(b) The spectrum of behaviour in the tendency of the soils to flocculate, was as predicted. Including the later findings for Podzol C and Amlaird $B_{2g}$, this at first appeared to follow the order:-

Dunlop $B_{2g}(H_2O_2) >$ Tirau $B(H_2O_2) >$ Dunlop $B_{3gx}(H_2O_2)$
$>$ Tirau B $>$ Dunlop $C_g$ (1971 $H_2O_2$) $\approx$ Podzol C ($H_2O_2$)
$>$ Amlaird $B_{2g}(H_2O_2) >$ Dunlop $A_1$ ($H_2O_2$).

Dunlop $A_1$ is of course misplaced in the series, since it was inhibited from flocculating by incomplete removal of organic matter. $C_g$ as seen later, is also misplaced.

The order suggests it was not only the amount but also the nature of the allophane which dictated the degree of flocculation. The order of response to fluoride, measured by hydroxyl release was found to be:-

Dunlop $B_{2g} >$ Dunlop $B_{3gx} >$ Tirau B $>$ Podzol C
$>$ Dunlop $C_g$ (1971) $>$ Dunlop $C_g$ (1969)
$>$ Dunlop $A_1 \gg$ Amlaird $B_{2g}$.

If one is to account for the much smaller response of Tirau B than Dunlop $B_{2g}$ and $B_{3gx}$, this reaction must measure surface alumina rather than allophane content. It could be argued that the degree of flocculation at high pH depended on the extent to which the allophane surface is dominated by alumina groups. Removal of organic matter from Dunlop $B_{2g}$, for instance, exposed an allophane most dominated by alumina groups and most prone to flocculate, while Dunlop $C_g$ was least prone to flocculate at high pH, because having low organic matter, its aluminous sites are more silicated. This accords with Mattson's evidence (1930a, b:1931a) that in the absence of humate, siliceous allophanes form under acid conditions. His findings were described in Chapter III 4 (iii) p.72 and VII 2 p.295.

(c) In the more slowly flocculating $B_{3gx}$ and $C_g$ cases, gibbsite was shown to have an inhibiting effect. (Table 73 p.566).

(d) Silica was shown to have a strongly dispersive effect on the flocs of all four soils provided the suspensions were alkaline. This was considered due to the uptake of silica on the aluminous sites and the masking of these reactive centres. The number of sites requiring silication was reflected in the relative degree of flocculation of the suspensions. Complete dispersion appeared to have been achieved for Dunlop $C_g$, $B_{3gx}$ and possibly also for Tirau B, using 2 drops of Baylis sol. Dunlop $B_{2g}$ flocculation was inhibited for about six days and peroxidised Tirau B remained flocculated, requiring 1 ml $SiO_2$ for dispersion. These results are broadly in agreement with those for the rate of flocculation in ammonia solution, except that peroxidised Tirau B appears here to have a greater number of aluminous sites than Dunlop $B_{2g}$, reflecting the amount of allophane present rather than its nature.

Mattson's experiments (1930b, 1931a) with silica, humate and phosphate alumino-silicate complexes leads one to predict that addition of humate or phosphate should have a similar dispersive effect, for he showed that dispersion was a consequence of the high electronegativity conferred on the colloid when large amounts of these anions were present, provided the cations of the free electrolyte were univalent. Organic matter does indeed help to peptise an alkaline suspension. It might then be argued that sesquioxides themselves become negatively charged at high pH and therefore should be dispersive in alkali. Since this does not appear to be the case, at least when they are combined in alumino-silicate, a further explanation must be sought.

## Exp. 71 Mechanical analysis of soil dispersions in alkaline silica solution.

The next step was to study the silica dispersions quantitatively by mechanical analysis.

Method: 10 g air dry soil suspended in 25 ml water was made alkaline to ~pH 10 with 1:1 ammonia solution. Drops of silica sol were added and the suspension was given sonic treatment, sieved, diluted to ~990 ml and shaken. Further silica sol was added so long as a tendency to flocculate was perceived. When the suspension appeared stable for at least an overnight period, the silt + clay and clay samples were pipetted. An aliquot of silica sol was taken concurrently and the appropriate weight of the oven dry material subtracted from the weights of the silt + clay and clay samples.

## Results and discussion.

The silica dispersions for Dunlop $C_g$ (1971) yielded almost the same amount of clay as in ammonia alone, 29% and 29.5% respectively (Table 66 p.527), and only a small increase was obtained for the peroxidised soil, which gave 27% in $NH_3$ and 29.3% in $NH_3 + SiO_2$. The peroxidised podzol C gave exactly the same clay yield in $NH_3$ and $NH_3 + SiO_2$, 13.3%. It was at first thought the similarity of these results was due to the fact that the soils were siliceous already. Later it was realised that only 5 ml $H_2O_2$ had been added in each case and that further peroxidation would have led to flocculation in ammonia and dispersion on silica addition as was found for Dunlop $B_{2g}$.

Dunlop $B_{2g}$ was peroxidised with a total of 20 ml

$H_2O_2$. Vigorous flocculation persisted until 5 ml $SiO_2$ had been added. The suspension then appeared dispersed, but some flocs were noted after two days. A total addition of 7 ml produced a stable dispersion yielding 27.3% clay (Table 64 p.525). This was the highest obtained for this horizon by any method. There was no sign of flocculation in the ensuing 5 months. The clay sedimented to a compact coagulum.

The unperoxidised Tirau B required 15 ml $SiO_2$ to stabilise the suspension, again reflecting the influence of the amount of allophane present in contradistinction to an aluminous nature. Table 68 p.529 shows that the clay yield was 25.7%, or the second highest obtained by any method.

10 ml $H_2O_2$ was used for peroxidised Tirau B. It appeared to disperse after addition of 17 ml $SiO_2$ and formed a compacted sediment, yet the yield of clay remained small. Cumulative additions of 17, 27 and 33 ml $SiO_2$ gave 8, 10 and 11.9% clay respectively. The observations suggest there was a subsidence of very small flocs. The experiment was abandoned.

It was concluded that silica dispersions could assist in the mechanical analysis of soils containing allophane. They suffered from the same defect as the zirconium nitrate dispersions in that the clay properties would be changed by adsorption of the dispersing agent. Moreover, there was no possibility of restoring them by dialysis. On the other hand, valuable knowledge might be obtained from a comparative study of the silicated and original clay. These might include a comparison of their cation exchange properties, and of their uptake of phosphate, pectin, organic matter extracts and leaf leachates; also of their infra red spectra and DTA properties.

## 6. Silica-alumina ratios in the allophane of Dunlop and Tirau B soils.

It has been postulated that the tendency of the peroxidised Dunlop and Amlaird soils to flocculate and their relative response to sodium fluoride were determined by (a) the amount of allophane in the soil and (b) its relatively aluminous character. There was no evidence yet however, which could separate these two effects. The subdued response of Amlaird $B_{2g}$ was almost certainly due to low total allophane; and the behaviour of Tirau B, known to be mainly allophane in the clay fraction, suggested that this was siliceous. But among the Dunlop soils themselves there was no information upon which one could build a case that the high pH flocculation mechanism was connected with aluminous character, rather than with allophane content, although it could be reasoned that soils low in organic matter would be more siliceous than soils high in organic matter, where the silica was displaced. This question could be settled by extracting the allophane and determining its percent and $SiO_2$:$Al_2O_3$ ratio for each horizon.

The relative merits of procedures for the selective extraction of allophane were discussed in Chapter V 2 p.214. Follett et al. (1965) compared the results obtained with cold 5% $Na_2CO_3$, cold followed by hot 5% $Na_2CO_3$ and a 2½ minute boiling procedure in 0.5 N NaOH recommended by Hashimoto and Jackson (1960) for allophane extraction. Follett et al. concluded that soil clays were a continuum ranging from completely disordered to well crystallised material, and the range extracted depended on the reagent employed. The writer proposed to begin by using their mildest reagent, cold 5% $Na_2CO_3$. Extractions might be on the low side and silica:alumina ratios would also be low, if results followed a similar pattern observed for their standard clay and Baidland and Dunwan extractions (Table 35 p.217). It was hoped however, the findings would reflect the relative state of each horizon correctly.

## Exp. 72 Alumino-silicate extraction with cold 5% $Na_2CO_3$.

Two attempts at extraction were made. In extraction I 50 ml dispersed clays were pipetted as for mechanical analysis to recover $< 2\mu$ esd fractions from the Dunlop soils. 10 ml quantities were taken at the same time to obtain the oven dry weights. These varied between 76 and 120 mg/50 ml. The suspensions were peroxidised in 10 ml $H_2O_2$ on a water bath, then made to 100 ml and transferred to plastic centriguge bottles where 5 g $Na_2CO_3$ was added to each. They were shaken on a reciprocating shaker for 16 hours, centrifuged and the supernatants stored in plastic bottles. A second extraction was done with a further 100 ml 5% $Na_2CO_3$, and the two extracts were combined, made to 250 ml and stored in plastic bottles. Finally, a third extraction was done with 90 ml 5% $Na_2CO_3$, the supernatants made to 100 ml and stored in plastic bottles.

In extraction II, 50 ml aliquots of dispersed Dunlop clay were pipetted to recover the $< 1.4\mu$esd fraction. The suspensions were peroxidised in 5 ml $H_2O_2$, evaporated, the air dry samples weighed and their oven dry weights calculated. These varied between 49 and 103 mg. The dry clays were shaken with 100 ml 5% $Na_2CO_3$ for 16 hours and the procedure was continued as described for extraction I. These extractions were both exploratory and further extractions under chosen and well-defined conditions have not yet been made. Samples were taken from dispersions that were available and their pretreatments varied as shown in Table 74 p.580. In the main, they had been sonic dispersed in $NH_3$, but $C_g$ (I) and $B_{3g}$ ( II) had been vibrated in water and $A_1$ (II) had been dispersed with a cation exchange resin and then shaken in ammonia. Tirau B clays were also extracted, samples being obtained from suspensions which had been dispersed by resin and shaken in ammonia. In Tirau B (I) 50 mg of a peroxidised oven dry sample was used and the heating may have affected its behaviour in extraction. In Tirau B (II) the same procedure was followed as for the rest of the second extraction except that 20 ml was pipetted, yielding 51 mg air dry clay. Since the resin, as described later in Section 7 p.587, itself extracts considerable silica and alumina, these amounts have been calculated from the values in Table 76 p.596 and added to the $Na_2CO_3$ extractions.

A mistake was made in neglecting to wash the peroxidised suspensions with hot water in order to remove oxalate as ammonium oxalate. This was recommended by Farmer and Mitchell (1963) as a routine pretreatment to prevent subsequent oxalate interference. Oxalate may thus have interfered with the analyses, particularly of alumina, although it is possible the presence of ammonia minimised the effect. One sample however, received this treatment. The $B_{2g}$ (II) peroxidised suspension was centrifuged and the residue washed three times in hot water.

The extracts were analysed using methods described in Section 2 p.541.

## Results and discussion.

Table 74 shows the results for extractions I and II. Examining I, it is seen that the percent total extraction of the alumino-silicate material follows the order:

Tirau B $> B_{2g} > A_1 > B_{3gx} > C_g$

and the $SiO_2 : Al_2O_3$ ratios follow the order:-

Tirau B $> C_g > B_{3gx} > A_1 > B_{2g}$

Thus among the Dunlop soils, $B_{2g}$ released the most allophane and its composition was the most aluminous, $C_g$ released the smallest amount of allophane and its composition was the most siliceous. Tirau B was more siliceous than any of the Dunlop soils. These results are in broad agreement with the spectrum of behaviour noted in sodium fluoride dissolution and flocculation tests (p.431). All the soils had very low silica: alumina ratios (1.01 - 0.30) and this may be attributed to the method of extraction, since they agree with the low values found by Follett et al. (1965) for cold 5% $Na_2CO_3$ extractions in contradistinction to the higher values obtained for hot $Na_2CO_3$ and NaOH extractions (Table 35 p.217). The efficiency of extraction I can be gauged by comparing the Tirau B results with those of Follett et al. Converting their percent total silica and alumina figures to percent total clay, one finds they extracted 12.64% $SiO_2$ and 21.52% $Al_2O_3$, whereas extraction I only yielded 5.51 and 8.68%. The molecular ratios are similar, 1.01 for extraction I and 1.00 for Follett et al., but the reason for the inefficiency of extraction I is not understood unless their original Tirau clay was much dissimilar.

Table 74 % Silica and alumina extracted by cold 5% $Na_2CO_3$ from Dunlop and Tirau B clays.

| Soil | dispersion pretreatment | esd μ | state of clay | % $SiO_2$ | % $Al_2O_3$ | %total | $SiO_2$:$Al_2O_3$ (molecular) |
|---|---|---|---|---|---|---|---|
| | | | I | | | | |
| Dunlop A1 | $H_2O_2$ ‖ $NH_3$ | < 2 | suspension | 0.86 | 3.31 | 4.19 | 0.44 |
| B2g | $NH_3$ | < 2 | suspension | 0.86 | 4.87 | 5.73 | 0.30 |
| B3gx | $NH_3$ | < 2 | suspension | 1.02 | 2.97 | 3.99 | 0.58 |
| Cg | $H_2O$ | < 2 | suspension | 0.62 | 1.25 | 1.87 | 0.84 |
| Tirau B | Resin ‖ $NH_3$ | < 1.4 | oven dry | 5.51 | 8.68 | 14.19 | 1.01 |
| | | | II | | | | |
| Dunlop A1 | Resin ‖ $NH_3$ | < 1.4 | dry | 3.74 | 4.69 | 8.43 | 1.35 |
| B2g | $NH_3$ | < 1.4 | dry | 1.57 | 5.65 | 7.22 | 0.47 |
| B3gx | $H_2O$ | < 1.4 | dry | 2.16 | 2.49 | 4.65 | 1.47 |
| Cg | $NH_3$ | < 1.4 | dry | 1.50 | 1.94 | 3.44 | 1.31 |
| Tirau B | $H_2O_2$ ‖ resin ‖ $NH_3$ | < 1.4 | dry | 7.42 | 6.94 | 14.36 | 1.81 |

When extraction II is examined, the results are very different. Percent total extraction follows the order:

Tirau B $> A_1 > B_{2g} > B_{3gx} > C_g$,

and $SiO_2 : Al_2O_3$ ratios follow the order:

Tirau B $> B_{3gx} > A_1 > C_g > B_{2g}$.

Thus, while $C_g$ still released the smallest amount of allophane and $B_{2g}$ released the most aluminous material, the other relationships among the Dunlop soils were different. Moreover all the silica : alumina ratios were increased due to large or very large increases in dissolved silica.

In seeking the cause for these spectacular differences one considers in turn how far they may be due to (a) analytical error (b) dispersion pretreatment (c) sample size (d) sample weight (e) sample treatment.

(a) Analytical error always remains a possibility, particularly when results depend on single determinations .

(b) Dispersion of $B_{3g}$ (II) in water almost certainly accounts for the anomalously low alumina extracted and the high $SiO_2 : AlO_3$ ratio, if one postulates oxalate interference. Pretreatments also varied for $A_1$ (II) which was not a peroxidised dispersion, and the 5 ml $H_2O_2$ used to peroxidise the 50 ml sample may have been

insufficient. $A_1$ (II)also differed in being predispersed by cation exchange resin, but the amounts of silica and alumina removed by the resin have been included in the $Na_2CO_3$ extraction figures. Corrections due to resin uptake for $A_1$ (II) and Tirau B are shown in Table 75 p.583
(c) On sample size, one would expect the total percent extraction to be slightly more for the $< 1.4\,\mu$ fraction than the $< 2\,\mu$ fraction. Differences between them in terms of clay percent of soil are of the order of 0.5 to 5.1% as shown in Table 75 and do not strike one as responsible for the difference in silica extracted.
(d) Sample weights are given in Table 75 . None of them exceeds the 100 mg/80 ml solution used by Follett et al. and recommended as the safe limit before precipitation problems occur. The major difference between extractions I and II appears to be in (e) sample preparation. The writer puts the greatest weight on this, bearing in mind an earlier discovery, and suggests the following explanation.

It will be recalled from Chapter X 4 p.439 that the rise in pH when sodium fluoride was added to dry soil was considerably greater than when it was added to a vibrated suspension. For instance the pH was 11.4 and 10.5 respectively when Dunlop $B_{2g}$ was treated with NaF

Table 75 Additional information on $Na_2CO_3$ extrations.

| Soil | % clay in dispersion sampled | | OD wt. clay sample (mg/100 ml) | |
|---|---|---|---|---|
| | $<2\mu$ | $<1.4\mu$ | I | II |
| Dunlop $A_1$ | 39.4 | 34.3 | 76.0 | 49.9 |
| $B_{2g}$ | 29.5 | 27.3 | 104.5 | 90.3 |
| $B_{3gx}$ | 24.7 | 22.0 | 117.5 | 83.1 |
| $C_g$ | 25.5 | 25.0 | 121.0 | 103.8 |
| Tirau B | - | 25.0 | 50.0 | 48.1 |

| Soil | Correction due to resin uptake (added to $Na_2CO_3$ figures). | |
|---|---|---|
| | $SiO_2$% | $Al_2O_3$% |
| Resin $A_1$ | 0.21 | 1.62 |
| Tirau B (I) | 0.28 | 0.73 |
| Tirau B (II) | 0.40 | 0.65 |

for 30 minutes. This was attributed to the way in which additional energy provided by the heat of wetting was able to break bonds resistant in the 'cold' suspension. The same phenomenon would be expected to produce differences between extraction I where $Na_2CO_3$ was added to a clay suspension, and extraction II where water was added to dry clay and solid $Na_2CO_3$. (It would have been better to have added liquid 5% $Na_2CO_3$). One could postulate that the heat of wetting caused both silica and alumina to be relaeased in greater quantity. The results however, show the interesting fact that far higher amounts of silica than alumina were released ie. it was the silica bonds which were the most susceptible to the input of energy. The figures of Follett et al. (Table 35 p.217) bear out this statement. At higher temperatures, greater amounts of silica were released and the consistently low $SiO_2 : Al_2O_3$ values obtained for the cold extractions were raised. Tirau B, for example yielded a $SiO_2 : Al_2O_3$ ratio of 1.12, 1.44 and 1.75 from the cold $Na_2CO_3$, cold + hot $Na_2CO_3$ and 0.5 N NaOH $2\frac{1}{2}$ minute-boil treatments respectively (the results are for % original oxide). A comparison cannot be made unfortunately, for extractions I and II, because although both clays were in the dry state Tirau B (I) had been oven-dried and its low $SiO_2 : Al_2O_3$ ratio may be due to that pretreatment. However the 1.81 value for extraction II is of interest, in that it approaches the 2.2 value reported for the same profile and horizon in "Soils of New Zealand" (1968 3 p.80), and also the 1.75 value obtained by Follett et al. for their NaOH extraction.

Table 35 p.217 shows the low $SiO_2 : Al_2O_3$ values obtained by Follett et al. for their cold $Na_2CO_3$ extraction, but it is not crystal clear from the reported procedure whether they added their 5% $Na_2CO_3$ solution to dry or wet soil so that their figures cannot be used to test the writer's hypothesis. Experiments are planned to investigate it under conditions which eliminate the other sources of variation. Meanwhile one may only conclude speculatively that if the heat of wetting indeed assists a cold 5% $Na_2CO_3$ extraction in the manner suggested, then as a method for the selective removal of allophane it could prove superior to hot extractions on grounds both of mildness and efficiency.

Returning now to the investigation of the relative amounts and aluminousness of the allophane in Dunlop soils, the results from extraction I confirmed the original prediction, but those from extraction II confused some of the argument. Further evidence however is available from experiments described in later pages. These include analyses of the resins used to disperse the soils (Section 8) and analyses of the citric-soluble extracts (Chapter XV 4). Table 76 p.596 shows that the alumina taken up from the soils by the resins follows the order:-

Dunlop $B_{2g} > A_1 > C_g >$ Tirau B $\gg$ Amlaird $B_{2g}$,

while the silica uptake follows the order:

Tirau B > Dunlop $A_1 > B_{2g} \gg$ Amlaird $B_{2g}$.

Table 98 p.733 shows the amounts of alumina extracted from the soil by citric acid follows the order:

Dunlop $B_{2g} > B_{3gx} > C_g > A_1 >$ Amlaird $B_{2g}$.

while silica : alumina ratios followed the order:

Amlaird $B_{2g} >$ Dunlop $C_g > B_{3gx} > B_{2g} > A_1$.

Thus taken together, the evidence confirms that the gradation of behaviour exhibited by the soils in the flocculation and sodium fluoride tests was determined both by their relative amounts of allophane and its aluminous character. For both properties the order was:

Dunlop $B_{2g} > B_{3gx} > C_g >$ Amlaird $B_{2g}$.

The position of Dunlop $A_1$ was indeterminate. Tirau B was a siliceous allophane.

## 7. Dispersion of soils with Na-cation exchange resin.

It will be remembered that Edwards and Bremner (1965, 1967) reported that cation exchange resins in the sodium form proved excellent dispersing agents for soils. Their findings were described in Chapter IV A p.125. They suggested that di- and trivalent cations which linked clay and organic matter in micro-aggregate complexes were taken up by the resin in exchange for sodium ions, but gave no experimental evidence to support their statement. The resin method had been tried by the writer. (Chapter XI p.483). Resin in the $H^+$ form had given successful dispersion, and in the $Na^+$ form it had failed. The success of the $H^+$ resin experiment however, was due in this case to the effective disruption of the aggregates by peroxide treatment prior to rotary shaking, and the failure of the $Na^+$ resin was due to the inefficiency of rotary shaking in disrupting aggregates. Hence it was decided to experiment with the resin method again, using the reciprocating shaker.

Method: Amberlite IRC - 50 cation exchange resin in the sodium form was sieved through a 52 mesh sieve and the coarse fraction used for the experiments. Its cation exchange capacity was determined from the sodium in the eluate after leaching 5 ml samples of resin with

HCl, and was found to vary between 0.3 and 0.45 me/ml. This was about one tenth of the 3.5 ml advertised for the unsieved resin and the difference was attributed to the discarding of the fine material.

5 to 10 g samples of soil were suspended in ~60 ml water in 250 ml plastic jars and 10 to 25 ml of the coarse resin (pH 5.45) was added. The available exchangeable $Na^+$ for 5 to 10 g soil was thus 30 to 60 me/100 g respectively, assuming a CEC of 0.3 me/ml. The samples were shaken for 16 hours at ambient temperature on a reciprocating shaker.

The soils were sieved, and a clean separation was made by decanting resin beads, silt and clay with the help of a jet of water. The resin beads were washed on the 100 mesh sieve before setting them aside for analysis and the sands were then virtually free of resin. If the soils had any tendency to flocculate on the sieve, the silt and clay was decanted straight into the cylinder, and the resin held back and removed separately.

### Exp. 73 Mechanical analysis of soils after dispersion by Na - cation exchange resins.

Dispersion by cation exchange resin was highly successful. Considering first the normal, or non-flocculating soils, Dunlop $C_g$ (1971) yielded 29.9% clay

(Table 66 p.527) and Amlaird $B_{2g}$ 43.6% (Table 67 p.528) both of which are the highest values obtained by any routine method. For some reason, the Amlaird $B_{2g}$ clay increased to 45.5% after standing two months, just as it had done after NaF ‖ Sonic|$H_2O$ treatment. Dunlop $B_{2g}$ yielded 24.5% clay, the fourth highest value (Table 64 p.525). Disruption of the coarse sand aggregates was not quite so efficient as by the sonic method. Dunlop $A_1$ (5 g soil shaken with 25 ml resin) yielded 27.1% clay, but the dispersion was incomplete, since 32.1% was obtained after the suspension had been hand shaken in ammonia (Table 62 p.523). It was not established whether the 120 me/100 g of available cation exchange capacity was simply insufficient, or whether organic rich soils should be peptised in ammonia following resin treatment.

The triumph of the resin method was its success in dispersing flocculating soils ie. the Tirau B and Dunlop peroxidised soils. Tirau B resin/water (pH 5.5 for 5 g/500 ml) yielded 20.4% clay (Table 68 p.259). It was seen to flocculate slightly. When it was handshaken a week later in ammonia (pH 10.5) 24.9% clay was obtained, and flocculation was not observed for several weeks. Peroxidised Tirau B (pH 6.35 for 5 g/500 ml) flocculated on sieving, but dispersed when hand shaken in ammonia (pH 9.7) to give 26.8% clay, the highest yield obtained by any method. Addition of silica sol (5 ml) at a later date brought no further improvement. The suspension was also stable for several weeks, but gradually flocculated.

Peroxidised Dunlop $B_{2g}$ yielded 22.2% clay (pH 6.0). It appeared to be very stable, but after two days a spectacular subsidence set in. The flocs were too small to be visible but the clay sank slowly, over the period of about a week, like a thick curd, and sharply demarced from the clear supernatant (plate 3 ). A further sample was peroxidised and shaken with resin and flocs were seen to develop after a few hours standing in the cylinder (pH 4.42). It was hand shaken in ammonia (pH 9.75) and yielded 25% clay, comparable to the unperoxidised resin dispersed sample (24.4%). This suspension remained stable. After three months it sedimented to form zones of turbidity, although there were some very slight flocs at the base.

Thus the peroxidised Dunlop $B_{2g}$ soil and the Tirau B soil flocculated only slowly in mildly acid conditions after resin dispersion. Peroxidised Tirau B flocculated more readily but this may have been due to its pH being closer to the isoelectric point. The flocs were dispersed by shaking them in ammonia solution but the stability was not permenant for the Tirau soils.

## Plate 3

## Stable and flocculated suspensions of Dunlop soils.

1 Stable dispersion: Dunlop $C_g | H_2O_2 \| \text{sonic} | NH_3$ (3 days old)

2 Stable dispersion: Dunlop $B_{2g} | \text{sonic}$ (3 years old)

3 Flocs, immediate subsidence: Dunlop $B_{2g} | H_2O_2 \| \text{sonic} | H_2O$

4 Subsidence of invisible flocs: Dunlop $B_{2g} | H_2O_2 \| \text{Na-resin}$ (5 days old)

The next step was to ignite the resins and analyse them in order to see whether in fact sesquioxides had been taken up, as proposed by Edwards and Bremner (1965). Ignition was necessary in view of statements that the hydrolysis products of iron and aluminium could not be removed from resin even with the aid of complexing agents (Hsu and Rich 1960).

### 8. Exp. 74 Chemical analysis of the cation exchange resins.

#### Method.

The resin beads were contaminated with silt sized particles and their removal posed a problem. The bulk of them could be separated by decanting repeatedly in water and by spreading the beads on a watch glass to pick out the remaining grains. An efficient method appeared to be to float the beads off in $CHCl_3$, dry and rewet them in water, and again to pick out any remaining grains; but at the time of writing it is suspected that this leads to a worse result, because fine silt seemed to adhere to the particles with the $CHCl_3$ treatment. The problem has not yet been solved.

The volume of the resin in water was measured and the dried beads were weighed in a vitreosil crucible and ignited in a muffle furnace at 800°C. over a period of two days. The residue was dissolved in hot 2N HCl until the disappearance of a haze which was probably alumina, while at the same time the treatment was kept as short as possible in order not to attack the silt particles, now made visible and readily identified under the microscope as hematite, quartz and felspar, together with a few black grains. The solution was filtered and made to 100 ml in acid solution of 1 to 2N HCl.

Three controls were done. Control (a) was 5 ml fresh resin which was similarly ignited. Control (b) was 10 ml resin beads shaken up with freshly precipitated $Fe(OH)_3$ (pH 3.9), then washed copiously on a 52 mesh sieve, dried and ignited. This was to discover the ease with which the resin could take up amorphous sesquioxide. Control (c) was an aliquot of resin beads used for the

Dunlop $B_{2g}$ dispersion. It was shaken in the complexing solutions of buffered bipyridyl and oxine/chloroform. Controls (b) and (c) were designed to allay some of the anxiety that results were spurious and due to silt dissolution in HCl.

Results.

The ignited resins left a substantial papery residue, except for control (a) of fresh resin which was a mere scraping of white ash. The $Fe(OH)_3$ treated resin was tinged a deep red-brown and the Dunlop $S_1$ resin was a dirty fawn colour. The other resins were white or pale grey. Despite the care exercised in the separation earlier, there were always a few grains of mineral adhering to the residue, and which required filtering.

The results of the analyses are given in Tables 76 and 77. Control (a) of 'resin-only' contained no Fe, Al or Si and trace amounts of Ca, Mg, Na and K. Control (b) showed that 0.325 mg $Fe_2O_3$ suspension at pH 3.88 had been taken up from a $Fe(OH)_3$ suspension by 20 ml resin. Control (c) extracted iron, as seen from the pink colour of the resin when shaken with bipyridyl. This was not measured. However, the beads and bipyridyl solution were left in contact with oxine/$CHCl_3$ for a day and the aluminium extracted was found to be one tenth of that for the ignited beads. These results dismissed any fears that the figures shown in Tables 77 and 76 were altogether illusory and due to silt contamination. The results are not definitive however. Some contamination certainly occurred. For example, the Tirau B/$H_2O_2$ excess sodium and potassium figures indicate dissolution or partial dissolution of a mineral, and the high calcium in Tirau B and high calcium and magnesium in Dunlop $B_{2g}$ suggest the same. As a result, and for these cases in particular, the silica and/or alumina figures may be too high. Nevertheless, they form a basis for discussion.

## Discussion.

The first point of interest is the high alumina extracted from Dunlop $B_{2g}$ (528.9 - 761 mg $Al_2O_3$/100 g soil) together with much lower silica (17.2 - 37.7 mg). By contrast, Tirau B released only 175.8 - 182.9 mg $Al_2O_3$ but its silica figures were comparatively high (69.4 - 101.6 mg). These results agree with those found from $Na_2CO_3$ extractions, which established Dunlop $B_{2g}$ allophane as aluminous and Tirau B allophane as siliceous. Very little alumina (28.7 mg/100g) and silica (12.1 mg) were extracted from the Amlaird soil, in agreement with its low allophane content.

Table 76 Oxides and cations extracted from soil by cation exchange resin.

(mg/100 g OD soil).

| Soil | Dunlop | | | | | Amlaird | Tirau | |
|---|---|---|---|---|---|---|---|---|
| Horizon | Cg/$H_2O_2$ | $B_{2g}$/$H_2O_2$ | $B_{2g}$/$H_2O_2$ | $B_{2g}$ | $A_1$ | $B_{2g}$ | B | B/$H_2O_2$ |
| Oxide | | | | | | | | |
| $Al_2O_3$ | 238.4 | 654.8 | 528.9 | 761.0 | 487.0 | 28.7 | 182.9 | 175.8 |
| $Fe_2O_3$ | 24.6 | 49.2 | 30.8 | 23.0 | 102.0 | 12.1 | 16.5 | 16.6 |
| $SiO_2$ | n.d. | n.d. | 17.2 | 37.7 | 63.8 | 12.1 | 69.4 | 101.6 |
| cation | | | | | | | | |
| $Al^{3+}$ | 126.2 | 346.2 | 280.0 | 403 | 257.8 | 14.9 | 96.9 | 93.1 |
| $Fe^{3+}$ | 17.1 | 17.1 | 21.6 | 16.1 | 71.3 | 8.4 | 11.5 | 11.6 |
| $Si^{4+}$ | n.d. | n.d. | 8.1 | 17.6 | 29.8 | 5.7 | 32.4 | 47.5 |
| $Ca^{2+}$ | 32.6 | 57.8 | 18.1 | 134.1 | 340.0 | 51.3 | 74.2 | 16.6 |
| $Mg^{2+}$ | 6.9 | 4.1 | 4.7 | 31.6 | 30.8 | 22.3 | 18.4 | 10.2 |
| $K^+$ | 1.1 | n.d. | 1.6 | 6.0 | 4.3 | 1.4 | 3.9 | 230.0 |
| $Na^+$ (resin) | 6.2 | n.d. | 3.3 | 61.5 | 14.5 | 4.7 | 18.1 | excess |

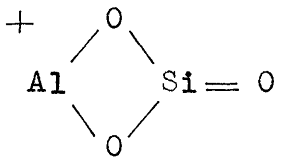
Table 77 Cations extracted from soil by cation exchange resins.

(me/100 g OD soil).

| Soil | —— Dunlop —— | | | | | Amlaird | Tirau —— | |
|---|---|---|---|---|---|---|---|---|
| Horizon | $C_g/H_2O_2$ | $B_{2g}/H_2O_2$ | $B_{2g}/H_2O_2$ | $B_{2g}$ | $A_1$ | $B_{2g}$ | B | $B/H_2O_2$ |
| Cation | | | | | | | | |
| $Al^{3+}$ | 14.02 | 38.35 | 31.10 | 44.80 | 28.60 | 1.65 | 10.76 | 10.34 |
| $Fe^{3+}$ | 0.92 | 1.85 | 1.16 | 0.87 | 3.37 | 0.46 | 0.67 | 0.62 |
| $Ca^{2+}$ | 1.63 | 2.98 | 0.91 | 6.70 | 17.00 | 2.60 | 3.70 | 0.83 |
| $Mg^{2+}$ | 0.57 | 0.35 | 0.40 | 2.63 | 2.57 | 1.84 | 1.60 | 0.86 |
| $K^+$ | 0.05 | 0.63 | 0.04 | 0.15 | 0.11 | 0.04 | 0.01 | 5.6 |
| $Na^+$ (remaining on resin) | 0.27 | n.d. | 0.14 | 2.67 | 0.63 | 0.21 | 0.80 | excess |

The amount of iron oxide removed from the Dunlop subsoils (24.6 - 49.2 mg/100g) was very small in comparison with the alumina, and bears out other observations that despite their ferruginous nature, the soils' reactivity is not due to the iron oxide. In the $A_1$ (102 mg/100g) it was more active and this one attributes to its association with or complexing by organic matter. The low iron oxide figure for Amlaird $B_{2g}$ (12.1 mg/100g) appears anomalous.

The uptake of negatively charged silica by the cation exchange resin agrees with Mattson's observations (1928b, 1933) that during the electrodialysis of a soil or mineral, silica accompanies alumina to the cathode compartment. Mattson postulated a cationic silico-alumina complex of the form:



as described in Chapter III 4 p.75. The resin extractions indicate that this or a similar entity is an important complex, and that when silica is brought into solution together with sesquioxides, as for example during dithionite, citric-soluble or other extractions, it may be largely associated with alumina in cationic form. Mattson and Hester (1933) made the important suggestion that this might have significant effects in acid soils susceptible to aluminium toxicity "if the Al ion is less toxic (less diffusible through the cell membranes?) in association with the silicate ion than in the free condition."

Turning now to the mechanism of the dispersion, the writer suggested in Chapter IV A 2 p.132 that the cation exchange resin might be acting like a mild Tamm oxalate extraction. Such extractions have been used to facilitate dispersion of allophane soils. Figures for the Tamm oxalate extraction of the Tirau B soil are available from the profile description ("Soils of New Zealand" 1968 3 p.80) and can be compared with those obtained for the resin extraction. A 13 inch depth sample yielded 4.24% Tamm Al and 1.10% Tamm Fe, or 8.0% Tamm $Al_2O_3$ and 1.57% Tamm $Fe_2O_3$, with a $Al_2O_3$:$Fe_2O_3$ molecular ratio of 7.98. The resin extractions gave an average of 0.180% resin -$Al_2O_3$ and 0.016% resin-$Fe_2O_3$, with a molecular ratio of 17.62. Hence the resin extractions represent about one fortieth of Tamm Al and one hundredth of Tamm Fe, or a very mild extraction.

The Dunlop resin extractions are fiercer by comparison. Tamm oxalate figures have not yet been obtained, but if one uses the comparable citric soluble figures given in Table 98 p.733, citric -$Al_2O_3$ is 1.58% compared with ~ 0.6% resin -$Al_2O_3$ and citric -$Fe_2O_3$ is 0.38% compared with ~ 0.03% resin $Fe_2O_3$. Thus citric -$Al_2O_3$ is only between two and three times more soluble than resin -$Al_2O_3$ and citric -$Fe_2O_3$ ten times more soluble than resin $Fe_2O_3$. This partly reflects the smaller quantities of allophane removed from Dunlop soils by the citric acid then was dissolved from Tirau B by Tamm oxalate. But it also reflects the greater 'activity' of the aluminium and iron in the Dunlop soils.

The success of the dispersion however, does not necessarily follow from the removal of the sesquioxides. Edwards and Bremner postulated this, on the grounds that linkages between clay-sesquioxide-organic matter complexes were thereby broken. But one must account for the fact that while other soil suspensions remained stable after resin dispersion, the allophane soils flocculated, either slowly, as in the Tirau B case, or in the spectacular fashion described on p.590 for Dunlop $B_{2g}$. This suggests that the flocculation mechanism was regenerated, either by rearrangement of active sites or by diffusion of cations from internal positions in the allophane gel to the adsorbed surface water layer or by hydrolysis. The success of the resin in bringing about maximum dispersion of normal soils may have been simply due to its removal of flocculating cations such as $Ca^{2+}$, $Mg^{2+}$ and exchangeable $Al^{3+}$, with substitution of $Na^+$. Its success in inhibiting the flocculation of allophane and peroxidised Dunlop soils may have been for the same reason.

## 9. Exp. 75 The effect of dialysis on Tirau B soil.

It was stated by Birrell and Fieldes ("Soils of New Zealand" 1968 2 p.40) that 'allophane will disperse partially in both weakly acid and fairly strong alkaline media provided the total electrolyte concentration is sufficiently low'. In this way they obtained 13% <2μ clay from a Tirau B sample dispersed in NaOH at pH 12 and 13% from one dispersed in HCl at pH 3.8. They did not mention how the excess electrolyte was removed, but it is assumed from their earlier work (1952) that it was by shaking in water and centrifuging off.

The writer decided to check on the effects of dialysis on the Tirau B soil in order to discover the degree to which this might disperse the soil and the range of pH over which it was made possible. In particular it was planned to recover the dialysate and find out if it contained aluminium, or any other constituent suspected of flocculating the soil in alkaline suspension.

Method.

5 g Tirau B soil was given sonic treatment for 30 mins. and silt + clay was decanted into a length of visking tubing. The samds were washed and discarded. The suspension was left to dialyse in 600 ml water for 20 hrs. (dialysate I) after which the water was changed. The suspension remained heavily flocculated. It was dialysed a further three days, and then it appeared the flocs were dispersing, for the tubing became filled with cloudy material. However, when the tubing was hung up momentarily like a stocking, although there was a persistent turbid supernatant, the rest of the soil was heavily flocculated. Dialysate II was removed and replaced by fresh water.

During some time in the next 12 days, the tubing was hung up for examination and then forgotten about, so that for several days only a small part of it was in water. It was then noticed that the amount of material seemed to have shrunk considerably, although there was no sign of sediment in the water (dialysate III). The soil was washed out of the tubing and made to 500 ml (pH 5.18). It had a strongly turbid supernatant but was flocculating slightly. Mechanical analysis yielded a silt + clay value of 52.7% and a clay value of 11.0%. The silt + clay value was as high as that achieved by other methods, but this may have been partly due to hindered settling. The clay percent was less than half that normally achieved. The suspension sedimented slowly to a coagulum which contained flocs. It was put aside for further experiments.

## Exp. 76 Analysis of the dialysates.

On standing, all three dialysates produced a white precipitate. These were at first thought to be alumina but since they failed to dissolve in HCl, it was considered they might be artefacts from the visking tubing (see Chapter XVI p.751 ). $H_2O_2$ was added to oxidise them. This was a mistake, because the $H_2O_2$ oxidised the HCl to $Cl_2$, which then had to be removed prior to analysis. The white precipitate eventually disappeared after the solutions had boiled for a long period, but was never identified. Subsequent analysis also ruled out silica, whose highest concentration was

5µg/ ml. The dialysates were filtered and made to 100 ml. The $Cl_2$ was reduced to chloride by adding hydroxylamine hydrochloride and allowing them to stand a few days. They were then analysed for calcium, magnesium, sodium, potassium and also for silica, alumina and iron oxide.

## Results and discussion.

The results are shown in Table 78 p.605. The first point to note is that the dialysate-calcium (19.2 mg/100 g) correlated closely with the resin-calcium (16.6 mg/100 g), and dialysate-magnesium (34.9 mg/100 g) was but two to three times greater. This contrasts with the potassium and sodium levels which were very much higher in the dialysate than in the resin extract. Dialysate-potassium was 194.7 mg/100 g in comparison with 18.1 mg/100 g resin-potassium (unperoxidised Tirau B, Table 76 p.596). Dialysate I sodium was not analysed, because NaOH was added to it at one stage, but from II and III total sodium could be expected similar to total potassium. The second point to note is that alumina was scarcely removed at all (21.3 mg/100 g), but silica was dialysed in a large amount (227.6 mg/100 g). This is in agreement with Mattson's finding, described in Chapter VII 2 (ii) p.299 that "a silicate gel containing a high proportion of

Table 78 <u>Concentration of sesquioxides, silica and cations found in the dialysates of Tirau B silt + clay</u>.

(mg/100 g OD soil).

| Cation or oxide | I<br>(after 20 hrs.) | II<br>(after 4 days) | III<br>(after 16 days) | Total |
|---|---|---|---|---|
| Calcium | 7.5 | 2.1 | 9.6 | 19.2 |
| magnesium | 29.8 | 2.1 | 3.0 | 34.9 |
| potassium | 151.4 | 24.5 | 18.8 | 194.7 |
| sodium | n.d. | 40.5 | 39.4 | 79.9 + I |
| $SiO_2$ | 93.7 | 53.3 | 80.6 | 227.6 |
| $Al_2O_3$ | nil | 12.8 | 8.5 | 21.3 |
| $Fe_2O_3$ | trace | trace | trace | trace |

bases and therefore also a high proportion of silica must, upon removal of the bases by leaching, lose as much of its silica as is in excess of that proportion which the sesquioxides at the prevailing pH are able to neutralise" (Mattson 1928 b).

These results suggested that it was the loss of bases which allowed the partial dispersion obtained at pH 5.18. It might also have been due to the loss of silica; not because the silica itself caused flocculation, for the stability of the silicated suspensions (Exp. 70) has already shown it inhibits it; but because loss of silica would have raised the isoelectric point of the allophane to where the suspension pH of 5.18 was further removed from the point at which it would self-flocculate by the simple electrostatic mechanism.

Exp. 77 Investigation of (a) the isoleectric pH of dialysed Tirau B and (b) whether flocculation occurs at high pH.

The dialysed Tirau B suspension was reshaken and sampled after standing $1\frac{1}{2}$ hours. Its pH was 5.62. 5 ml aliquots were pipetted into test tubes and NaOH or $NH_3$ solution of suitable concentration was added dropwise. The results are shown in Table 79. At pH 6.05

Table 79 Exp. 77 Investigation of the isoelectric pH of dialysed Tirau B and of flocculation at high pH.

| Hydroxide | pH | observation |
|---|---|---|
| control | 5.62 | turbid suspension |
| NaOH | 6.05 | turbid suspension |
| NaOH | 6.45 | flocculation 10 min. |
| NaOH | 6.55 | flocculation 10 min. |
| NaOH | 7.0 | precipitate in 3 min, flocculation in 8 min. |
| NaOH | 8.6 | slight ppt. in 5 min, slow flocculation |
| NaOH | 9.0 | clear rim 1 ml in 3 hours |
| NaOH | 10.9 | clear rim 0.5 ml in 3 hours |
| $NH_3$ | 10.05 | clear rim 0.5 ml in 3 hours |

and below the suspension was stable and positively charged. The isoelectric pH was in the region 6.45, but its upward range was indeterminate. It may have persisted to pH 8.6. At pH 9.0 and above subsidence seemed to take place, although this needs confirmation by analysis.

Thus the original undialysed suspension which was stable at pH 4.4 presumably flocculated isoelectrically at a pH a little higher than this. On removal of silica by dialysis, isoelectric flocculation did not begin until close on pH 6.4. When the pH was raised eg. to 9.0 the unknown mechanism appeared to operate. However since the clay recovery from the dialysed soil was only 11% compared to 24% for the HCl and 25 - 27% for the resin dispersions, it would appear that the unknown mechanism was also operating at pH 5.18, albeit to a modified extent. Since the main difference in the composition of the resin and the dialysate extracts lay in the large amounts of alumina taken up by the resin, one concludes that the unknown mechanism which produced the flocculation was connected with the continuing presence of active alumina, whose activity was enhanced at high pH. This is in agreement with the other results: namely the correlation of the greatest tendency to flocculate with highest mobile alumina content; and the

Table 80 Exp. 78 <u>The effect of alumina additions to Tirau B dispersions</u>.

| Suspension | Concentration in 5 ml (added as $Al(OH)_4^-$) | Observation |
|---|---|---|
| | mM $Al^{3+}$/l | |
| Tirau B/resin/$NH_3$,$SiO_2$<br>(pH 10.3, $NH_3$) | 0.038 | no reaction |
| | 0.15 | precipitate in 2½ hrs. |
| | 0.45 | turbidity 15 min, precipitate in 1½ hrs. |
| | nil | no reaction |
| Tirau B/dialysed<br>(pH 10.4, $NH_3$) | 0.038 | precipitate before 30 min. |
| | nil | no reaction |
| (pH 11.3, NaOH) | 0.038 | cloudy 30 min, precipitate 1 hr. |
| | nil | no reaction |

stability of suspensions whose active aluminium was masked either with silica or organic matter. In order to test this idea, alumina was added to the resin and dialysate dispersions.

### Exp.78 The effect of alumina addition to Tirau B dispersions.

Of the two resin dispersions, the silicated sample proved the most stable over a period of months and flocculated very little on reshaking. Hence 5 ml aliquots of this suspension were pipetted into test tubes and the pH was raised from 9.5 to 10.3 with a drop of ammonia. 5 ml aliquots of the dialysed suspension were made to pH 10.4 and 11.3 with $NH_3$ and NaOH respectively. Aluminate was prepared by making a solution of potassium aluminium sulphate alkaline with NaOH and separating the supernatant. Analysis showed its concentration was 0.91 mmole $Al^{3+}/l$. The aluminate was added to the suspensions and the results are shown in Table 80.

Addition of $Al(OH)_4^-$ thus initiated a slow precipitation. 0.15 mmole $Al^{3+}/l$ was required for the resin-dispersed silicated sample and 0.038 mmole $Al^{3+}/l$ for the dialysed sample. It seemed to indicate that aluminium ion indeed promoted flocculation at high pH. This conclusion must remain tentative however, because the solution also contained potassium ions and the possibility of their playing a role cannot be ruled out.

## 10. Coagulation by alumina : discussion of a new hypothesis.

It was now required to find a hypothesis which fitted the following observations:

(a) The aluminous allophanes were most effectively flocculated. Flocculating properties were removed by:

(b) masking the active aluminium with organic matter or silica;

(c) extracting the active aluminium with a cation exchange resin, or a deferration process such as was used by Birrell and Fieldes (1952).

(d) Flocculation returned to stabilised suspensions on addition of alumina.

(e) There was an increase in the vigour of the flocculation between pH 7.5 and 10.0.

(f) Boiling in NaOH and centrifuging off achieved dispersion. Flocculation reappeared at pH 9.6 on adding HCl (Birrell and Fieldes 1952).

(g) Dispersion for an allophane soil ie. with minimum crystalline clay present, was achieved in HCl at pH 4.3.

(h) Dispersion was achieved for a soil with allophane on addition of charge-reversing hydrolysed metal ions.

At this stage it appeared that a hypothesis which best fitted these observations could be derived from the work of Matijević et al. (1961a). It will be recalled from Chapter III 5 (iv) p.106 that these authors found the "critical coagulation" concentrations of aluminium for halide sols as a function of pH. This allowed them to calculate the charge on the polymer using the Schultze-Hardy rule, and from this and potentiometric evidence they were able to determine the polymer composition. Fig. 19 p.107 shows that the critical coagulation concentration rose steeply above pH 7 and levelled off in the region pH 9 to 10 at a concentration 0.3 mmoles/l. This suggested that a divalent ion was formed by the hydrolysis step:

$$Al_8(OH)_{20}{}^{4+} + 2OH^- \rightleftharpoons Al_8(OH)_{22}{}^{2+},$$

Higher pH regions could not be examined with the silver halide sols, but Matijević et al. assumed that additional $OH^-$ uptake would give the neutral complex, $Al(OH)_{24}$.

Thus it was conceivable that the flocculation of allophane at high pH was due to the coagulating effect of the active alumina on the clay surface, which remained as positively charged cations in suspensions as alkaline as pH 10 or more. The stability of allophane soil dispersions at pH 4.3 was explained by the fact that the alumina could not coagulate a positive sol (although as mentioned earlier, it possibly played a role in reversing the charge on small amounts of kaolinite present). The reported stability of allophane dispersions at pH 12, with electrolyte removed ("Soils of New Zealand" 1968 2 p.40), could be due to the formation of the neutral polymer, and the reported reappearance of flocculation at pH 9.6 (Birrell and Fieldes 1952) to the re-formation of the divalent polymer.

There were still some points however to be cleared up:

(a) Critical coagulation concentrations could not of course, be compared in the halide and clay sols. Nevertheless if the hypothesis was correct, the alumina concentration must either increase after pH 7.0 to allow the divalent ion to form, or it must retain a lower valency despite the increased pH.

(b) Birrell and Fieldes (1952) reported that addition of HCl to the electrolyte-free dispersion at pH 12 initiated flocculation at pH 9.6 and this persisted at least till pH 2.5 when dispersion was only achieved after centrifuging off and shaking in dilute HCl.

(c) What was the role of the free electrolyte?

(d) What was the role of the hydroxyl ion?

Mattson's studies on the alumino-silicates and his comments were always in mind. Question (c) was prompted by his observation that "The presence of divalent cations also extends the zone of flocculation on the negative side of the isoelectric point. No matter how strongly negative the sol may be, it will flocculate at once if sufficient $Ca(OH)_2$ is added." (Mattson 1930 a). This was connected with the presence of the $OH^-$ ion, and question (d) was promted by his statement on a general rule that: "The more strongly adsorbed the anion, the higher the charge at which an electronegative sol is precipitated by a cation. For an explanation of this behaviour, the author will refer here merely to his theory of ionic linkage." (Mattson 1928 b).

The explanation was not immediately available because it was given in a long paper in German (Mattson 1922) entitled "The relationship between flocculation, adsorption and particle charge, with special reference to hydroxyl ions." The writer was certain that this contained important evidence for the understanding of allophane. While a translation was being prepared, a few studies of the behaviour of electrolytes and hydroxyl ion were made. These included (a) the coagulation of sols by $CaCl_2$; (b) the flocculation of sols by starch; (c) the effect of raising the pH of the peroxidised suspensions to 11 and 12.

## 11. Flocculation experiments with electrolytes.

It was decided to compare the effects of coagulation and flocculation. At this time, the writer understood, wrongly, that there was a difference between the coagulation of a sol by an electrolyte and the flocculation of a sol by a polyelectrolyte which could be detected visually. The belief derived from the distinction drawn by La Mer (1964, 1967) who contended that:

> "If colloid chemistry is to maintain its position as a science, we can no longer treat coagulation and flocculation indiscriminately as synonymous or interchangeable terms. Instead, they should be distinguished in terms of the active agent and its molecular characteristics, microscopic examination, final sediment volume, and particularly dependence of rate of filtration upon concentration of additive."

From La Mer's descriptions (1967) the writer assumed that coagulated sols sedimented as aggregates, formed compact final volumes and resisted filtration, while flocculated sols showed hindered settling, subsided, formed voluminous sediments and were easily filtrable. La Mer and indeed most of the contributors to the recent literature identified the coagulation process as governed by the laws of the DLVO (Double Layer Verwey-Overbeek) theory, and as bringing about direct adhesion between particles; and they identified the flocculation process as governed by a bridging mechanism. There were cases in which both processes took part (Somasundaran et al. 1966). Chapter III 2; 7

and IV B 3 discussed these approaches.

Exp. 79 Flocculation of soils with $CaCl_2$.

The original object of this experiment was to provide a control for an early experiment (Chapter XI 4 p.476) in which the rate of filtration of peroxidised Dunlop $B_{2g}$ flocs was measured and compared with the rates found by La Mer and Smellie (1956 b) for starch flocculated slimes. The Dunlop flocs were assumed to be formed by the interaction of positive allophane with negative crystalline clay. The filtration time of Exp. 24 was found to be of the same order as that for starch flocculated slimes, and a control experiment, in which unperoxidised Dunlop $B_{2g}$ was precipitated by excess electrolyte and filtered, remained to be done for the sake of completeness.

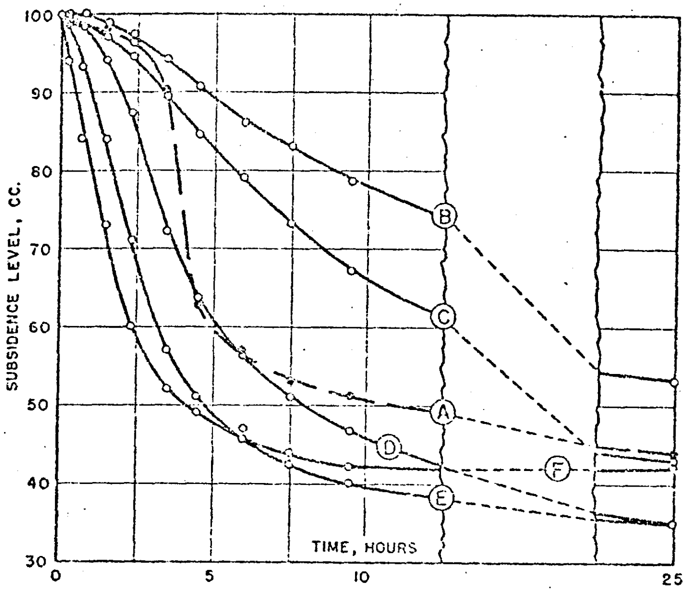
790 ml Dunlop $B_{2g}$ dispersion was reshaken in the cylinder and a few ml saturated $CaCl_2$ solution were added. The dispersion flocculated immediately with hindered settling, counter streaming and subsidence, ie. with all the characteristics noted in the flocculation of peroxidised soils. It subsided to a volume of 380 ml in 40 minutes and sank through time to a volume of 150 ml. At first it was thought the massive flocculation

might in some way be connected with the allophane content. Hence, saturated $CaCl_2$ solution was added to a Keuper marl dispersion and also to an Amlaird $B_{2g}$ which had been previously treated with sodium fluoride. Both soils responded in the same manner, forming bulky long-lived flocs and clear supernatants. Finally, in order to see if a low $Ca^{2+}$ concentration had the same effect, a solution containing 118 mg $CaCl_2$ was added to 400 ml of an untreated Amlaird $B_{2g}$ vibrated sol, so that the suspension contained a slight excess of the 2 mmole/l upper threshold limit for a divalent ion. Flocculation with hindered settling began at once and the suspension subsided to 200 ml of flocs.

On close examination it was found that La Mer's sweeping distinctions (1967) were not borne out by the evidence given in the original papers on which his conclusions were based. The Hopewell slime examined by Smellie and La Mer (1956) produced as voluminous flocs when precipitated by 10 ml saturated $Ca(OH)_2$ as when precipitated by 200 ml Flocgel in the presence of 10 ml $Ca(OH)_2$ and this comes out clearly in their diagram (Fig. 42 p.619). The authors merely drew attention to the fact that curve A for $Ca(OH)_2$ alone showed an initially low subsidence rate reflecting a slow

Fig. 42 Subsidence of Hopewell slime suspension on addition of various amounts of Flocgel and $Ca(OH)_2$ or $Ca(OH)_2$ only.

(Smellie and La Mer 1956)



Shows subsidence level (in terms of the graduations on the cylinder) vs. the time in hours after adding reagents. Hopewell slime (I) 5% solids. Each sample contains 10 ml. of added saturated $Ca(OH)_2$ per 100 ml. of slime and various amounts of added Flocgel to give the following final concentrations in p.p.m. *A*—0 p.p.m. *B*—10 p.p.m. *C*—20 p.p.m. *D*—40 p.p.m. *E*—70 p.p.m. *F*—200 p.p.m.

flocculation process, and claimed that it was a typical curve for behaviour that led to the formation of a compact floc. All the experiments (Exp.79 ) above however, showed much swifter flocculation than that given by any of the curves in Fig.42 , and though the flocs sank under their own weight to smaller volumes through time, they never became compacted. They showed indeed, all the characteristics depicted by Russell (1961) in his review of the literature on electrolyte flocculation of soils, (p.200).

### Exp. 80 Filtration of the flocs precipitated by $CaCl_2$.

La Mer laid great stress on the importance of operational methods in distinguishing flocculation from coagulation and emphasised that the most important of these was concerned with the filtration properties of the precipitates. The following experiment examined this proposition, while at the same time it provided a control to Exp.24 p.476, allowing comparison of the filtration behaviour of flocs produced by electrolyte to flocs produced by the activity of the allophane.

The clear supernatant above the Dunlop $B_{2g}$ - $CaCl_2$ precipitated flocs was poured into a leaching tube and the sediment was transferred to a large filter funnel fitted with 27 cm/Whatman No. 1 filter paper. The supernatant was leached through the flocs in the same way as in Exp. 24 p.476, with the rate of addition controlled to keep pace with the rate of filtration. The first 650 ml filtrate took 4½ hours to be collected. The last 100 ml or so filtered much more slowly so that the total time for collection was 7½ hours.

## Discussion.

The bulk of the liquid therefore filtered at a rate 10 ml/4 minutes and this was similar to that found for the peroxidised Dunlop in Exp. 24. La Mer and Smellie (1956 b) gave results as one-off collections in ml/time in minutes, rather than as averages. They did not say whether filtration rates slowed down with time. However, a broad comparison can be attempted. The authors found that the filtration rate varied with the starch and $Ca(OH)_2$ concentration; for a given $Ca(OH)_2$ addition, the rate increased with increasing Flocgel (10 - 500 ppm) content, and for a given Flocgel content, it increased with increasing $Ca(OH)_2$ concentration. Examples from their data are shown in Table 81. The slime filtered slightly less rapidly when flocculated with 10 ml $Ca(OH)_2$ than with 10 ml $Ca(OH)_2$ + 10 ppm Flocgel, but slightly more rapidly than when flocculated

Table 81 <u>Times required to collect 10 ml filtrate from 100 ml flocculated Hopewell slime (5% solids)</u>.

(Compiled from La Mer and Smellie 1956 b).

| Flocgel ppm. | $Ca(OH)_2$ ml saturated | $Ca(OH)_2$ mmole/l (estimated) | time to collect 10 ml filtrate minutes |
|---|---|---|---|
| 500 | 2 | 0.2 | 2 |
| 50 | 2 | 0.2 | 4.5 |
| 10 | 2 | 0.2 | 3.25 |
| 10 | 10 | 1.0 | 1.3 |
| 0 | 10 | 1.0 | 1.7 |

<u>NOTE</u>: 'Saturated $Ca(OH)_2$' estimated as ~0.01 M, but it may have been as high as 0.02 M.

with only 2 ml $Ca(OH)_2$ and as much as 500 ppm Flocgel. This was not pointed out in the text. Indeed the role of the flocculating electrolyte seems to have been underplayed in the La Mer theory, and once again one finds that a closer scrutiny of the original experiment does not support the conclusion given.

According to La Mer and Smellie (1956 b), a di- or trivalent ion was required to link the starch polymers into a three dimensional network through their phosphate groups. Slimes failed to flocculate when univalent ions such as $NH_4^+$ , $K^+$, and $Na^+$ were substituted, and the success of the ions of higher valency and of $Ag^+$ was attributed to their ability to form insoluble phosphates. Thus one might suppose that only rather low concentrations of cation were needed for this function, similar to the concentration of calcium ions in natural waters (La Mer 1967). The experiment as reported however, showed that the flocculating effects of some 20 cations were determined using 20 ppm Flocgel and 0.005 N concentrations of each cation: ie. with 5, 2.5 and 1.6 mmoles/l for a uni-, di-, and trivalent ion respectively, or concentrations above the threshold limits for the di- and trivalent ion and below them for the univalent ion. The experiment proved nothing except that $Ag^+$ behaved as a multivalent ion in the presence of starch; its behaviour in the absence of starch was not reported.

Saturated $Ca(OH)_2$ was normally used by the authors as a source of electrolyte in their experiments with starch, and from the data given the $Ca^{2+}$ concentration could have been 0.2 to 1.0 mmole/l. The 0.2 value is below the lower limit of 0.5 mmole/l for a divalent ion, but this does not take account of the electrolyte already present. In addition it was shown by Mattson (1922) and will be demonstrated in the next section, that calcium hydroxide has greater flocculating power than calcium salt. It would appear then, that the free electrolyte was required to play its normal role in flocculating whatever the mechanism of that role might be.

The important distinction and the one that required proof was of the superiority of polyelectrolyte flocs over electrolyte flocs in the filtration process. This was given by La Mer and Healy (1963) who explained:

"We have found that the action of neutral simple salts ($CaCl_2$, $Ca(OH)_2$) on the same suspensions yields a 'coagulum' of small sediment volume, which filters very poorly compared to the product resulting from flocculation by polyelectrolytes where the final volume is larger and exhibits a greatly enhanced rate of refiltration - as müch as 200-fold in some cases."

The major distinguishing feature therefore was in floc behaviour during refiltration, a technique described in Chapter III 7 p.115, in which a reproducible and characteristic concentration/rate curve was produced for each flocculator/substrate pair (La Mer 1967). Thus of the several criteria put forward to distinguish flocs produced by electrolytes from flocs produced by polyelectrolytes, the only criterion based on their behaviour which seems to be valid is that of the refiltration rate; one assumes that behaviour on prolonged filtration would also be important. The difference is readily explained on the basis of the greater strength and permenance of the polyelectrolyte flocs. These are not aged and altered by handling, and their pores are more stable and less liable to be clogged by local redispersion than those of the electrolyte flocs. The mechanism of their formation might well be different, but one could not state from any of La Mer's operational criteria that it was so.

In past years colloid science has become equipped with the DLVO theory. This is the starting point for all investigations and its model has proved valuable in much applied work (Mackenzie 1971). La Mer and others discovered its limitations and found that polyelectrolyte-sol interactions could not be explained in its terms; nor could it fully account for the flocculating, dispersing and adsorption behaviour of hydrolysed metal cations, which are described as showing both flocculating and coagulating behaviour (Somasundaran et al. 1966). None of these authors however questioned the 'truth' of the DLVO theory itself as it applied to simple electrolytes.

In the writer's view it would be interesting to see what would happen if one took as a starting point the Mattson model described in Chapter IV B. According to this model, flocs are formed by the interaction, possibly via an ionic linkage, of the interfaces of clay micelles, and the process is highly sensitive to the concentration of adsorbed hydroxyl ions and the presence of free electrolyte (Mattson 1922, 1929 a,b). This is indeed a type of bridging model. The interest would be in whether both electrolyte and polyelectrolyte flocculation could be explained in its terms. If that were so, then the operational distinction based on refiltration rates would arise not from differences in the mechanism of floc formation, but on differences in the maintainance of floc stability. Large semi-rigid adsorbed molecules could supply this, while flocs dependent on the disposition of electrolyte and water would break down.

## 12. Flocculation experiments with starch.

### (i) Exp. 81 Attempts to flocculate Darleith sols with potato starch.

This experiment was designed to observe the difference in behaviour between starch flocculated suspensions and electrolyte or allophane flocculated suspensions.

Reagents.

1% potato starch was prepared by adding 1 g potato starch wetted with a little cold water, to 100 ml boiling water, and boiling for a few minutes. 0.1% potato starch was similarly made with 0.1 g/100 ml water.

1.0 and 0.01M solutions $CaCl_2$ .

Saturated $Ca(OH)_2$: the precipitate was centrifuged and the supernatant was filtered. It was titrated against N10 HCl and found to be 0.02N in $OH^-$. Similarly the $Ca^{2+}$ concentration was found to be 0.01M.

A total of 20 ml 0.1% starch solution was added with stirring to 400 ml vibrated Amlaird $B_{2g}$ suspension. This was thus ~ 0.4% in clay and ~ 50 ppm in starch. Since there was no reaction, 1 ml 0.01M $CaCl_2$ was added, to give a concentration of 0.02 mmole/l. At the time it was thought, wrongly as described in the preceeding pages, that only a small amount of $Ca^{2+}$ was required, and that it should be less than the threshold concentration. After about 1 hour a few small flocs settled to the base of the vessel. Addition of 15 ml 1% starch (giving 425 ppm total) did not increase the rate of flocculation, and the bulk of the suspension remained stable over a period of weeks. A few ml 1% starch was also added to 200 ml dilute Amlaird $B_{2g}$/NaF treated sol, together with 0.1 ml 0.01M $CaCl_2$. This remained a stable sol 'indefinitely'.

The reasons for the failure were attributed either to the suspensions being too dilute or the $Ca^{2+}$ ion concentration too low. La Mer and Smellie (1956 b) used 2.5 or 5% solid suspensions, and as estimated, 0.2 to 1.0 mmole $Ca^{2+}$/1.

Test tube experiments in which 0.01M $CaCl_2$ and 0.01M $Ca(OH)_2$ was added dropwise to 5 ml aliquots of the sols showed that 0.36 mmole $Ca^{2+}$/1 was just sufficient to initiate very slow flocculation. Accordingly the thick sol was divided into two portions of ~ 200 ml. 10 ml $CaCl_2$ was added to one and 10 ml $Ca(OH)_2$ to the other (0.5 mmole/1). There was no immediate reaction. On addition of 20 ml or 1.0 mmole $Ca^{2+}$/1, flocculation set in immediately and the usual characteristics of hindered settling and subsidence were noted. The pH of the $CaCl_2$ sol was 6.05 and of the $Ca(OH)_2$ sol 10.8. The filtration properties have not yet been examined.

The experiments suggested that when starch was used as the polyelectrolyte flocculator, threshold concentrations of electrolyte were required to enable flocculation to occur. Thus the role of the starch was not to produce the flocs per se, but to create flocs that were stable to filtration procedures.

### (ii) Exp. 82 Flocculation of kaolinite with starch solution.

100 mg BDH kaolinite was sonic dispersed and made to 100 ml. 5 ml aliquots were taken, some of these being made acid or alkaline as shown. 0.01M $CaCl_2$ and 1% starch solution were added dropwise as before. The results are given in Table 82 p.631.

## Discussion.

It is seen that the BDH kaolinite was flocculated by starch at all pH values tested and did not require addition of $Ca^{2+}$. It may however have contained calcium ion, and this has not yet been investigated. It was most noticeable however, that flocculation was much more marked at low and neutral pH than at high pH, suggesting that as in the allophane case below, the presence of positive sites assisted the interaction of the starch with clay. This in turn suggests that the flocculation was promoted by adsorption of phosphate, carboxyl or other negatively charged groups on the positive sites of the clays, allowing as it were, the polymer to gain a foothold for the effective adsorption of the hydroxyl groups. One notes that "with the exception of the polyacrylamides, the polymers most

Table 82 Exp. 82 Flocculation of kaolinite with starch solution.

| |
|---|
| kaolinite + 0.05 ml starch + 0.05 ml $CaCl_2$ (pH 4.3) ⟶ massive flocs, fairly clear supernatant. No return of turbidity on shaking. |
| kaolinite + 0.05 ml $CaCl_2$ (pH 4.25) ⟶ flocculation. Return of some turbidity on shaking. |
| kaolinite + 0.05 ml starch (pH 5.95) ⟶ flocculation. |
| kaolinite + 0.05 ml starch + 0.25 ml NaOH (pH 9.55) ⟶ flocculation after half hour. |
| kaolinite + 0.05 ml starch + 0.25 ml NaOH + 0.05 ml $CaCl_2$ (pH 9.55) ⟶ flocculation after half hour. |

successful in flocculating clay dispersions acted as stabilising agents in the silica suspensions" (Kane et al. 1963), so that the absence of positive adsorption sites in silica may account for its difference in behaviour.

The hypothesis requires verification, for La Mer and his colleagues, as described in Chapter III 7 p.118 did not interpret the role of phosphate in this way. They noted that the phosphorylated starches produced flocs which were more readily filterable than the non-phosphorylated starches, and thus assigned phosphate a role in the three dimensional cross-linking of starch through bridging cations that formed insoluble phosphates. They did not however account for the fact that carboxylated starches were as successful as phosphorylated starches.

### (iii) Exp. 83 Flocculation of Tirau B clay with starch solution.

5 ml aliquots of Tirau B dialysed suspension were pipetted into test tubes. Two samples were at suspension pH 5.85 and the rest were made alkaline with 0.1N NaOH or 1:1 $NH_3$. When one drop of starch (0.05 ml) was added, the sample contained 100 ppm starch. When 1 drop of 0.01M $CaCl_2$ was added, the suspension contained 0.1 mmole $Ca^{2+}/l$. The results are given in Table 83.

Table 83 Exp. 83 <u>Flocculation of Tirau B with 100 ppm starch solution</u>.

| Suspension (5 ml) | alkali ml | pH | starch added | | 0.01M $CaCl_2$ added | | Observations |
|---|---|---|---|---|---|---|---|
| | | | ml | ppm | ml | mmole $Ca^{2+}/l$ | |
| 1 | - | 5.58 | 0.05 | 100 | - | - | slow immediate ppt. |
| 2 | - | 5.58 | 0.05 | 100 | 0.1 | 0.2 | immediate ppt. |
| 3 | 0.05 1:1$NH_3$ | 10.0 | 0.05 | 100 | 0.05 | 0.1 | immediate massive ppt. |
| 4 | 0.05 1:1$NH_3$ | 10.0 | - | - | 0.05 | 0.1 | no immediate ppt. slight wispy deposit after 1 hour. |
| 5 | 0.05 1:1$NH_3$ | 10.0 | 0.05 | 100 | - | - | immediate ppt. |
| 6 | 0.05 N10 NaOH | 10.4 | 0.05 | 100 | - | - | no reaction |
| 7 | 0.05 N10 NaOH | 10.4 | 0.05 | 100 | 0.05 | 0.1 | ppt. after 5 mins. |
| 8 | 0.05 N10 NaOH | 10.4 | 0.05 | 100 | 0.10 | 0.2 | immediate ppt. |
| 9 | 0.05 N10 NaOH | 10.4 | - | - | 0.10 | 0.2 | a cloudiness after 10 mins. |

0.05 ml N10 NaOH ≡ 1 mM $Na^+/l$ final concentration

It is seen that below the isoelectric pH of the suspension, the starch flocculated the allophane immediately, whether $Ca^{2+}$ was present or not. This could be attributed to the mutual flocculation of positive and negative soils. At pH 10.4 in the presence of NaOH, the allophane required 0.1 mmole $Ca^{2+}/l$ for precipitation. This was a smaller amount than appeared to have been required to precipitate the Amlaird $B_{2g}$/starch in Exp. 81 p. 627, where 0.36 mmole $Ca(OH)_2/l$ was required for very slow flocculation and 1 mmole $CaCl_2$ or $Ca(OH)_2/l$ for immediate flocculation. At pH 10.0 in the presence of 0.05 ml 1:1 $NH_3$, precipitation occurred with starch in the absence of $Ca^{2+}$ ions. In pure water the concentration of $NH_4^+$ in 1:1 $NH_3$ can be calculated from the $pK_b$ of ammonia (4.75) as 0.011M, and allowing for further dissociation when diluted in 5 ml the final concentration would be ~ 1.4 mmoles $NH_4$ /l. This takes no account of the extent to which the soil displaced the equilibrium and increased the dissociation. The effect may be considerable. Nevertheless one can conclude that at high pH, $NH_4^+$ in concentrations less than its Schultze-Hardy threshold value, can replace $Ca^{2+}$ in bringing about the flocculation of allophane with starch, illustrating a further difference between allophane behaviour and that of crystalline clay.

### (iv) Exp. 84 Investigation of the effects of high pH on the flocculation of an Amlaird sol by starch solution

Mattson (1922) showed that the presence of hydroxyl ion dramatically increased the ability of $Ca^{2+}$ to flocculate: 90 times more calcium as $CaCl_2$ was required to flocculate quartz, for instance, than when NaOH was added to the $CaCl_2$ solution (Chapter IV B 1 p.167). Starch polyelectrolyte itself of course contributes hydroxyl groups, but these are not charged and therefore might not hold $Ca^{2+}$ ions as ionic linkages. Moreover as has been shown, Schultze-Hardy threshold quantities of electrolyte were demanded for flocculation. La Mer and his colleagues included pH as a variable (Smellie and La Mer 1956) in the flocculation process, but they recorded no values. Since they used saturated $Ca(OH)_2$ in their experiments, the suspensions must have been alkaline, but they did not comment on this, or on whether any difference was observed when "in some series of experiments, the pH was adjusted to that of the stock slime to control this variable." (Smellie and La Mer 1956).

In the following experiment a dilute Amlaird $B_2g$ - NaF treated sol was used. It was thus hoped to remove the influence of allophane from the test; and moreover since the sol was very dilute it was thought flocculation might be inhibited to some extent, so that any difference in response to variations in treatment might be shown more clearly.

50 ml aliquots of the sol were taken and to each was added 0.5 ml 1% starch solution corresponding to 100 ppm concentration. Sols were made alkaline with ammonia, sodium hydroxide or when calcium was added as $Ca(OH)_2$. Calcium was added as 0.01M $CaCl_2$ or 0.01M $Ca(OH)_2$ in 1 ml aliquots, with swirling, and the sol was examined for flocculation, about a quarter of a minute being allowed before each further addition. The results are shown in Table 84 and the following conclusions may be drawn from them:-

(a) At high pH the amount of $Ca^{2+}$ required to flocculate the sol was indeed greatly reduced. 1.0, 1.2, 2.1, 2.4 and 4.0 mmoles $Ca^{2+}/1$ were required at pH 10.9, 11.3, 10.4, 9.9 and 7.4 respectively. The results are in complete agreement with Mattson's (1922) observations on the flocculation of quartz and base-saturated clay.

Table 84 Exp. 84 The effects of high pH on the flocculation of a dilute Amlaird $B_{2g}$ sol by 100 ppm starch solution.

| System | pH | alkali | | | 0.01 M $Ca^{2+}$ | |
|---|---|---|---|---|---|---|
| | | ion | mls | mmoles/1 | ml | mmoles/1 |
| $CaCl_2$ | 7.4 | - | - | - | 20.0 | 4.0 |
| 6N $NH_3/CaCl_2$ | 9.9 | $NH_4^+$ | 0.25 | n.d. | 12.0 | 2.4 |
| 0.1N $NaOH/CaCl_2$ | 10.4 | $Na^+$ | 0.5 | 1.0 | 10.5 | 2.1 |
| $Ca(OH)_2$ | 10.9 | $Ca^{2+}$ | 5.0 | 1.0 | 5.0 | 1.0 |
| 5N $NaOH/CaCl_2$ | 11.3 | $Na^+$ | 0.10 | 5.0 | 6.0 | 1.2 |

(b) The $Ca^{2+}$ concentrations are all high in comparison with those found for the more concentrated sol (Exp.81 p.627) where only 0.36 to 0.5 mmole $Ca^{2+}$/1 was required, or for La Mer and Smellie's much more concentrated slimes where 0.2 to 1.0 mmole was used. On Mattson's hypothesis the calcium ion plays a double part, first in suppressing the charge on the colloid in its role as free electrolyte, second in supplying linking ions between micelles, and it is in this latter capacity that the increase in threshold value could be explained, for the more dilute the sol the greater the number of linking ions required.

(c) It is also interesting to compare these results with those of allophane in Exp.83 p.632, where only 0.1 mmole $Ca^{2+}$/1 was required for a dilute suspension. Since this suspension was dialysed and therefore contained a minimum of free electrolyte, one could postulate that the precipitation reflected the degree to which the allophane surface is itself dominated by hydroxyl groups. In the next section it will be shown that the hydroxyl ion has a profound effect on the flocculation of certain soils, and the above experiment anticipates it.

(d) It is possible that in the thick suspensions of slime examined by La Mer and his colleagues, the pH variations were not important in practice. In other operations such as those of mineral separation reviewed by Mackenzie (1971), every subtle difference in property is valuable as an aid; and to bring order into this field of empirical research, systematic investigations into the behaviour of variables such as substrate, polyelectrolyte, electrolyte and pH are required.

## 13. The effects of intensive peroxidation on the flocculation of soils containing allophane, particularly in alkaline suspension.

### (i) Introduction.

It has been noted earlier (p.559) that the persistence of flocs in alkaline suspension depended (a) on the relative allophane content of the soil and (b) on the degree of peroxide pretreatment. Flocs persisting in alkali were readily detected in the case of Dunlop $B_{2g}$ and $B_{3gx}$ soils, less readily in the $C_g$ case on account of slow flocculation, and of course were prominent in unperoxidised Tirau subsoil. It remained to test whether the same result was obtained by intensive peroxidation of (a) Loch Lomond podzol C (b) Amlaird subsoils (c) soils from which allophane had been removed with NaF.

These experiments were run concurrently with experiments to determine the behaviour of the flocs at pH 11 to 12. For this the following objectives were in mind:-

(a) To investigate the advice given by Birrell and Fieldes ("Soils of New Zealand" 1968 2 p.40) that partial dispersion could be achieved at pH 12. provided the electrolyte concentration was low enough.

(b) To test the hypothesis proposed on p.611 that it was the coagulating effect of surface alumina cations which accounted for the flocculation at high pH, and that in stronger alkali the formation of a neutral polymer would allow the soils to disperse.

(c) To test an alternative hypothesis which the writer now proposed after studying an early paper by Mattson (1922) "The relationship between flocculation, adsorption and particle charge with special reference to hydroxyl ions.", whose theme was the way in which, contrary to accepted belief, hydroxyl ions in the presence of divalent ions, promoted the flocculation of quartz and of clay, provided the clay was saturated. The greater the adsorption of the $OH^-$ ions, the smaller the amount of divalent ion required for flocculation. The writer proposed that this might allow an explanation for the behaviour of allophane, firstly because allophane itself was known to contain a high proportion of hydroxyl groups; secondly because it was aluminous. On the basis of another Mattson premise "in alkaline solutions in which they are electronegative these (sesquioxide) materials adsorb quantities of bases and exceed in this respect the soil colloidal materials having the highest proportion of silica" (Mattson 1927 b, 1928 b) and. . . .

"the adsorption of the cations is due to and follows the adsorption of the $OH^-$ ions" (Mattson 1928 b), the writer's proposal for the mechanism of allophane flocculation was that the aluminous sites adsorbed large quantities of $OH^-$ ion in alkaline solution, and in the presence of divalent ions flocculation took place, perhaps by the mechanism of ionic linkage (Mattson 1922, 1929 b). For a full discussion of Mattson's observations and ideas, relevant to this section, reference should be made to Chapter IV B. p. 164.

### (ii) Exp. 85 The effect of intensive peroxidation on Loch Lomond podzol C and its flocculation in alkali.

10 g podzol C soil was peroxidised for 2 days in 50 ml water at 90°C., 60 ml 30% analar $H_2O_2$ being added progressively. The suspension was vibrated for 30 minutes and the silt + clay decanted without sieving into a litre cylinder. The pH in 910 ml was 4.5. Small flocs were seen to be forming slowly. $NH_3$ solution was added dropwise and the rise in pH and flocculation behaviour is recorded in Table 85.

Table 85 Exp. 85 The buffering and flocculation effects in peroxidised Loch Lomond Podzol C soil on addition of $NH_3$ solution.

| Cumulative ml 1:1 $NH_3$ | pH | observation |
|---|---|---|
| 0 | 4.5 | slow flocculation |
| 0.55 | 7.4 | slow flocculation |
| 1.2 | 9.0 | slow flocculation |
| 2.2 | 9.35 | massive flocculation |
| 2.9 | 9.6 | massive flocculation |
| 3.9 | 9.75 | massive flocculation |
| 4.9 | 9.8 | massive flocculation |

Discussion.

The first point to note is that at low pH the flocculation was mild, while at pH $\sim 9.3$ or at pH assumed well above the system's isoelectric pH, massive flocculation set in. It was wondered whether this was due to a 'Matijević' type of mechanism ie. coagulation by alumina divalent polymers, or a 'Mattson' type of mechanism following adsorption of some critical amount of hydroxyl ion and flocculation by the free electrolyte present. To test the relative feasabilities of these ideas, the pH was raised to 12.18 with 5 ml 5N NaOH. The massive flocculation persisted, even when an aliquot of suspension was shaken overnight.

The second point was the extensive buffering power of the soil, Most soil suspensions required only 0.6 to 2.0 ml 1:1 $NH_3$ solution to raise the pH to 10. The podzol C contained much organic matter (6.75%) and the buffering power suggests that its removal unmasked a large number of aluminous sites.

It might then be argued that it was the extensive buffering which caused a high concentration of $NH_4^+$ to be added and that this then exceeded the Schultze-Hardy threshold amount. Massive flocculation however began in the region of the addition of 2.2 ml 1:1 $NH_3$, which was about the same amount as that often added to soil suspensions for alkaline dispersion (1.5 ml were added - pH 9.9 - to the podzol dispersions analysed for silt and clay.) Calculations using $pK_b = 4.75$ show that in pure water the $NH_4^+$ concentration would have been 0.4 mmoles/l. Once again one does not know the extent to which the soil dissociated the ammonia. Since the pH was 9.35 and in pure water it would have been 10.69, its influence was considerable. Nevertheless even with complete dissociation, the $NH_4^+$ concentration would only have been $\sim$ 13 mmole/l.

In order to understand why the unperoxidised and the peroxidised soils behaved so differently, it is necessary to consider Mattson's evidence (1922, 1929 b) that flocculation was governed by the CEC, the percent base saturation of the colloid, the valence and concentration of the free electrolyte and in particular by the hydroxyl concentration. It could be argued that the effect of peroxidation was to unmask aluminous sites, so that on addition of alkali hydroxyl was adsorbed in large amounts. This effect was seen indeed in the greatly increased buffer capacity of the soil. Then on Mattson's hypothesis, the adsorbed $OH^-$ ions enabled the divalent cations present to function as ionic links bridging the micelles.

### Exp. 86 The effect of adding HCl to the flocculated alkaline podzol.

After six weeks the pH of the suspension fell to 10.82, and when shaken by hand it flocculated only slowly. Two $\sim$ 50 ml aliquots were taken; one was reserved as control and to the other N HCl or N10 HCl was added as appropriate. At pH 9.52 flocculation grew more vigorous and flocs developed like snowflakes until the pH fell to $\sim$ 6.9, when they again became more subdued. The sample was made to pH 6.4, a total of 5.9 mmole HCl having been used.

The control sample was made to pH 12.08 with NaOH. No massive flocs developed. Both samples were shaken overnight on a rotary shaker. Next day the control (pH 12.08) flocculated slowly and the HCl sample (pH 6.4) over the period of a day.

### Discussion.

One of the most interesting points about the experiment was the reappearance of massive flocs in the region pH 9.52, corresponding to their original appearance at $\sim$ pH 9.35 when $OH^-$ ion was originally added (p.643). This might be taken as supporting the proposed 'Matijević' mechanism, ie. coagulation by divalent polymeric alumina. The writer however is inclined to prefer Mattson's working hypothesis (Chapter IV B 1 p.174) and to suggest that it corresponds to a critical concentration of $OH^-$ ions and divalent cations in which the hydroxyls attract sufficient cations for maximum development of ionic links, while at the same time the charge is still low enough for the particles not to repel too strongly. In Mattson's words, at this stage the links between the chains no longer tear.

### Exp. 87 The removal of free electrolyte from the flocculated podzol and the effect on its alkaline dispersion.

It is not clear why the flocculation became more subdued after the suspension was allowed to stand. It may have been due to a partial adsorption of free electrolyte by the clay. The effect of the near total removal of electrolyte, together with any other soluble flocculating agent was next examined. An alkaline sample was shaken in water and centrifuged six times, until the conductivity of the supernatant registered zero on a soil "CF" conductivity meter. The residue (pH 7.55), then flocculating strongly, was divided into two aliquots of 60 ml and these were made alkaline with

NaOH or $NH_3$.

(a) NaOH: 0.1 ml 5 N NaOH, equivalent to a final concentration 1.9 mmole $Na^+$/l, brought the sample pH to 11.6. After about one minute the shaken suspension appeared stable. It was shaken for 45 minutes on a wrist shaker and remained stable. In order to see whether it was necessary, as recommended for allophane by Birrell and Fieldes (1968), to disperse in strongly alkaline solution, the pH was lowered to 9.8 with 0.15 ml N1 HCl. During the next few days the suspension still appeared stable, being strongly turbid with a thin deposit of silt and coarse clay.

(b) $NH_3$: 0.05 ml 0.5 N $NH_3$ brought the sample pH to 9.2. The suspension was shaken for 45 minutes and flocculated to some extent on standing. A total 0.2 ml $NH_3$ brought the pH to 9.65. This at first appeared to be stable, but flocculated slightly over 3 days to give a sediment containing flocs.

### Exp. 88 The effect of adding a low concentration of $Ca^{2+}$ to the alkaline dispersions.

0.1 ml 0.1M $CaCl_2$ was added to the above alkaline dispersions, corresponding to a concentration of 0.16 mmole $Ca^{2+}$/l and a precipitate appeared at once. There was no hindered settling however. The flocs merely rained through the suspension, and after about 1½ hours a certain stability was re-established.

## Discussion.

The results suggest that a flocculated soil with allophane could be dispersed if free electrolyte was removed and the suspension was then made alkaline to about pH 10.0 or higher. The following points have still to be ascertained:

(a) Whether the inefficiency of the $NH_3$ was due to the pH being too low or to the presence of the $NH_4^+$ rather than the $Na^+$ ion.

(b) Whether it was only the removal of simple free electrolyte, and not of some other soluble constituent also, such as $Al(OH)_4^-$, which was decisive. Exp. 88 in which 0.16 mmole $Ca^{2+}$/1 reflocculated the dispersion, suggests the removal of simple cations was all that was required, but analysis of the water-washings has still to be done to comfirm this.

(c) Whether mechanical analysis would confirm the stability of the NaOH dispersion.

(d) Whether the same procedures could be used on allophane soils such as Tirau. Birrell and Fieldes only obtained partial dispersion at pH 12, yielding 13%

clay from a total calculated by surface area measurements to be 39% (Table 17 p. 152); but one does not know the extent to which their clay was washed. The writer for example found that after four washings the podzol continued to flocculate, but achieved dispersion in alkali after six washings.

(iii) Exp. 89 The effect of intensive peroxidation of Amlaird $B_{2g}$ on its flocculation in alkali.

10 g Amlaird $B_{2g}$ soil was peroxidised for 2 days in 50 ml water at 90°C., with progressive addition of 50 ml 30% analar $H_2O_2$. The suspension was divided into two for separate dispersion in $NH_3$ at pH 10 and NaOH at pH 12. One aliquot was vibrated in 30 ml water containing 1.0 ml 1:1 $NH_3$ for 15 minutes. It was sieved and a deep bank of flocs formed in the cylinder. The suspension was made to 500 ml (pH 9.7) and the pH raised to 10 with a total 1.6 ml $NH_3$. At first its appearance was stable, but after 3 hours slow flocculation began, and it settled to a deep bank of flocs over a period of days.

The second aliquot was vibrated in 30 ml water containing 0.6 ml 5 N NaOH for 15 minutes (pH 12.15). It was decanted without sieving and made to 500 ml (pH 11.2, 6 mmole NaOH/1) and was seen to be flocculating slowly. It was made to pH 12.05 with a further 2 ml 0.5N NaOH, equivalent to a total 26 mmole/1 NaOH. Massive flocculation set in and in 30 minutes the flocs had settled ~190 ml deep.

These results showed that even the Amlaird soil contained sufficient allophane to develop alkaline flocs provided it was intensively peroxidised. The $NH_3$ sample continued to flocculate after vibration in 1.0 ml 1:1 $NH_3$/5g soil, equivalent to the 2.0 ml/10g normally used in soil dispersion, and the NaOH sample continued to flocculate when the suspension contained only 6 mmoles/1 NaOH.

Examples of the quantities of peroxide and alkali whose addition led to either dispersion or flocculation of the Darleith soils are given in Table 86. Mild peroxidation, such as when Amlaird $B_{2g}$ was treated with 5 ml $H_2O_2$ led to flocculation at suspension pH by the electrostatic mechanism, but addition of 2 ml $NH_3$/1 dispersed the flocs. Vigorous peroxidation however produced (a) extensive buffering ie. hydroxyl uptake; and (b) continuous flocculation, and these two effects may be causally related. With Dunlop $B_{2g}$, for example, 1.5 ml $NH_3$ was sufficient to raise the pH of an unperoxidised sample to 10.1, while a sample treated with 20 ml $H_2O_2$

Table 86 Examples of the relationship between soil (10g/1) pretreatment, alkali addition, pH and suspension behaviour.

| Soil | pretreatment | ml 1:1 $NH_3$ | mM $Na^+$/1 | pH | suspension behaviour |
|---|---|---|---|---|---|
| Dunlop $B_{2g}$ | sonic | 1.5 | - | 10.1 | dispersion |
| Dunlop $B_{2g}$ | $H_2O_2$(20 ml)sonic | 5.1 | - | 9.8 | flocculation |
| Dunlop $B_{2g}$ | $H_2O_2$(10 ml)resin | 2.0 | - | 9.75 | dispersion |
| Dunlop $C_g$ | $H_2O_2$(5 ml)sonic | 1.1 | - | 10.3 | dispersion |
| Dunlop $C_g$ | $H_2O_2$(62 ml)sonic | 0.15 | - | 8.6 | dispersion |
| Amlaird $B_{2g}$ | sonic | 2.0 | - | 10.15 | dispersion |
| Amlaird $B_{2g}$ | $H_2O_2$(5 ml)sonic | 2.0 | - | n.d. | dispersion |
| Amlaird $B_{2g}$ | $H_2O_2$(50 ml)sonic | 5g 1.0 | - | 9.7 | flocculation |
| | | 3.2 | - | 10.0 | flocculation |
| | | 5g - | 6 | 11.2 | flocculation |
| | | - | 26 | 12.05 | flocculation |
| Podzol C | sonic | 1.5 | - | 10.0 | dispersion |
| Podzol C | $H_2O_2$(9 ml)sonic | 1.5 | - | 9.9 | dispersion |
| Podzol C | $H_2O_2$(60 ml)sonic | 2.2 | - | 9.8 | flocculation |

required 5.1 ml $NH_3$ to raise the pH to 9.8. Podzol C showed a similar effect. Hence in these cases, it is not the adsorption of cations which causes flocculation, but the adsorption of hydroxyl, made possible, in agreement with Mattson's hypothesis, by the negatively charged sesquioxide sites (p.641). Thus when the first requirement for flocculation is satisfied ie. the presence of aluminous sites capable of adsorbing hydroxyl ions, the free electrolyte and/or divalent cations can then play their flocculating role. In unperoxidised suspensions the hydroxyl ions quickly raise the pH because they are less adsorbed and much larger quantities of free electrolyte are required to initiate flocculation. Allophane soils resemble peroxidised soils-with-allophane in that their high concentration of aluminous sites cannot be adequately masked by organic matter except in surface horizons. Thus flocculation is the norm.

### Exp. 90 The effect of low concentrations of $Ca^{2+}$ on Tirau B dispersions.

It was decided to test this hypothesis by observing the effect of low ie. less than Schultze-Hardy concentrations of $Ca^{2+}$ ion on Tirau B dispersions. The samples used were dialysed Tirau B, Tirau B/$H_2O_2$/resin/$NH_3$ which was subsequently silicated and was still fairly stable, and

Tirau B/resin/$NH_3$ which was now unstable. It was found that the dialysed Tirau B suspension when at pH 5.8 flocculated only slowly on addition of 0.2 mmole $Ca^{2+}$/1, but on raising the pH of a sample to 11.0, 0.2 mmole initiated cloudiness in 10 minutes. The resin/$NH_3$ sample was affected by 0.1 mmole $Ca^{2+}$/1, but the resin/$NH_3$ + $SiO_2$ was only marginally affected by 0.3 mmole. This would be consistent with the masking of a proportion of aluminous sites by silica, and a smaller degree of $OH^-$ adsorption. Thus one concludes that small amounts of $Ca^{2+}$ are sufficient to cause flocculation of the highly hydroxylated allophane at field pH, and even more markedly at high pH. Similarly in Exp. 88 p.647, 0.16 mmole $Ca^{2+}$/1 reflocculated an alkaline dispersion of peroxidised podzol C.

### (iv) Exp. 91 The effect of intensive peroxidation of Dunlop $C_g$ on its flocculation in alkali.

Previous results suggested that intensive peroxidation was required to obtain Dunlop $C_g$ flocs. Three successful mechanical analyses had been made on soils peroxidised in up to 8 ml $H_2O_2$/10g, after the pH had been raised severally to 6.8, 8.5 and 10.3. Flocculation at high pH had so far only been observed to occur at a very slow rate, as in Exp. 70 p.564, when 5 ml $H_2O_2$/5g soil had been used in the pretreatment. However it was confidently expected that the same result would be obtained as for podzol C and Amlaird $B_{2g}$ once excess $H_2O_2$ had been added.

10g Dunlop $C_g$ (1971) was peroxidised for 2 days in 50 ml water at 90°C, 62 ml 30% analar $H_2O_2$ being added progressively. It was divided into two portions and the first portion was vibrated for 15 minutes in 30 ml water containing 0.15 ml 1:1 $NH_3$ (pH 9.2). It was decanted and appeared to flocculate slightly, but on being made to 400 ml (pH 8.6) and shaken by hand, it remained stable. It was stood under observation and after 6 weeks had formed a compact sediment and the zoned supernatant associated with stable suspensions (p.473).

Two 100 ml aliquots of the reshaken suspension were then transferred to cylinders. To one sample NaOH was added dropwise until at pH 12.1 (41.5 mmole Na /l), a few dark flakes like tea-leaves began falling through the turbid suspension. The second sample was made to pH 9.8 with dropwise addition of 1.5 ml 1:1 $NH_3$ and again the tea-leaf aggregates appeared. In both cases these settled to a compacted sediment, but the flakes formed in only small amounts, the bulk of the suspensions remaining thickly turbid. After 4 days they were each peroxidised with a further 2.5 ml $H_2O_2$, equivalent to a total 87 ml $H_2O_2$/10g soil. The suspensions remained turbid for several weeks.

The results of this experiment conflicted with that achieved earlier (Exp. 70 p.564) where 5g $C_g$ was peroxidised in only 5 ml $H_2O_2$ and yet flocculation in ammonia (pH 10.2) was complete in about 10 days. Further aliquots of these same peroxidised flocs made alkaline with $NH_3$ or NaOH gave the same result. The extreme stability of the present sample when subjected to 87 ml $H_2O_2$/10g soil is difficult to explain. Its relative stability compared with the other Dunlop subsoils has so far been attributed to the silication of alumina groups. It now appeared that peroxidised $C_g$ was also more stable than peroxidised Amlaird $B_{2g}$. The stability could be due (a) to silication and (b) to its low % base saturation, an effect described by Mattson (1922, 1929b) and discussed on p.172. $C_g$ was 18.1% saturated compared to Amlaird $B_{2g}$ which was 61.4% saturated (Table 87). The tea-leaf like aggregates which formed a limited coagulum were also a puzzling feature. Perhaps they resembled the coagulates that La Mer distinguished from subsiding flocs.

### (v) Exp. 92 The continuous flocculation of peroxidised Dunlop $B_{2g}$ throughout the pH range.

It was wondered whether there might be a pH region above the isoelectric point and below that of alkaline flocculation, in which dispersion took place. To check that such a region had not been missed 10g Dunlop $B_{2g}$ was peroxidised in 70 ml $H_2O_2$, vibrated and made to

Table 87 Comparison of the base saturation of Dunlop $C_g$ and Amlaird $B_{2g}$ soils.

(Compiled from analyses made by I. Pulford and M. Wilson)

| Soil | Exchangeable divalent base me/100g | | % base saturation | pH 1:2.5 |
|---|---|---|---|---|
| | $Ca^{2+}$ | $M_g^{2+}$ | | |
| Dunlop $C_g$ | 6.8 | 1.3 | 18.1 | 4.9 |
| Amlaird $B_{2g}$ | 12.3 | 8.9 | 61.4 | 5.5 |

1 litre. 100 ml aliquots of the flocs were taken for dropwise addition of N10 NaOH or 0.5N $NH_3$. No dispersion was obtained with either reagent up to pH 9.5. In one sample NaOH was added to pH 12.6, and flocculation occurred continuously.

(iv) Exp. 93 The effect of extended peroxidation on the sodium fluoride treated Dunlop $C_g$ and Amlaird $B_{2g}$ suspensions.

In Chapter XI p.486 and 487 it was described how allophane was removed from Amlaird $B_{2g}$ and Dunlop $C_g$ respectively by exhaustive NaF treatment. Peroxidation of the suspensions with 10 ml $H_2O_2$ each followed by vibration produced stable suspensions which yielded 41% clay. This was a normal yield for the Amlaird and about 13% higher than normal for the Dunlop. The suspension appeared to be sedimenting in the usual manner. It was now wondered whether further peroxidation, similar to that which had been given the untreated soils, would induce these sols to flocculate. To check this point a total of 20 ml 30% analar $H_2O_2$ was added to 200 ml of the silt + clay suspensions and they were heated at 90°C for one day.

The Dunlop $C_g$ precipitated voluminous flocs on cooling. The Amlaird $B_{2g}$ showed slight flocculation on standing for a day and this continued over the period of one week, after which it too developed a clear supernatant and voluminous flocs.

This perplexing result might be given one of several explanations. (a) All or many soils behave similarly if peroxidised intensively: to the writer's knowledge no such effects have been reported; (b) peroxidation produced artefacts which brought on flocculation: this can now be dismissed in view of the ability of calgon to disperse alkaline flocs (see p.669); (c) The NaF failed to remove all the allophane and peroxidation exposed fresh aluminous sites. One notes the NaF treated $C_g$ released 11% more clay than was in the original sample (Table 66 p.527). Perhaps this fraction when severely peroxidised, exposed fresh alumina groups.

### (vii) Exp. 94 The effect of alkali on the NaF- treated peroxidised flocs.

The flocs from each suspension were diluted to their original volume of 200 ml and divided into two 100 ml aliquots which were hand shaken before addition of alkali. The treatments and their effects are summarised in Table 88. Alkali additions are comulative, and concentrations refer to those in 100 ml suspension.

Table 88 Exp. 94 <u>The effect of alkali on the NaF- treated peroxidised flocs</u>.

| | |
|---|---|
| Amlaird $B_{2g}$ :<br>(1:1 $NH_3$) | handshaken (pH 6.6), appeared dispersed $\xrightarrow{1.2\text{ ml }NH_3}$ pH 9.8, $\longrightarrow$<br>remained dispersed $\xrightarrow{\text{shake 90 min.}}$ Remained stable $\xrightarrow{\text{12 days}}$ pH 9.4<br>$\xrightarrow{0.5\text{ ml }NH_3}$ pH 10.6 $\xrightarrow{\text{shake 30 min}}$ stable? $\xrightarrow{\text{next day}}$ flocculated. |
| Dunlop $C_g$ :<br>(1:1 $NH_3$) | handshaken (pH 6.85), fine precipitate $\xrightarrow{0.55\text{ ml }NH_3}$ pH 9.6, $\longrightarrow$<br>flocculation $\xrightarrow{\text{shake 90 min}}$ flocculation. $\xrightarrow{1.55\text{ ml }NH_3}$ pH 10.7 $\longrightarrow$<br>$\xrightarrow{\text{shake 30 min}}$ flocculated. |
| Amlaird $B_{2g}$ :<br>(NaOH) | handshaken (pH 6.6), appeared dispersed $\xrightarrow{0.65\text{ mM }Na^+/1}$ pH 9.2, $\longrightarrow$<br>dispersed? $\xrightarrow{13.2\text{ mM }Na^+/1}$ pH 11.85, $\rightarrow$ immediate heavy flocculation<br>$\xrightarrow{\text{shake 90 min}}$ flocculation. |
| Dunlop $C_g$ :<br>(NaOH) | handshaken (pH 6.85), fine precipitate $\xrightarrow{5.8\text{ mM }Na^+/1}$ pH 9.5, $\longrightarrow$<br>flocculation $\xrightarrow{18.3\text{ mM }Na^+/1}$ pH 11.55, precipitate finer.<br>$\xrightarrow{18.8\text{ mM }Na^+/1}$ pH 11.85, dispersion? $\xrightarrow{\text{shake 90 min.}}$ Remained<br>stable $\xrightarrow{\text{12 days}}$ flocculated pH 11.0 $\xrightarrow{44.2\text{ mM }Na^+/1}$ pH 12.5<br>$\xrightarrow{\text{shake 30 min}}$ stable? $\xrightarrow{\text{next day}}$ flocculated. |

Dunlop $C_g$ failed to disperse in ammonia at any pH, even though this was taken as high as 10.7. In NaOH however it finally dispersed on addition of 18.8 mmole $Na^+/l$ (pH 11.95) and remained stable for over a week. Its pH had then dropped to 11.0 and redispersion was obtained for a day by raising the pH. Thus it appeared that this soil could be dispersed at least temporarily, but only at very high pH.

Amlaird $B_{2g}$ behaved differently. It had flocculated slowly at pH 6.6, and was stabilised on addition of $NH_3$ (pH 9.8) for over a week. Its pH was then 9.4 and it was redispersed for a day on further addition of ammonia (pH 10.6). In NaOH however, the dispersion suddenly flocculated after 13.2 mmole $Na^+/l$ had been added (pH 11.85). This was unexpected. In searching for an explanation one again recalls that Mattson (1922,1929b) showed that a $Ca^{2+}$ saturated soil flocculated with lower concentrations of alkali than an unsaturated soil. Amlaird $B_{2g}$ contained higher amounts of exchangeable $Ca^{2+}$ and much higher $M_g^{2+}$ than the Dunlop $C_g$ (Table 87). These would be displaced into solution on addition of large amounts of alkali ion, where they would perform the role of ionic links. This may also explain the more rapid flocculation of Tirau B in NaOH than the less dissociated $NH_3$ solution (p.558).

## 14. Inhibited flocculation.

### Exp. 95a The effect of alkaline electrolyte on an unperoxidised Dunlop $B_{2g}$ (1969) dispersion.

The following experiment was designed to compare the amount of alkaline electrolyte required to precipitate a Dunlop $B_{2g}$ suspension: (a) with the amount of neutral $CaCl_2$ required to precipitate it as found in Exp. 79, p.617; (b) with the amount required for reprecipitation of peroxidised soils. (Exps. 88,90,94).

A Dunlop $B_{2g}$ (1969) suspension which had been recently dispersed by vibration in ~ 2 ml 1:1 $NH_3$ (pH now 7.85) was reshaken and transferred in 100 ml aliquots to cylinders. Dropwise additions were made of one of the following:- 5N NaOH, 1:1 $NH_3$, 0.01M $Ca(OH)_2$ and 5N NaOH + 1M $CaCl_2$ and 1M $CaCl_2$. The various amounts and subsequent observations are shown in Table 89. Volumes, concentrations and days are cumulative.

The first point to note was the stability of the sol to a large excess of alkali or calcium ion in the presence of alkali. Active flocculation did not occur until 72 - 122 mmole NaOH/l or 4.0 - 4.5 mmole $Ca^{2+}$/l had been added. The second point was the very different course of flocculation to that observed in other sols. The features

Table 89 The effect of alkaline electrolyte (Exp. 95a) and neutral $CaCl_2$ (Exp. 95b) on an unperoxidised Dunlop $B_{2g}$ (1969) dispersion.

| Electrolyte | Observation |
|---|---|
| 1:1 $NH_3$ | 1.0 ml (pH 11.0) → v. fine flakes visible falling at base, halting after some minutes — 2.0 ml → (pH 11.0) v. fine granular ppt. visible at rim? — 1 day → zoning into "clear brown (5 ml) opaque (15 ml), v. opaque (78 ml). Compact sediment. A few flocs." |
| 5 N NaOH | 30 mM/1 (pH 12.1) → No flocs to this point, but now v. fine flocs falling at base and v. fine granular ppt. at rim — 45 mM/1 → (pH 12.5) → as before — 1 day → Zoned turbid supernatant, sediment with small "tea leaf" flocs on lower walls — 72.5 mM/1 → as before. — 122 mM/1 → as before. — 2 days → 4 ml flocs — 3 days → 7 ml flocs, supernatant clear brown. |
| 0.01M $Ca(OH)_2$ | 2 mM/1 (pH 9.45) Stable suspension — 2 days → stable suspension. |
| 5 N NaOH<br>+<br>1 M $CaCl_2$ | 50 mM Na /1 0.5 mM $Ca^{2+}$/1 (pH 12.5) → immediate thin trickle of flocs down sides and slight granular ppt. at rim. — 0.1 mM $Ca^{2+}$/1 → slow trickle continues — 1 day → zoning into "clear brown (5 ml) sharp interface with turbidity (93 ml), coagulum." — 2 mM $Ca^{2+}$/1 → rain of v. fine flocs — 2 days → "clear brown (5 ml), turbidity 92 ml), flocs (3 ml)" — 3.5 mM $Ca^{2+}$/1 → granular ppt at rim, slight fall of flocs at base — 4.5 mM/1 → as before — 5.5 mM/1 → slow pile up of flocs. |
| 1 M $CaCl_2$ | 3.0 mM/1 → flocs at rim? – $1\frac{1}{2}$ hrs → stable? — 4 mM/1 → small flocs at rim. — 4.5 mM/1 → strong granular ppt. at rim, none visible at base for 2 - 3 mins, then flocs pile up slowly, leaving clear supernatant. |

of streaming, counter-streaming and massive subsidence were absent. Instead of the whole suspension being involved, small flocs rained down through the turbid suspension for a period, and then the 'rain' ceased and the stability returned. In the early stages, flocs were often sparse, and like tea leaves in colour and shape. A mental picture is formed of particles coalescing, and then as their numbers in suspension were reduced, of effective collisions no longer occurring, but the suspension regaining stability until fresh additions of electrolyte renewed the process. The sediment so formed was of compacted flocs, at least until excess electrolyte was added, and would probably not be easily filtrable. Here indeed perhaps was the suspension behaviour that resembled La Mer's description of a coagulated sol.

In searching for an explanation for this difference in behaviour to that of the peroxidised sols, one might attribute it (a) to the presence of alkaline organic matter since this is generally thought to assist peptisation; or (b) to the masking effect of organic matter. Absence of exposed alumina groups would restrict hydroxyl uptake and inhibit the flocculating role of free electrolyte.

In passing one notes that a rather similar, though more subdued behaviour was shown by Dunlop $C_g$, where in this case the alumina groups were thought to be silicated.

### Exp. 95b The effect of $CaCl_2$ on an unperoxidised Dunlop $B_{2g}$ (1969) dispersion.

1M $CaCl_2$ solution was added dropwise to 100 ml Dunlop $B_{2g}$ suspension and the result is shown in Table 89. It is seen that the $CaCl_2$ produced the same type of flocculation with clear supernatant as was observed with the 1971 sample in Exp. 79, but that 4.0 - 4.5 mmole $Ca^{2+}/l$ was required for a sluggish precipitation, whereas ~ 2mmole $Ca^{2+}/l$ brought on immediate flocculation in the 1971 case. The difference in behaviour might be attributed to a higher organic matter content (5.9% and 4.5% respectively) or perhaps to a higher percent base saturation in the 1971 sample, following liming of the soil in summer 1970.

### Exp. 96a The effect of starch + $Ca(OH)_2$ solution on an unperoxidised Dunlop $B_{2g}$ (1969) dispersion.

It was expected that when starch was added together with $Ca(OH)_2$, the stable Dunlop $B_{2g}$ dispersion would flocculate in the manner described by La Mer (1967), and that for this sol at least, the behaviour might be distinguished from that in $Ca(OH)_2$ alone.

Table 90 Exps.96a and 96b <u>The effect of potato starch + $Ca(OH)_2$ and starch + $CaCl_2$ addition on an unperoxidised Dunlop $B_{2g}$ (1969) dispersion.</u> (Cumulative additions and $Ca^{2+}$ final conc. in mM/l).

| Electrolyte | Observations. |
|---|---|
| Exp 96a<br>$Ca(OH)_2$ | 100 ml suspension + 100 ppm starch + 1 mM $Ca(OH)_2$ ⟶ no reaction.<br>2 mM $Ca(OH)_2$ ⟶ very small granules at rim, 'tea-leaf' ppt. at base.<br>200 ppm starch ⟶ slight ppt. at rim. 300 ppm starch ⟶ as before.<br>3 mM $Ca(OH)_2$ ⟶ as before. 4 mM $Ca(OH)_2$ (pH 11.2) ⟶ stronger ppt at rim, small flocs falling at base then coming to a halt.<br>5 mM $Ca(OH)_2$ + 400 ppm starch ⟶ ppt. still only v. small, fuzzy, peppery, just visible at rim. 500 ppm starch ⟶ no change.<br>Next day ⟶ Strongly turbid suspension, fine 'tea-leaf' ppt on walls, coagulated sediment. |
| Exp.96b<br>$CaCl_2$ | 50 ml suspension + 100 ppm starch + 1 mM $CaCl_2$ ⟶ no reaction.<br>2 mM $CaCl_2$ ⟶ v. few 'tea-leaves'. 3,4,5,6,7, mM $CaCl_2$ ⟶ No reaction.<br>200 ppm starch ⟶ immediate granular ppt. followed by subsidence of flocs and clear supernatant. |

Dropwise additions of 1% potato starch solution and 10 ml additions 0.01M $Ca(OH)_2$ were made to 100 ml Dunlop $B_{2g}$ (1969) dispersion, with stirring. The cumulative concentrations and observations are shown in Table 90.

Despite the addition of up to $\sim$ 500 ppm starch and 5 mmole $Ca(OH)_2$, there was no development of 'flocs' in La Mer's sense, nor of their subsidence. Instead a few dark 'tea-leaf' flakes drifted through the turbid supernatant in the same manner as in Exp. 95a, and at the rim the turbidity became a 'fuzz' of very fine white precipitate. This did not appear to unite into flocs but must have sedimented by free fall, for the turbidity decreased over a period of days and a compact coagulum formed.

### Exp. 96b The effect of starch + $CaCl_2$ solution on the unperoxidised Dunlop $B_{2g}$ (1969) dispersion.

Exp. 96a above was repeated, using 1M $CaCl_2$ as a source of $Ca^{2+}$ instead of $Ca(OH)_2$. The results are also shown in Table 90. It is seen that there was no sign of flocculation on addition of 7 mmole $Ca^{2+}/l$ and 100 ppm potato starch, except for a few stray 'tea-leaves'. A total 200 ppm starch however, brought on heavy flocculation together with a clear supernatant.

## Discussion.

Combinations of starch and $Ca(OH)_2$ which failed to flocculate are not cited by La Mer, and this again lends support to the proposition that the inhibited behaviour of the alkaline sols was connected with the presence of organic matter. In the starch/$Ca(OH)_2$ suspension an exceedingly fine precipitate was visible in the rim of the liquid which had all the appearance of an incipient precipitation. Its failure to flocculate may have been due to the fact that, unlike the $CaCl_2$ sample above, it was highly charged, perhaps by strongly negative organic matter. It has still to be checked whether further addition of $Ca(OH)_2$ ie. > 5 mmole/l, would have produced flocculation instead of sedimentation.

It is not clear whether the mechanism for the type of precipitation described in this section is sufficiently different to merit calling it 'aggregation' or 'coagulation' as distinct from 'flocculation'. An abortion of flocs appeared to take place. One important conclusion however can be drawn: the interference was the same whether in the presence of electrolyte or polyelectrolyte, and it was most marked at high pH. This in turn reinforces the suggestion made on p.629 that their flocculation mechanism is of a similar nature.

## 15. Dispersion of soils containing allophane using sodium hexametaphosphate.

An earlier dispersion of peroxidised Dunlop $B_{2g}$ (1971) made by shaking with calgon had yielded only 16.7% clay in contrast to the 23 - 25% normally achieved (Table 66 p. 525). There had been no visible sign of flocculation however, and it was necessary to check on its poor performance by using a sonic/calgon instead of a shake calgon treatment.

### Exp. 97a Dispersion of peroxidised Dunlop $B_{2g}$ by vibration in calgon.

10 g soil was suspended in 100 ml water, peroxidised with 18 ml 30% $H_2O_2$ and vibrated in a suspension containing 10 ml calgon. When made to 1 litre, the suspension was stable (pH 8.0) while a control peroxidised sample flocculated. The clay yield was 32.5% which can be compared with the 30.1% obtained for $H_2O_2$/sonic/Zr pH 3.4 (Table 65 p.524).

Further experiments confirmed the stability of the dispersion. These included: (a) extended peroxidation of 130 ml with an additional 10 ml $H_2O_2$; (b) shaking 50 ml dispersion with 0.2 ml 1:1 $NH_3$ (pH 10.55); (c) shaking 50 ml dispersion with 0.2 ml 5 N NaOH (20 mmole

$Na^+/l$, pH 11.8). None of these treatments brought about flocculation of the soil.

The success of the calgon was considered due to the ability of hexametaphosphate to sequester $Ca^{2+}$ and substitute $Na^+$ ions; ie. it removed flocculating cations and prevented them from exerting their bridging function. Since calgon is a widely used reagent, it helped explain why the flocculating properties of soils similar to the Darleith soils had apparently till now been unobserved. Edwards and Bremner (1967) pointed out that when used in conjunction with $H_2O_2$, calgon produced negligible effect (p.129), ie. it played little part in disruption. The above experiment showed its important role was in preventing flocculation.

Exp. 97b <u>Limited dispersion of Tirau B with sodium hexametaphosphate</u>.

The inefficiency of calgon in dispersing allophane soils has been widely reported (p.146) and was confirmed by experiment, using an excess:-10 ml càlgon/20 ml Tirau B of 10 g/l flocs. It was thought that the difference in behaviour might be due to the greater hydroxylation of the Tirau clay than the Dunlop $B_{2g}$, and that the very small concentration of free $Ca^{2+}$ in equilibrium with sequestered $Ca^{2+}$ must be sufficient to interact with the OH groups. Dispersion would obviously be promoted if the OH concentration was lowered eg. by omitting the $Na_2CO_3$. Contrary to the statement on p.123, the sequestering action of the $(NaPO_3)_6$ is effective at low pH. It is used, for example, in the extraction of pectin at pH 4 - 5, where it is assumed to act by removing the $Ca^{2+}$ linkage between the pectin and the cell walls. However, in order to observe its effect with Tirau B, the pH required to be higher than 4.3, and it was also essential to avoid the self-flocculating region of isoelectric pH.

Unfortunately, only 0.85g of the Tirau B sample was left. This was vibrated in water containing 0.39g $(NaPO_3)_6$ and made to 100 ml (pH 7.5). It did not appear to flocculate but settled slowly to a fairly compact sediment. The silt content was found to be 51.4%, but the clay content was only 9.1%, or not much more than the 5 - 7% found in the profile analysis by calgon (Table 16 p.150). It is still hoped however, that a suitable pH for calgon dispersion may be found. Addition of a little HCl for example, may depress the isoelectric pH and allow better dispersion at say pH 6.5 where the hydroxyl concentration will be further reduced.

## 16. Conclusions : dispersion methods and flocculation mechanisms of soils containing allophane.

Allophane flocculates in the region of its isoelectric pH due to the interaction of positive and negative charges. When soils contain both allophane and clay minerals, flocculation persists on the acid side of the isoelectric region for the same reason. On the alkaline side allophane continues to flocculate by some other mechanism. The cause of this has never been satisfactorily explained. To the writer's knowledge such behaviour has been assumed a rare property restricted to allophane soils. The foregoing experiments demonstrated that the Darleith soils and the C horizon of a podzol behave in exactly the same manner as allophane soils if they are peroxidised to some critical extent. Even the surface water gley which contains only minute amounts of allophane, when peroxidised severely flocculates throughout the pH range. To date, no other soils have been examined, so that it is not yet known whether the behaviour is more widespread than supposed.

It is postulated that the cause of the alkaline flocculation is due to the combined influence of (a) surface active alumina (b) hydroxyl ion (c) free electrolyte. Soils most prone to flocculate either contain large amounts of allophane clay or hold considerable aluminous allophane as a coating on clay surfaces. Order of flocculating power has been shown to correlate not only with the relative amounts of allophane present, but with its $SiO_2 : Al_2O_3$ ratio. Soils with the highest amounts of 'active' easily extractable alumina are the most sensitive to flocculation. This was shown using NaF, $Na_2CO_3$, cation exchange resin and citric acid extraction techniques.

The role of the alumina in bringing about flocculation is thought to lie in its ability to adsorb large quantities of hydroxyl ion rather than to any coagulating effect. In the presence of adsorbed hydroxyls, very small amounts of divalent cation are able to flocculate the soil. In this respect the behaviour of allophane is exactly similar to the behaviour of quartz and base-saturated clay suspensions discovered by Mattson (1922). Contrary to the accepted belief that hydroxyl ions act as dispersing agents, Mattson found that their principal role was as flocculating agents, in that much smaller quantities of $Ca^{2+}$ were required as $Ca(OH)_2$ or $CaCl_2$ in the presence of NaOH, than as $CaCl_2$ alone to flocculate soil colloids. Only as univalent hydroxides and in the absence of critical concentrations of divalent cations did the $OH^-$ ions have a dispersing function.

Dispersion of the flocculated soils can thus be accomplished by any technique which interferes either with the reactivity of the surface alumina, or the uptake of hydroxyl ions or the presence of free electrolyte. These techniques were found to include:

(a) Masking of the aluminous sites with organic matter. ie. avoidance of the peroxide step. The Darleith soils are readily dispersed in water or alkali, with the exception of certain samples of Dunlop Cg. These last when low in organic matter cannot be dispersed in water because their positively charged allophane is free to flocculate with the clay minerals; but they can be dispersed in alkali, suggesting that the $C_g$ is not sufficiently aluminous for the unperoxidised soil to flocculate at high pH. With allophane soils aluminous sites are too numerous to be masked by organic matter, except in the A horizon; thus the subsoils flocculate but the surface horizon can usually be alkali dispersed.

(b) Masking of the aluminous sites with silica. Addition of alkaline silica sol to the suspension allows uptake of silica by the aluminous sites. It was found a feasible dispersion method except in the case of peroxidised Tirau B where the sites were too numerous. In certain soils the silica is already present: the relative stability of peroxidised Dunlop $C_g$ alkaline suspensions may be due to siliceous allophane.

(c) Removal of electrolyte by shaking with Na-exchange resin.

The resin removes divalent ions from the suspension and substitutes the less flocculating $Na^+$ ions. It also removes considerable surface alumina, but it is not clear how far this too contributes to the dispersion, since a certain amount of silica is taken up as well. After separating the resin the suspension pH is raised to avoid the isoelectric region and dispersion takes place in alkali. The resin method was found the preferred method for mechanical analysis of allophane. Unlike other resin soil dispersions however, the allophane dispersion is unstable and redevelops its flocculating property with time. This is thought due either to exposure of fresh alumina groups or diffusion of divalent cations from within the mineral into solution. The dispersion can be stabilised as in (b) by silication of the alumina groups.

(d) Removal of the electrolyte by washing.

After intensive washing, the flocs can be dispersed in alkali at pH 9.8 or above. In the experiment described the soil was first saturated with NaOH at pH 12 and it is probable that the divalent ions, having been displaced by $Na^+$, were more readily removed than if the untreated soil had been washed. In this case, NaOH was found a more effective dispersing agent than $NH_3$, which produced slow flocculation. Quantitative assessment of the efficiency of the dispersion by mechanical analysis, and analysis of the water washings have still to be made.

(e) Removal of electrolyte by dialysis.

Electrolyte is leached out of the soil. A proportionate amount of silica is also leached so that the alumino-silicate complex can maintain electrical neutrality. As a result the isoelectric pH is raised and a partial dispersion can be achieved at pH 5 - 6. With Tirau B, under 50% of the clay content dispersed. From test tube trials (Exp. 77 p.606) dispersion did not appear possible as in (c) and (d) on addition of alkali, but this has yet to be confirmed with larger samples.

(f) Removal of $Ca^{2+}$ ions by sequestering with $(NaPO_3)_6$.

Peroxidised Dunlop $B_{2g}$ was dispersed with calgon between pH 8 and 11.8, probably due to the flocculating divalent ions being sequestered by $(NaPO_3)_6$. All pretreatments with $H_2O_2$ should thus be followed by shaking or vibration in calgon in routine mechanical analysis. Allophane soils are too highly hydroxylated to be dispersed in this way. It is thought the small amount of free $Ca^{2+}$ in equilibrium with the Ca in the polyphosphate complex is still sufficient for flocculation. Evidence suggests however, that if the OH concentration is reduced and slightly acidified instead of alkaline $(NaPO_3)_6$ is used, dispersion may be possible at some critical pH, which at the same time avoids the isoelectric region.

(g) Destruction of the $OH^-$ groups by acid dispersion.

Allophane soils which contain only small amounts of clay mineral can be dispersed in dilute HCl at approx. pH 4.3. On Mattson's hypothesis this is the result of the destruction of $OH^-$ ions by the $H^+$ ions. It will be recalled from Chapter IV B 1 p.166 that he found quartz flocs were stabilised in acid and even in $NH_4Cl$, and this was attributed to the property of $H^+$ and $NH_4^+$ ions reacting with $OH^-$ ions to form water.

(h) Charge reversal of negative colloids.

Tirau B contains a small amount of kaolinite and this is not flocculated, despite its negative charge, but remains suspended in even very fine sols. It is thought to be stabilised against flocculation by charge reversal due to hydrolysed alumina. When a soil contains much clay mineral together with allophane, dispersion in acid alone is no longer possible, but can be achieved on addition of certain metal salts (eg. Zr, Th, Zn, Al, Fe) whose hydrolysis products are capable of reversing the charge on negative sols when present in some range of concentration. It was not found necessary to disperse at low pH and risk damaging the clay. Charge reversal and dispersion of the Darleith soils was achieved at pH 4.3-4.5. It should be noted however, that the quantities of charge reversing cation required increase dramatically with rising pH, due to the continuous formation of negative charge; and perhaps also to the requirements for higher concentrations of dispersing agent at high pH noted on p.163. Thorium nitrate was found preferable to zirconium nitrate, because smaller amounts were needed to stabilise suspensions.

All the mechanisms that allow dispersion by the methods outlined in a to h above, were in essence investigated and explained by Mattson in his 1922 paper. Thus in searching for an explanation of the flocculation of allophane, and indeed of soil colloids in general, the writer proposes to use as a working hypothesis his theory of ionic linkage, suggested in 1922 and re-affirmed in the Laws of Colloidal Behaviour (1929b). In this theory, divalent cations present in the free electrolyte are held electrostatically to the adsorbed hydroxyl ions, and when present in sufficient quantity they link the clay micelles into a three dimensional network. Flocs are formed by the interaction of the micelles and not their particle nuclei. Sol stability is maintained if the supply of hydroxyl ions is either too small or too large for the cations to function in this way. Hence one can postulate that the sensitivity of allophane to flocculation above the isoelectric pH is due to its active alumina whose strong adsorption of hydroxyl ions allows the linking of clay micelles by very small amounts of divalent cation.

The writer suggests that the DLVO (double layer Verwey-Overbeek) theory is not applicable to flocculation, but only to aggregation, and that Mattson's evidence (1929a, b) described in Chapter IV B 2 p.186 on the role of the dissociated cations, free electrolyte and osmotically imbibed water in controlling sol stability, should be re-examined and tested. It may be possible to develop a theory of more universal applicability than the DLVO theory, particularly when the properties and functions of the all-pervasive OH group are better understood, and to interpret in its terms what are now distinguished as 'electrolyte coagulation' and 'polyelectrolyte flocculation'. In the writer's view the term coagulation is confusing, and experiments suggest that electrolyte flocculation differs from polyelectrolyte flocculation chiefly in the greater vulnerability of the flocs. With electrolytes, the individual $OH^-$ ions act as the 'bridgeheads' to the bridging cations, and displacement and local dispersion leading to poorer filtration properties can occur. With polyelectrolytes the hydroxy polymers are adsorbed irreversibly and their bridging of the micelles provide a network of stable flocs and pores.

An 'abortive' type of flocculation has been observed in which small flocs descend through the turbid suspension forming a compact coagulum, and where after a while floc formation ceases and the rest of the sol remains stable. Both electrolytes and starch polyelectrolyte produced this effect in a stable unperoxidised Dunlop $B_{2g}$ suspension, and the result was attributed to the masking of alumina groups by organic matter and the inhibition of hydroxyl uptake.

In conclusion the writer suggests that perhaps a study of the flocculation of allophane may lead to a better understanding of the phenomenon of flocculation itself.

POSTSCRIPT. SRC Report on Colloid Science, see Appendix C, p.787.

# CHAPTER XIV : THE EXTRACTION OF ORGANIC MATTER FROM SOILS CONTAINING ALLOPHANE.

## 1. Introduction.

### Exp.98 Release of organic matter from soil suspensions in NaF solution.

Soil suspensions were often left to steep a few days in sodium fluoride solution after their rise in pH had been recorded. The supernatants developed colours ranging from cherry black, deep red, deep orange and deep yellow for Dunlop $A_1$, $B_{2g}$, $B_{3gx}$ and $C_g$ horizons respectively, and suggested in this vivid fashion, that sodium fluoride might be an efficient extractant of soils containing allophane. It was possible of course, that the organic matter had been released from the clay fraction as a result of the alkaline conditions produced, rather than from the allophane fraction by the fluoride complexing agent. It was planned to hold the pH between 6 and 7 with HCl.. In the event of a successful extraction, the major points of interest were:-

(a) Sodium fluoride would almost certainly selectively extract allophane-held organic matter. From this one could learn the proportion of organic matter held by soil allophane.

(b) Comparative analysis of the organic extract with that obtained by NaOH extraction, might suggest whether organic matter held by allophane was different in composition to that held by crystalline clay.

(c) Polymers extracted at pH 6 - 7 should be virtually unaltered, allowing analysis of undegraded material.

(d) The degree of alkali degradation in the soil situation could then be assessed by comparing the analytical results for NaF and NaOH extracted samples. The need to obtain information on the degradation of soil organic matter by alkali was discussed in Chapter VI 2 (vi) p263.

It was proposed to concentrate on the polysaccharide fraction, since this could be estimated semi-quantitatively and its components were readily identified. Moreover, it was an important constituent of soil organic matter and was known to influence strongly the creation of soil structure.

## 2. Methods.

### (i) Sodium fluoride addition.

5 or 10 g samples of soil were sonic-dispersed in 25 ml water and 100 ml aliquots of saturated sodium fluoride solution ( $\sim$1 M) were added. The pH was either allowed to rise, or it was controlled at some desired value by adding N/10 HCl from a burette. The amounts of HCl used were recorded. The suspension was usually magnetically stirred for some hours until the upward drift in pH was very small, and then rotary shaken for 16 hours overnight. The soil was in a glass vessel for these operations and spent only brief periods in a plastic one when centrifuging. The suspension was centrifuged at 10,000 rpm for 30 minutes, and the organic matter was removed in the supernatant, made to volume and stored in a frig. Then either a second 100 ml aliquot NaF was added to the residue, or it was shaken in water to wash out the excess salts. In each case, extracts were obtained from these and further treatments until the process was thought complete.

### (ii) Removal of salts.

Salts were removed from the residue by washing in water with overnight shaking and centrifuging off until there was negligible $Na^+$ or $Cl^-$ in the supernatant. It was essential to centrifuge at high speed eg. 10,000 rpm. Colloidal suspensions were obtained at 3,000 rpm. Attempts to remove salts from the extracts by dialysis were a failure because as shown in Chapter XVI, artefacts from the visking tubing interfered with the polysaccharide determinations and the sugar chromatograms. Hence, the extracts were rotary-evaporated to dryness and their purification left until after the hydrolysis step.

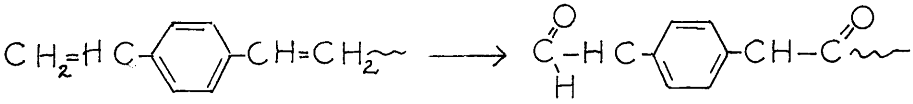
### (iii) Hydrolysis.

Whole soils, extracts and residues were hydrolysed under conditions which would cleave polysaccharides to monosaccharides. 1 g soil or residue, or an aliquot of extract brought to dryness on a rotary evaporator, was steeped in 3 ml 72% $H_2SO_4$ for 2 hours. 75 ml $H_2O$ was added to dilute the $H_2SO_4$ to a 1N solution. This was heated for 16 hours under reflux condenser and allowed to cool. The coloured organic components were removed by stirring 2 - 3 spatulas of B.D.H. activated charcoal into the hydrolysate. The suspension was filtered through No. 42 Whatman filter paper, washed with water, and the clear eluate made to a convenient volume such as 100 ml. In practice it was found that whole soils and residues required only one filtration, but the organic extracts required two and perhaps three, in order to remove a turbidity produced by salt interference. Reproducible results were best achieved even then by allowing the liquid to stand for two days before sampling, so that any remaining turbidity could settle.

## (iv) Semi-quantitative measurement of polysaccharide content by the phenol-sulphuric method.

The phenol-sulphuric method (Dubois et al. 1951, 1956) was used to obtain a semi-quantitative measurement of the polysaccharide content of the soil or fraction. 1 ml sample, containing 10 - 90 µg polysaccharide was mixed in a test tube with 1 ml 5% phenol solution, and 5 ml conc. analar $H_2SO_4$ was then added rapidly and directly into the solution from a wide bore pipette, with shaking, the object being to generate the maximum amount of heat. The samples were cooled and their yellow colour measured on an Eel colorimeter with 603 filter (490 mµ ) vs a reagent blank. Per cent transmission was calibrated with a glucose standard curve. The method is intrinsically semi-quantitative for polysaccharides since these contain a variety of sugars which each react to give a slightly different colour intensity at any one concentration. In addition, errors can arise from differences in the rate of mixing of the concentrated

$H_2SO_4$, from dust contamination and from differences in the sample itself, such as bubbles due to HF. These can be minimised with practice. The most important limitation of the phenol-sulphuric method is that it does not detect sugars per se. It detects reducing agents. Aldehydes and potential aldehydes for example give the same response. Chapter XVI describes the spurious results which were obtained due to the presence of plastic artefacts in the organic extracts. Cross-linkages associated with plastic would be a source of aldehydes and ketones as in the figure below:-



Fortunately the effects of the plastic artefacts were so large that interference was obvious. Had they been smaller, grave mistakes in the analysis and its interpretation might have been made.

### (v) Semi-quantitative measurement of polysaccharide content by its reducing power.

This method, due to Somogyi (1952), and like the phenol-sulphuric method, is quantitative for sugars but only semi-quantitative for polysaccharides, and can similarly be interfered with by other reducing agents.

## Reagents.

(a) Copper solution: 12 g Rochelle salt and 24 g anhydrous sodium carbonate were dissolved in 250 ml water. A solution containing 4 g copper pentahydrate in water was added, followed by 16 g sodium bicarbonate. A solution containing 180 g anhydrous sodium sulphate/ 500 ml water was boiled to expel air, and the two solutions were combined and diluted to 1 litre. The solution was stored at a slightly elevated temperature (37°C).
(b) Arsenomolybdate solution: 25 g ammonium molybdate was dissolved in 450 ml water and 21 ml conc. analar sulphuric acid added. 3 g disodium hydrogen arsenate dissolved in 25 ml water was added and the solution kept at 37°C. for 24 - 48 hours. The solution was stabilised by storage in a brown glass bottle.

## Procedure.

1 ml aliquots of the sample solution and copper reagent respectively were mixed in narrow pyrex tubes and heated in a boiling water bath for 20 minutes, the tubes being loosely stoppered with marbles. After cooling for 5 minutes in a bath of cold water 1 ml arsenomolybdate reagent was added with shaking. The resulting solution

was made to 10 ml with water and after 10 minutes, the colour was measured on an Eel colorimeter with 608 filter (660 $m\mu$ ) vs a reagent blank. Per cent transmission was calibrated with a glucose standard curve.

### (vi) Qualitative identification of polysaccharide by the Molisch ($\alpha$- naphthol) test.

1 ml sample was mixed in a test tube with 2 to 3 drops of a 1% alcohol solution of $\alpha$- napthol. 2 ml conc. analar $H_2SO_4$ was added down the side of the tube, and the tube rotated without allowing the solutions to mix. A purple interphase denoted the presence of polysaccharide. Like the quantitative methods, this test also can be interfered with by other reducing agents.

### (vii) Identification of monosaccharides by paper chromatography.

Sulphate was removed from the hydrolysed solutions by precipitating it out as barium sulphate. 15 g $Ba(OH)_2$ was ground in a mortar and stirred into the 1N $H_2SO_4$ solution gradually until the pH was just on the acid side of neutral. The precipitate was centrifuged and the supernatant retained. The residue was washed once in water to release any co-precipitated sugars, centrifuged and the combined supernatants were passed through biodeminirolit resin until all salts were eliminated. The liquid was rotary evaporated down to approx. 1 ml and this together with glucose, mannose, galactose, xylose, arabinose, fucose and rhamnose samples were spotted in two sets on Whatman No. 1 chromatography paper. The paper was irrigated by a descending solvent of pyridine : ethylene acetate: water (50:120:40 by vol) for 16 hours. The paper was hung to dry, examined by ultra-violet light for fluorescent and salt contaminants, and then halved so that one set was developed by the alkaline silver nitrate method (Trevelyan et al. 1950) and the other by aniline oxalate (Wilson 1959).

## Alkaline silver nitrate method.

### Reagents.

(a) 1 ml saturated silver nitrate solution was diluted with 100 ml acetone and water was added dropwise until the precipitate formed just dissolved.

(b) 2 g sodium hydroxide was dissolved in 5 ml water and diluted to 100 ml with ethanol to give a 0.5 M alcoholic solution.

### Procedure.

The paper was dipped rapidly through the silver nitrate reagent, hung to dry for 15 minutes, then dipped through sodium hydroxide solution until the spots had developed a required intensity. Continued development causes the background colour to darken and the excess reagents were removed by dipping the paper through 6 N ammonia solution and then washing it under running water for 2 hours. It was stiffened with a rinse of ethanol and hung to dry.

### Aniline oxalate method.

### Reagents.

4.5 ml aniline and 6.3 g oxalic acid were dissolved in 100 ml water. 5 g trichloroacetic acid was added and the mixture was poured into 500 ml acetone and made to one litre with the same. The paper was dipped through this solution and hung to dry in a hot cupboard at 100°C. for 5 to 10 minutes or until the spots developed maximum intensity.

The aniline oxalate method is to be preferred to the alkaline silver nitrate method because the sugar spots can be distinguished more readily. Pentoses develop an orange colour and hexoses a yellow colour, so that by spotting the standards on either side of the sample thus: glucose + mannose + xylose + rhamnose and galactose + arabinose + fucose, a clear separation is obtained (plate 4 p705). The advantages of the silver nitrate method are its stronger sensitivity and ability to show up low sugar concentrations, and also the permenance of the developed colour.

### (viii) Carbon determinations.

Organic matter was determined as carbon, using the Walkley-Black (1947) wet-oxidation method. 0.2 - 1.0 g soil or soil residue was ground to 100 mesh and placed in a 600 ml erlenmeyer flask. 10 ml 1N $KCr_2O_7$ was added followed by 20 ml conc. $H_2SO_4$. The mixture was swirled for a minute and stood for 30 minutes. 10 ml 80% $H_3PO_4$, a spatula of solid NaF and a few drops of ferroin were added in order. The excess $KCr_2O_7$ was back-titrated with 0.5 N ferrous ammonium sulphate and the percent organic matter calculated from the Walkley-Black formula:-

$$\% \text{ OM} = \text{ml x N } KCr_2O_7 \left\{ 1 - \frac{\text{ml titre}}{\text{ml blank}} \right\} \frac{12}{4000} \text{ x } \frac{1.72}{0.77} \text{ x } \frac{100}{\text{wt. sample}}$$

where 1.72 is the conversion factor which assumes the organic matter is 58% carbon, and 0.77 is the percent oxidation found to be valid for most soils. Neither of these assumptions can be taken for granted, particularly in the case of the soil residues, but the calculation has been used for comparative and semi-quantitative measurements.

### (xi) Use of anion exchange resins as a source of fluoride.

Amberlite IRA 400 (1 me/ml), a strong base resin, and Amberlite IRA 45 (2 me/ml), a weak base resin were saturated with fluoride and then sieved to remove resin finer than 300 mesh. 10 g soil was added to various amounts (4 to 16 ml) resin and shaken gently by hand to avoid breaking up the resin which appeared rather fragile. The resin + soil were centrifuged and the supernatant was removed. In one case resin + residue were washed with NaOH at pH ~ 8.4 and then centrifuged, although it would have been better at that point to have separated the resin before attempting to remove adsorbed organic matter with dilute NaOH.

## 3. Search for optimum conditions for the extraction of organic matter with sodium fluoride.

The following experiments were exploratory. Many early results had to be discarded because of interference by plastic artefacts as described in Chapter XVI. The results shown in Tables 91 and 92 are for a limited number of experiments, made during the search for optimum conditions of extraction and reproducible conditions for analysis.

Exp 99 Comparison of extractions made at pH 6 - 7 and pH 10 - 11.

The primary interest had been to see whether organic matter could be extracted quantitatively from allophane soils by sodium fluoride at neutral pH. Table 91 shows that the polysaccharide content obtained from Dunlop $B_{2g}$ when the pH was controlled between 6 and 7 with HCl, was about the same as that obtained when the pH was allowed to rise to 10 or 11. In each case approx. 2 mg polysaccharide/g soil or $\sim$ 27% of the total soil polysaccharide was extracted. Analysis of the residues suggested that at neutral pH slightly more polysaccharide and organic matter had been extracted than at raised pH. The alkaline extracts were a darker colour than the neutral extracts and this probably reflected changes made in the organic polymers by the alkali.

Table 91 % extractions of soil polysaccharide and organic matter by saturated sodium fluoride solution (200 ml/10g soil).

| Soil and extraction pH | Treatments | Extractions | | | | |
|---|---|---|---|---|---|---|
| | | polysaccharide | | | organic matter | |
| | | mg/g soil | % soil | % total p.s. | % in residue | %extract |
| Dunlop $B_{2g}$<br>pH 6 - 7 | NaF 1st | 1.70 | | | | |
| | $H_2O$ wash | 0.36 | | | | |
| | NaF 2nd | 0.075 | | | | |
| | Total | 2.035 | 0.20 | 27.5 | | 58.21 |
| | Residue | ~4.5 | 0.45 | ~61.0 | 1.30 | |
| Dunlop $B_{2g}$<br>pH 10 - 11 | NaF 1st | 1.60 | | | | |
| | $H_2O$ wash | 0.36 | | | | |
| | NaF 2nd | 0.02 | | | | |
| | Total | 1.98 | 0.20 | 26.8 | | 53.38 |
| | Residue | ~5.1 | 0.51 | ~69.0 | 1.45 | |
| Dunlop $B_{2g}$<br>pH 7 - 7.8 | NaF 1st | 1.60 | | | | |
| | NaF 2nd | 0.11 | | | | |
| | Wash 1-6 | 0.74 | | | | |
| | Total | 2.45 | 0.25 | 33.1 | 1.41 | 54.67 |
| Dunlop $B_{2g}$<br>pH 8.2 | NaF 1st | 1.2 | | | | |
| | NaF 2nd | 0.33 | | | | |
| | $H_2O$ wash | 0.47 | | | | |
| | NaF 3rd | 0.1 | | | | |
| | Total | 2.1 | 0.21 | 28.38 | n.d. | n.d. |

Table 92 <u>% extractions of soil polysaccharides by sodium fluoride, F-anion exchange resins and control solutions.</u>

| Soil and extraction pH | Treatments | Polysaccharide extractions. | | |
|---|---|---|---|---|
| | | mg/g soil | % soil | % total p.s. |
| Dunlop $B_{2g}$<br>pH ~ 5.2 | Strong resin | 0.1 | | |
| | NaOH wash 1st (pH 8.0) | 0.35 | | |
| | NaOH wash 2nd (pH 8.0) | 0.1 | | |
| | Total. . . . . . . . . . | 0.55. . . | 0.06. . | 7.4 |
| pH ~ 5.6 | Weak resin | 0.1 | 0.01 | 1.4 |
| pH ~ 5.7 | $H_2O$ | 0.24 | 0.02 | 3.24 |
| pH ~ 5.7 | 1M NaCl | 0.13 | 0.01 | 1.76 |
| Dunlop $A_1$<br>pH ~ 8.0 | NaF 1st | 5.28 | | |
| | $H_2O$ wash | 2.28 | | |
| | Total. . . . . . . . . . | 7.56. . . | 0.76. . | 25.2 |
| | Residue | 14.4 | 1.44 | 48.0 |
| Amlaird $B_{2g}$<br>pH 6-7 | NaF 1st | 1.15 | 0.12 | 19.5 |

### Exp. 100 Comparison of the influence of charge effects on the extractions.

Allophane becomes negatively charged in the region pH 6 to 7 and it was assumed that at this pH there would be negligible positive charge to inhibit the release of organic matter. One of the products of the NaF - allophane reaction however was found to be $\kappa$-$Al_2O_3$ (Chapter X p. 448) with a positive charge retained to pH 8.0. If the role of positive charge in holding organic matter was important in the extraction, pH 8.0 - 8.5 might be more favourable than pH 6 - 7. Table 91 shows that for two NaF extractions and one water-wash, the amount of polysaccharide obtained was exactly the same as for the extractions at pH 6 - 7 and pH 10 - 11 ie. 2 mg/g. Hence in this case the charge effect was not significant.

### Exp. 101 Extraction of organic matter with F-anion exchange resins.

It was thought that the use of F-anion exchange resins might provide an alternative source of fluoride and an alternative sink for hydroxyl ions. In addition they would dispense with the inconvenience of large salt concentrations. The problem was to have the resins take up the $OH^-$ ions without at the same time taking up organic matter. Preliminary trials, as shown in Table 92 p.695 were not successful. It was hoped to pursue the experiments and control organic matter uptake either by increasing the suspension acidity to lower the organic matter negative charge and/or by introducing minimum quantities of resin sufficient to take up the strongly adsorbed $OH^-$ ions only. The resin experiments were temporarily abandoned however, because through them, the writer came to realise the importance of controlling equilibria and the possibility of obtaining optimum conditions for the sodium fluoride extraction by considering the various equilibria carefully as outlined below.

### Exp.102 Control of the equilibria in sodium fluoride extractions.

The formation of cryolite in the suspension when alumino-silicates are treated with sodium fluoride indicates that the reaction is of the form:-

$$Al(OH)_3 + 6\,Na^+ + 6F^- \longrightarrow Na_3AlF_6 + 3Na^+ + 3OH^-,$$

but cryolite dissolves in alkali, so that addition of acid is necessary for it to precipitate as an insoluble salt. The reaction is thus sustained by introduction of $H^+$ ions to the suspension. This displaces the equilibrium to the right by removing the $OH^-$ ions as water and the other products as precipitate. The principle is inherent in the methods used by Romo and Roy (1957), Birrell (1961) and Bracewell et al. (1970). Alternatively or in addition, one can reinitiate the reaction by physically removing the reaction products ie. by centrifuging off the supernatant and adding fresh NaF to the residue (Huang and Jackson 1965). These procedures of sodium fluoride dissolution of allophane were discussed in Chapter II 12 p.40.

It is clearly desirable to choose the fluoride salt which gives rise to the most insoluble fluoaluminate. Table 93 p.699 shows their solubilities (Seidell and Linke 1958). The most insoluble of the series is sodium fluoaluminate with 0.417 g/1000 g water at 25°C. It is worth noting however, that this solubility is increased by addition of chloride which competes for aluminium.

One concludes that maximum displacement of the equilibrium would be achieved by using sodium fluoride and controlling the pH of the reaction with HF rather than HCl. A solution of NaF + HF was used by Birrell (1961).

Table 93 Solubilities of fluoaluminates at 25 °C.

(compiled from Seidell and Linke 1958).

| fluoaluminate in $H_2O$ | g/1000g saturated solution |
|---|---|
| $(NH_4)_3\ AlF_6$ | 7.66 |
| $K_3AlF_6$ | 1.43 |
| $Na_3\ AlF_6$ | 0.417 |
| fluoaluminate in aluminium chloride<br>mmoles/1000 moles $H_2O$ | |
| $Na_3AlF_6$ | $Al_2Cl_6$ |
| 0.66 | 0.5 |
| 1.14 | 1.02 |
| 2.94 | 3.23 |

Optimum pH conditions might be partly governed by the charge on the allophane and the relative importance of this in retention of organic matter remains to be examined.

Exp. 103 Minimum number of extractions required.

Table 91 p.694 shows that most of the extractable Dunlop $B_{2g}$ polysaccharide or 1.6 - 1.7 mg/g soil was mobilised in the first extraction, while only 0.11 mg/g was obtained when this was followed by a second NaF treatment. (The pH 8.2 results are less comparable since only 4 hours shaking were allowed for the extractions instead of 16). When the first extraction was followed by water washing however, 0.36 mg/g was obtained. This result was quite general and could be seen visually in the stronger colour of the water extracts compared to subsequent sodium fluoride extracts. High salt concentrations thus 'salted in' organic matter so that it was adsorbed on the clay. The same effect was shown in the smaller amount of polysaccharide extracted by the NaCl control than by the water-only control (Table 92 p.695). It was concluded from these findings that one NaF extraction, followed by one or possibly two water washings was sufficient to release most of the NaF- extractable organic matter in the B horizon. For the Dunlop $A_1$ horizon, polysaccharide content of a second NaF extraction is not shown in Table 92 because the sample was lost when the centrifuge bottle broke. The pH however, only rose from 6.7 to 7.6 during the second NaF addition, so that evidence suggests a surface horizon would require one extraction followed by two or three water washings.

## Conclusions on optimum extraction conditions.

It was noted in Chapter X p.439 that the reactivity of NaF with dry soil was greater than with wet soil, and that the reciprocating shaker was more efficient than the rotary shaker. These observations together with those made in the experiments described above, suggest that for optimum extraction conditions the following procedure should be used:-

### Extraction.

200 ml saturated NaF solution is added to 10g air dry soil and the pH maintained at approx. 6 with an HF solution. The suspension is shaken on a reciprocating shaker and the pH adjusted at intervals if necessary. It is centrifuged at 10,000 rpm and the supernatant removed for analysis. The residue is reshaken in water

for some hours, centrifuged at 10,000 rpm and the supernatant removed. This step is repeated where necessary and as gauged from the colour of the extract. It may be useful to give the final wash in NaOH at pH 8.2 in order to detach any organic matter held electrostatically by K - $Al_2O_3$.

Salt removal: At the extraction pH of 6 most of the fluoride will probably be in the form of cryolite and a simple method for removing this is required. One might use the property that it is soluble in alkali or the property that it is more insoluble in acid than in water. The latter is the most convenient, since cryolite would be precipitated during acid hydrolysis of the polysaccharide. Its subsequent peptisation during the charcoal washing step may be prevented by washing with dilute $H_2SO_4$ instead of water. The small amount of dissolved salt can be removed after precipitation of sulphate by leaching the solution through biodeminrolit resin.

Estimation of the non-humified organic matter: This fraction is obtained separately by the method of Ford, Greenland and Oades (1969), in which soil is vibrated in a bromoform-petroleum spirit mixture containing a surfactant such as Aerosol OT - 100, and the light fraction is removed by flotation. This method has not yet been tried by the writer. It is essential in future however, that the contribution particularly of inert cellulose, to the polysaccharide content of the whole soil should be measured, in order that the efficiency of the sodium fluoride in extracting clay-sorbed organic matter can be assessed.

## 4. Exp.104 Identification of the polysaccharide sugars by paper chromatography.

The sugar composition of soil polysaccharides is normally very uniform and it was wondered whether allophane-held polysaccharide would differ in this respect.

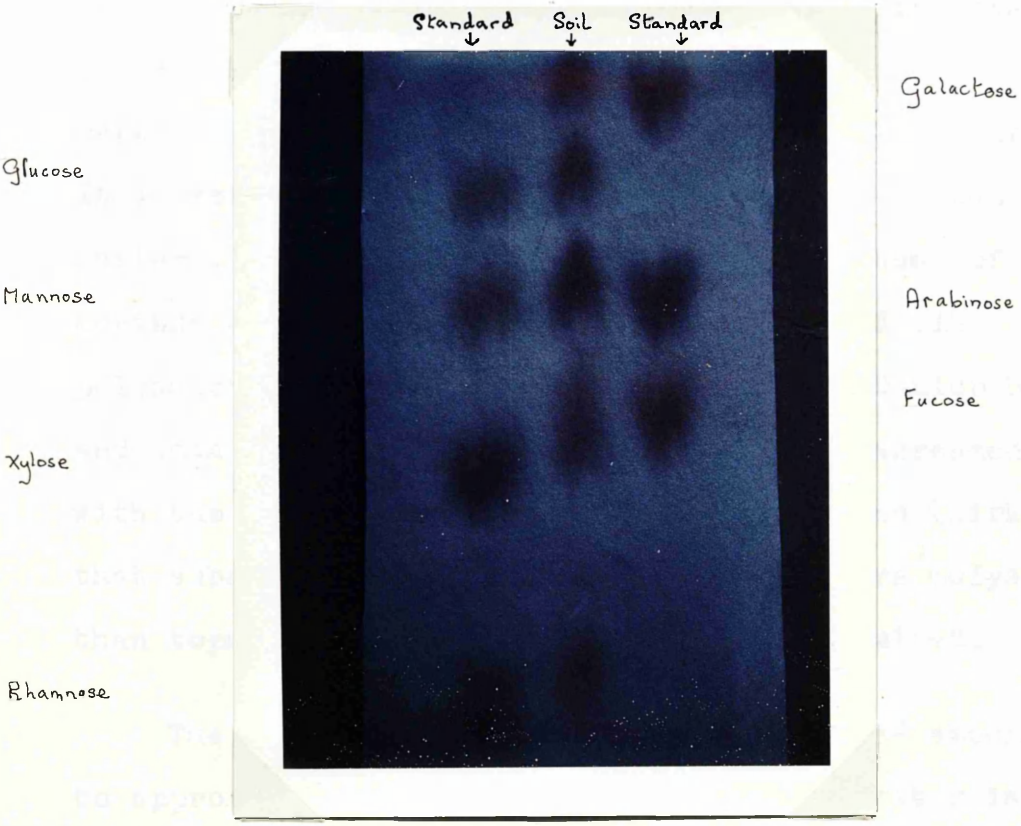
The hydrolysed polysaccharide extract, freed of salt, was evaporated down to ~ 1 ml on a rotary evaporator. 20 - 25 capillary drops normally proved optimum for a discernible reaction with aniline oxalate. Best sugar separation was achieved with pyridine : acetyl acetate : water solvent.

Whole soils and extracts of Dunlop $A_1$ and $B_{2g}$ horizons were found to contain glucose, galactose, mannose, rhamnose, fucose, xylose and arabinose (plate 4 p.705). These are the sugars normally found in soil. In Amlaird $A_1$, rhamnose, fucose, glucose and possibly galactose were identified. Of the remaining sugars, alkaline silver nitrate showed a spot whose position could be due to mannose or arabinose, but aniline oxalate failed to develop its colour to enable identification. Xylose appeared to be absent. The chromatogram requires repetition with stronger concentrations.

Plate 4

Chromatogram of Dunlop $A_1$ hydrolysed extract and standard sugars.

(solvent: pyridine/ethyl acetate/water
developer: aniline oxalate)



## 5. Discussion of the sodium fluoride-organic matter extraction.

Table 94 p. 707 shows the total percent organic matter and polysaccharide figures for the $A_1$ and $B_{2g}$ horizons of Dunlop (1970) and Amlaird together with the percent polysaccharide and organic matter extracted. (Dunlop $B_{2g}$ soil collected in 1970 was low in organic matter at 3.11% compared to that normally found ie. 5-6%). It is seen that the polysaccharide content of the organic matter increased as the organic matter content of the horizon decreased, with 18.5, 19.1, 23.8, 34.1% polysaccharide for Dunlop $A_1$, Amlaird $A_1$, Dunlop $B_{2g}$ and Amlaird $B_{2g}$ respectively. This is in agreement with the finding of Greenland, Lindstrom and Quirk (1962) that subsoils contained proportionately more polysaccharide than topsoils for the Australian soils examined.

The polysaccharide extracted by the NaF amounted to approx. 30% for the Dunlop soils (the writer is taking into account the incomplete extraction of $A_1$ mentioned on p.702), and approx. 20% for the Amlaird soil, although this figure, which depended on only one result, is less certain. In the case of the Dunlop soils, 30% would seem to account for all the allophane-held polysaccharide because further extractions yielded

Table 94 % total and NaF-extracted organic matter and polysaccharide in some Dunlop and Amlaird soils.

| Soil | % soil as OM | % soil as p.s. | % OM as p.s. | % OM extracted | % p.s. extracted |
|---|---|---|---|---|---|
| Dunlop (1970) $A_1$ | 16.20 | 3.00 | 18.5 | n.d. | 25.2 |
| Dunlop (1970) $B_{2g}$ | 3.11 | 0.74 | 23.8 | ~58.0 | 27.0 |
| Amlaird $A_1$ | 12.46 | 2.38 | 19.1 | n.d. | n.d. |
| Amlaird $B_{2g}$ | 1.72 | 0.59 | 34.1 | n.d. | 19.5 |

only negligible amounts, while hydroxyl release was as great for the second extraction as for the first, and continued on addition of several further aliquots of NaF. One may suppose then that about 30% of the polysaccharide was held by the allophane and the remaining 70% was present as inert cellulose, or held on crystalline clay, or enclosed within aggregates, or perhaps remained associated with $\kappa$-$Al_2O_3$. Swincer and Oades (1968) recovered two fifths of the soil carbohydrate in the light fraction ie. 40% of it was non-humified cellulose. If one assumes a similar proportion for the Dunlop soils, then $\sim$ 50% of the adsorbed soil polysaccharide was extracted by NaF.

Analysis of the residue estimated that $\sim$ 58% of the total soil organic matter was extracted. Too much weight should not be placed on the figure at this stage. The Walkley-Black method and its assumptions for example, may not be as applicable to 'residual' soils as to the original soils. Nevertheless and even with this caution, the percent organic matter extracted at pH 6 - 7 must be in the region of 50, and this is a high figure for such a mild technique.

It appears then that at least half the organic matter was held by allophane. This is in agreement with the observations of Jackman (1964), Wada and Inoue (1967) and in "Soils of New Zealand" (1968) that allophane has strong affinity for organic matter and allophane soils accumulate it in large amounts (Chapter V 5 p.258).

The results for the surface water gley soil are also interesting. Preliminary NaF tests showed (Chapter IX p.432) that it contained negligible allophanic material in all horizons. Later tests and its flocculation properties (Chapter XIII) indicated the presence of a significant amount and the organic matter extraction supports this. Sodium fluoride released 19.5% of the total polysaccharide, and although this figure is tentative, it would appear that an influential amount of allophane is present. It may be almost entirely associated with organic matter.

Perhaps of greatest interest to the organic chemist is the finding that a large and predictably representative fraction of soil organic matter can be made available for analysis in virtually undegraded form. To the writer's knowledge, sodium fluoride has never been used for this purpose, because of its inefficiency as a reagent for normal soils. However, if the procedure is reversed, and instead of starting off with a soil and looking for a suitable extractant, one starts off with an extractant and looks for a suitable soil ie. a soil containing allophane, then one can achieve the long-sought goal of separating organic matter from mineral soil in a form unaltered from its form in situ: unaltered that is, except with respect to the loss of bonding substrates such as metal ions and hydroxylated clay surfaces whose removal may to some extent affect polymer configuration and reactivity.

These soils are not rare soils as formerly supposed. In Scotland they are widely developed on the carboniferous and tertiary lavas, and are also found in the subsoils of podzols. The writer suggests that allophane soils provide an ideal starting point for the systematic study of soil organic matter.

# CHAPTER XV : PHOSPHATE PROBLEMS IN DARLEITH SOILS.

## 1. Introduction.

Chapter VIII p.322 should be referred to for discussion of the problems of phosphate availability in soils containing allophane. In brief, it was the finding of Forestry Commission workers that spruce checked on Darleith brown forest soils and their opinion that this was caused by phosphate deficiency which led the writer to suppose that the deficiency was connected with the soils' allophane content. Many New Zealand allophane soils are reported to have high phosphate retention and low phosphate availability, and it was thought the same situation might apply in the Darleith soils. Further investigation by the Forestry Commission however, found that phosphate availability in the soils was adequate, but that poor growth was almost certainly caused by phosphate deficiency, because P-levels in the spruce needles were very low. From this and other evidence outlined in Chapter VIII, the writer postulated that the deficiency might be caused by toxic levels of soluble aluminium in the soil produced as a result of its high allophane content. Experiments were thus conducted, first with the idea that phosphate fixation might be a problem in the soils, and later with the alternative idea that excess soluble aluminium might be the problem.

## 2. Exp.105 Determination of available phosphate by the citric-soluble method. (Dyer 1894).

Reagents.

1% citric acid

5% ammonium molybdate

60% perchloric acid

Reducing reagent: 0.125 g 1,2,4-aminonapthol sulphonic acid was mixed with 44 ml 15% sodium bisulphite. 20% sodium sulphite was added dropwise until the solution was clear.

Procedure.

10 g samples $<$ 2mm Dunlop and Amlaird soils were taken

in duplicate and shaken with 1 g citric acid in 100 ml water on a rotary shaker for 16 hours. The soils were filtered into 100 ml conical flasks through Whatman No. 42 filter paper. Filtrations were repeated through fresh filter paper until the filtrates were absolutely clear. The phosphate concentration was determined colorimetrically by King's method (King 1932). 1 ml sample, 1 ml $HClO_4$, 1 ml ammonium molybdate and 0.5 ml reducing agent were pipetted in order and made to 10 ml with water in volumetric tubes, the solutions being thoroughly mixed. Standards containing 0 - 5 μg P/ml were similarly prepared. Readings were made after 15 minutes on a Bausch and Lomb colorimeter at 622 mμ vs. a reagent blank. The readings were reproducible for at least a further 15 minutes.

## Results and Discussion.

Table 95 gives the available P as citric-soluble P in mg/100 g OD soil, and these figures are of the same order as those obtained in previous years. It is seen that all samples except Amlaird $A_1$ released high to very high citric-soluble P. These results are in disagreement with the findings of the Kilmarnock Soil Survey Memoir (Mitchell and Jarvis 1956) of low available P measured as acetic-soluble, in all the Drumboy Dunlop horizons

Table 95 Citric soluble phosphate in Dunlop and Amlaird soils.

| Soil | mg P/100 g OD soil | Soil | mg P/100 g OD soil |
|---|---|---|---|
| Dunlop $A_1$ | 33.5 | Amlaird $A_1$ | 6.3 |
| B2g | 52.4 | Aeg | 16.1 |
| B3gx | 47.4 | B2g | 17.3 |
| $C_g$ | 40.3 | C1G | 26.8 |
| | | C2 | 31.4 |

(pH 1% citric acid = 2.45. pH final suspensions 2.65 - 2.85).

Scale of values for available P as citric soluble P

| mg/100 g OD soil | value |
|---|---|
| > 16 | very high |
| 10 - 16 | high |
| 5 - 10 | satisfactory |
| 2.5 - 5 | low |
| < 2.5 | deficient |

except $C_g$; and also with the general observation that surface water gleys are low or deficient in P. The discrepancy might lie (a) in the method of analysis (b) in differences in the state of the soil analysed or (c) in the method of extraction. (a) The 1,2,4 amino-naphthol sulphonic acid method, of which the King's is a variant, is often preferred to other methods because of its relative freedom from difficulty and interference : for example, it is reproducible over a wider range of acidity than other molybdate methods, and it is unaffected by up to 200 μg/ml ferric iron. Hence it is not thought to be at fault. (b) Jackson (1962) maintained that an air-dried soil may increase extractable P by 10 - 30% and recommended soils should be analysed moist, as soon after sampling as possible. Some error therefore may have been introduced here. The most likely source however is (c), in the extraction technique.

Extraction methods aim to achieve the best correlation between the phosphate dissolved by the extractant and the phosphate taken up by the plant, or alternatively, the response of a crop to phosphate fertiliser. Hence an extractant valid in this respect for one type of soil and crop, may not give correlations for another type of soil, or for a different crop. There is indeed 'no chemical method of measuring available phosphorous in an unknown soil' Hesse (1971). 1% citric is one of several acid extractants but is also a strong complexing agent and its pH 2.45 is rather lower than the others. These include 0.002 N $H_2SO_4$ pH 3 (Truog 1930), and 2.5% acetic acid pH 3 (Williams and Stewart 1941). This last method is widely used in Scottish soil laboratories and was developed to meet the needs of advisory services in the north-east. The writer understands that no work has yet been done on the suitability of the 2.5% acetic acid extraction method for the particular case of Darleith soils. The New Zealand Soils Bureau however employs a 1% citric acid method (Metson 1961) for routine determination of available phosphate in all soils, including allophane soils, and one assumes correlations have been made.

Williams et al. (1958) showed that for a range of Scottish soils phosphate sorption was most highly correlated with Tamm-oxalate (pH 3.2) extractable aluminium and also with 2.5% acetic acid (pH 3.0) extractable aluminium. Thus soils dissolving large amounts of aluminium with these extractants might be expected to release considerable phosphate. Williams et al.

further showed that soils developed from basic igneous rocks dissolved the greatest quantities of $Al_2O_3$ ; 1.59% and 0.16% $Al_2O_3$ with Tamm oxalate and HOAc respectively, compared to 0.97 and 0.13% respectively for three other soil groups. The citric acid extracts of Exp. 105 were analysed for $Al_2O_3$ content in Exp. 108. Table 98 p.733 records that Dunlop $B_{2g}$ dissolved 1.58% $Al_2O_3$ and Amlaird $B_{2g}$ dissolved 0.36% $Al_2O_3$. In comparing a citric acid extraction with a Tamm-oxalate extraction one would normally expect that the oxalate ($pK_{a1} = 1.25$) would be more effective than the citrate ($pK_{a1} = 2.94$) so that this result would appear to indicate proportionately more extractable aluminium in the Darleith lava soil that the basic igneous soils investigated by Williams et al. A direct comparison with Tamm-oxalate (pH 3.2) is not possible however, because the pH of a 1% citric acid solution was found to be 2.45 and the final pH of the suspensions ranged between 2.62 and 2.85. Large amounts of aluminium would have been released as a result of the acidity, as well as of the complexing action.

The concentrations of citric-soluble phosphate can thus be interpreted as the direct result of the solubility of the aluminium in the citric acid medium. Unfortunately no information is yet available on how much alumina is dissolved from the Darleith soils by 2.5% acetic acid at pH 3.0. One can predict that it will be higher for the Dunlop soils than for other soils on two sources of evidence. In the first place, the resin extractions (Table 76 p.596) in which ~ 600 mg $Al_2O_3$/100 g soil was taken up from Dunlop $B_{2g}$ or about 20 times the amount taken up from Amlaird $B_{2g}$, suggest the Dunlop soil contains mobile aluminium. In the second place, it is relevant to recall the work of Mattson and Hester (1933) in their paper on "The amphoteric nature of soils in relation to aluminium toxicity." These authors showed that soils with low silica : sesquioxide ratios and high isoelectric point dissolved, at the same pH, dramatically larger quantities of alumina than did soils with a higher silica : sesquioxide ratio and lower isoelectric point. This was illustrated in Tables 50 and 51 pp 337 and 338. Sassafras soil, for example, with a $SiO_2 : R_2O_3$ ratio of 1.89 dissolved 5.2 mg $R_2O_3$ at pH 3.6, while Sharkey soil with a $SiO_2 : R_2O_3$ ratio of 3.18 dissolved only a trace. Although solubility differences between the two soils tended to narrow as the pH decreased, nevertheless the authors' observations lead one to expect that the aluminous allophanes in the Darleith soils would release larger amounts of aluminium to the extracting solvent than other soils. This is not only, as previously supposed, on account of their amorphous character, but the inevitable consequence of a high isoelectric pH and positive charge.

It must next be considered how far the acid-soluble results are relevant to phosphate availability. There are several effects to be separated to clarify discussion. (a) The excess dissolution of alumina due to the amount of allophane present. (b) The excess dissolution in cases where the $SiO_2 : Al_2O_3$ ratio is low. (c) The excess dissolution due to the low extraction pH of the citric acid : 2.62 - 2.85. (d) The excess dissolution due to the use of citric acid rather than the more widely used acetic acid. This latter effect is usually taken care of by correlating values for low and high available P with $< 5$ and $> 16$ mg/100g as citric soluble P and $< 1.3$ and $> 4.4$ mg/100g as acetic soluble P respectively. Table 98 shows Dunlop $B_{2g}$ released 52.4 mg citric-soluble P while only 0.46 mg was found as acetic-soluble P (Mitchell and Jarvis 1956), so that available P was extremely high in the first case and rather low in the second. The high results for both Dunlop and Darleith soils can be explained by the low extraction pH developed and suggest the unsuitability of citric acid as an extractant; but it is difficult to see why the acetic-soluble values obtained by Mitchell and Jarvis were so low for the Drumboy Dunlop profile. In general the Darleith brown forest soils are reported to have adequate acetic-soluble P (D.B. Patterson pers. comm. 1971), and this finding is consistent with the solubility of Darleith aluminium.

There appear to be two possibilities: either the acetic-soluble method does not correlate with phosphate availability, phosphate is unavailable and the pH in the neighbourhood of the plant root is less acid in these soils than broadly assumed in the acid extraction methods. Or there is a correlation in the direct sense of phosphate availability; but conditions are severely toxic due to soluble aluminium and plants are unable to take up and/or metabolise the phosphate, unless specially adapted.

## 3. Exp.106 Phosphate retention in Dunlop soils.

The object of this experiment was to determine the extent of phosphate sorption in each horizon of Dunlop soil and also the influence of both allophane and organic matter on the sorption capacity. The readiness of the soil to release the phosphate was also to be examined.

### Method.

10 g air-dry < 2mm samples were taken from each horizon. In addition (a) a $B_{2g}$ sample was peroxidised in 30 ml water with 10 ml $H_2O_2$ (b) $B_{2g}$ and $C_g$ samples were each treated with aliquots of saturated sodium fluoride solution, with water-washing between each treatment, until the pH of the suspensions failed to rise higher than 8.0 in 30 minutes. A total of 250 ml NaF solution was required. These three specially prepared samples were air-dried before use.

A series of 100 ml $KH_2PO_4$ solutions containing 10, 35 and 310 mg P/100 ml were added to the 10 g samples and these were shaken on a rotary shaker for 16 hours. The soils were centrifuged and the supernatants analysed for phosphate by King's method. The residues were shaken for a further 16 hours in 100 ml water, centrifuged and their supernatants analysed. The combined phosphate concentrations found in the 1st and 2nd supernatants represented unadsorbed phosphate, and the adsorbed phosphate was thus: phosphate added minus phosphate in supernatant.

An attempt was then made to determine the amount of phosphate retained by the soil ie. resistant to a 1% citric acid extraction. The soil residues were shaken for 16 hours in 100 ml 1% citric acid solution and the citric-soluble phosphate was measured. Citric-soluble P from the treated soils minus citric-soluble P from the untreated soils (shown in Table 95 p.714 but given air-dry values) represented the available -P which had been re-extracted from the added -P. This figure subtracted from the added -P gave the phosphate -P which the soil held in unavailable positions.

The experimental results are shown in Tables 96 and 97. Bearing in mind that the figures are the result of only one experiment in each case, the following observations can be made at this stage:-

(a) Phosphate uptake in the $A_1$ horizon was slightly less than for the subsoils at low and medium (10 and 35 mg) additions of phosphate. In the highly saturated

Table 96 Phosphate retention in Dunlop soils.

(10 g soil shaken 16 hrs. with 35 mg P/100 ml water).

| Soil | mg P/10g air-dry soil | | | | | % P-retained per 10 g OD soil |
|---|---|---|---|---|---|---|
| | P uptake | citric - soluble P | | | P-retained | |
| | | Total | original soil | P-saturated soil | | |
| A1 | 24.7 | 12.5 | 3.2 | 9.3 | 15.4 | 66.1 |
| B2g | 29.5 | 21.5 | 5.0 | 16.5 | 13.0 | 46.2 |
| B3gx | 27.3 | 18.5 | 4.6 | 13.9 | 13.4 | 50.7 |
| Cg | 28.6 | 19.5 | 3.9 | 15.6 | 13.0 | 47.4 |
| B2g NaF treated | 0.4 | 5.9 | 5.0 | 0.9 | -0.5 | nil |
| Cg NaF treated | 0.1 | 3.7 | 3.9 | -0.2 | 0.3 | nil |
| B2g $H_2O_2$ treated | 33.0 | 36.5 | 5.0 | 31.5 | 1.5 | 4.7 |

Table 97 Phosphate retention in Dunlop soils.

| Soil | mg P/10 g air-dry soil | | | | | % P retained per 10g OD soil |
|---|---|---|---|---|---|---|
| | P uptake | citric - soluble P | | | P retained | |
| | | Total | Original soil | P-Saturated soil | | |
| (10 g soil shaken with 10 mg P/100 ml water) | | | | | | |
| $A_1$ | 8.7 | 6.0 | 3.2 | 2.8 | 5.9 | 71.6 |
| $B_{2g}$ | 9.4 | 10.0 | 5.0 | 5.0 | 4.4 | 49.2 |
| $B_{3gx}$ | 9.3 | 8.7 | 4.6 | 4.1 | 5.2 | 57.9 |
| $C_g$ | 9.2 | 8.7 | 3.8 | 4.9 | 4.3 | 48.9 |
| (10 g soil shaken with 310 mg P/100 ml water) | | | | | | |
| $A_1$ | 66.6 | 31.9 | 3.2 | 28.7 | 37.9 | 60.3 |
| $B_{2g}$ | 100.7 | 53.4 | 5.0 | 48.4 | 52.3 | 54.5 |
| $B_{3gx}$ | 101.8 | 43.2 | 4.6 | 38.6 | 63.2 | 64.1 |
| $C_g$ | 59.7 | 41.4 | 3.8 | 37.6 | 22.1 | 38.7 |

(310 mg) case, the $A_1$ phosphate uptake was considerably less than for the $B_{2g}$ and $B_{3gx}$ soils, but more than for the $C_g$. These results are in rough agreement with the soils' comparative amounts of allophane content as measured by the sodium fluoride test. It will be recalled that the rise in pH for the $A_1$, $B_{2g}$, $B_{3gx}$ and $C_g$ soils after 30 minutes treatment was 9.9, 11.4, 11.1 and 10.4 respectively.

(b) In general % P retention followed the order $A_1 > B_{3gx} > B_{2g} \approx C_g$. There were two exceptions in the case of the highly saturated samples, where $B_{3gx} > A_1$ and $B_{2g} \gg C_g$. The order of retention was governed by the 'total citric-soluble' extractions. One notes from these figures that the $A_1$ soil was most prone to retain newly adsorbed phosphate. It released 12.5 mg/10 g soil or only 9.3 mg of the added P. The $B_{2g}$ soil was most prone to release the newly adsorbed phosphate; citric acid extracted a total of 21.5 mg, or 16.5 mg of the added P.

(c) This behaviour of the $B_{2g}$ soil in readily releasing the adsorbed phosphate was accentuated in the peroxidised sample. Table 96 shows that it took up almost all the phosphate that was offered it, but retained only 4.7% on citric acid extraction.

(d) The sodium fluoride treated soils were virtually inert to phosphate addition. Their total citric-soluble values were almost identical with the original ones, suggesting that the phosphate switched sites during the allophane extraction ie. became re-adsorbed by unextracted allophane.

(e) From an experimental point of view, the 35 mg P/10g soil was the most appropriate concentration for the untreated soils. Peroxidised soils required higher concentrations.

## Discussion.

Phosphate retention figures determined immediately after saturation of the soil with phosphate bear no relation to the powers of the soil to 'fix' phosphate over periods of time, and for this reason an experiment of this kind may not be of great significance. Unfortunately its validity could be still further discounted in view of the conclusions reached on p.719 above that the citric-soluble method was too drastic for allophane. On this evidence one would predict that higher percent retention figures would have been obtained by other methods such as the 2.5% acetic soluble method. Nevertheless the percent retention was still fairly high and at ~ 50%

in the subsoils, it is very comparable to the 40 - 50% retention given by Cloos et al. (1968) for their synthetic alumino-silicates of medium and low $SiO_2 : Al_2O_3$ ratio (Table 49 p.333). They extracted with 0.002 N $H_2SO_4$ ie. at pH 3. (Truog 1930).

Further information can be gained by taking the citric-soluble P figures together with the citric-soluble alumina figures given in Table 98 p.733. Dunlop $A_1$ lost least alumina (765 mg/100 g soil) and retained most phosphate P (66.1%). Dunlop $B_{2g}$ lost most alumina (1580 mg/100 g ) and retained least phosphate P (46.2%), and when its organic matter was removed by peroxide treatment, phosphate retention was reduced to 4.7%. Thus, the organic matter appeared to protect the alumina, and consequently the associated phosphate from being brought into solution, while the removal of humate appeared to make it vulnerable, dissolving it, together with the phosphate in large quantities. This might be interpreted as in agreement with the findings of Mattson and Hester (1933) that addition of humate increased the acidoid : basoid ratio of the clay complex, so that its isoelectric pH was lowered and alumina solubility decreased. The hypothesis has yet to be tested on the Darleith soils.

An important result in the retention experiments was that sodium fluoride treated soils were inert to phosphate uptake, suggesting that the allophane fraction accounted for the entire phosphate sorption. This accords with the finding of Williams et al. (1958) that active aluminium gave the highest correlation with phosphate sorption for a range of Scottish soils, and that this aluminium was closely associated with organic matter. One may suppose it was allophanic material. It also accords with the view held by Mattson and now becoming widely adopted, that the amorphous fraction in soils is the most chemically reactive fraction. The Dunlop soils' ferruginous and kaolinite content appear to have offered no alternative sites for immediate phosphate sorption. One concludes that allophane supplies high storage capacity for phosphate. Its usefulness in plant nutrition will depend on the extent to which the phosphate is transferred to less available forms; the rate at which it is released in available form; and the relative ability of plants to extract it under conditions where aluminium is unusually mobile. This last point may be of particular importance to plant husbandry.

## 4. Dissolution of alumina, silica and iron oxide from Dunlop and Amlaird soils in 1% citric acid suspensions.

The object of these analyses was to determine the levels of soluble aluminium in soils under the conditions which the citric-soluble method assumes to exist in the neighbourhood of the plant root surface. It was predicted that the comparative mobility of aluminium in allophane to that in crystalline clay might allow toxic amounts to be released in the environment of the root surface.

### Exp.107 Oxidation of the citric-acid extracts: observations and preparation for analysis.

(a) peroxidation: Citric soluble extracts from Exp.105 were used. It was at first tried removing the organic matter and citrate contents by peroxidation of extract aliquots. About 30 minutes after the addition of a few ml $H_2O_2$ to the extracts, the surface water gley samples and the brown forest soil $A_1$ had flocculated heavily. The other three horizon extracts flocculated some time later. The Amlaird flocs were reddish, Dunlop $A_1$ yellowish and $B_{2g}$, $B_{3gx}$ and $C_g$ were white. This spectacular result suggested that citric acid mobilised iron oxide in the Amlaird soils and alumina in the Dunlop soils.

The pH of the Dunlop $C_g$ extract rose from 2.65 to 5.55 the next day and 5.75 the following day. It must however have risen initially fairly quickly to allow the alumina to precipitate. Thus, the origin and order of flocculation of the extracts was explained. A citric acid blank containing 4 ml $H_2O_2$ had a pH 2.1. The reason for the increase in pH must have been due to the formation of bicarbonates as the citrate decomposed to $CO_2$.

The removal of citrate was monitored by tests with neutral silver nitrate solution, and when after two days, peroxidation failed to remove all the citrate, the method was abandoned in favour of wet-oxidation with oxidising acids.

(b) Acid oxidation: 25 ml aliquots of extract were pipetted into 100 ml conical flasks and evaporated to dryness. (It was noticed in passing, that Amlaird $C_2$ had a pink tinged residue suggesting high manganese content). 1 ml conc. $HNO_3$ was added to each flask and evaporated on a water bath. Then 5 ml of a ternary concentrated acid mixture containing $HNO_3 : H_2SO_4 : HClO_4$ in the proportions 100 : 10 : 40 was added to each flask and the mixture heated on a sandbath at $\sim$ 240°C. After 15 - 30 minutes white fumes appeared and evaporation was continued until these ceased. Unfortunately, the silica was dehydrated by this treatment, for an insoluble white precipitate formed on subsequent dilution and did not redissolve even though the diluted samples were left in the frig for three months.

The precipitates were separated by centrifuging the samples and washing the residues three times in dilute HCl. The combined supernatants were made to 100 ml in dilute HCl. Pellets of NaOH were added successively to the 1 - 2 ml liquid containing the residues until after some hours their precipitates dissolved. A blank containing ~6 pellets dissolved in 1 - 2 ml water was also made, to take account of any reactivity of the concentrated NaOH with the pyrex glass of the centrifuge tubes. The solutions were made to 100 ml and stored in plastic. It was concluded that sodium hydroxide fusion to remove the organic matter and citrate would have been a more convenient procedure.

### Exp.108 Analysis of the citric-acid extracts.

The samples were analysed for $Al_2O_3$, $SiO_2$ and $Fe_2O_3$ using the same analytical methods described in Chapter XIII p. 541 et sequitur. Silica was found mainly in the alkaline fraction, but also in the acid fraction. The blank was negligible. Alumina was found only in the acid fraction. The results are given in Table 98.

## Discussion.

It is seen that the alumina dissolved from the Dunlop soils by citric acid is very high indeed, amounting to 1.58 and 1.44 g/100 g OD soil in the $B_{2g}$ and $B_{3gx}$ soils respectively, and about half this amount or 0.77 and 0.85 g for the $A_1$ and $C_g$ soils. This correlates with their allophane content. The silica extracted was something less than one quarter of the alumina, by weight, except in the $A_1$ horizon. The proportionately lower figure for silica in the surface horizons of both soils could be attributed to the displacement of silica by humate in the allophane complex, but this should be weighed against the finding (Table 74 p.580) that alkaline extraction of the soils released three times more silica from Dunlop $A_1$ than $B_{2g}$ (Chapter XIII Table 74 p.580).

The Amlaird results were higher than might have been expected from preliminary NaF tests, but this is not surprising in view of later evidence from flocculation experiments (Chapter XIII p.649) and organic matter

Table 98 Sesquioxide content of the citric-soluble extracts of Dunlop and Amlaird soils.

| Soil | — mg/100g OD soil — | | | | $SiO_2 : Al_2O_3$ |
|---|---|---|---|---|---|
| | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $P_2O_5$ | |
| Dunlop $A_1$ | 765 | 92 | 400 | 76.7 | 0.20 |
| $B_{2g}$ | 1,580 | 384 | 96 | 119.9 | 0.41 |
| $B_{3gx}$ | 1,440 | 445 | 99 | 108.5 | 0.52 |
| $C_g$ | 848 | 189 | 109 | 92.3 | 0.38 |
| Amlaird $A_1$ | 452 | 113 | 515 | 14.4 | |
| $A_{eg}$ | 385 | 159 | 204 | 36.9 | |
| $B_{2g}$ | 361 | 192 | 304 | 39.6 | |
| $C_{1G}$ | 407 | 291 | 654 | 61.4 | |
| $C_2$ | 332 | 299 | 372 | 71.9 | |

extractions (Chapter XIV p.706) that the surface water gley contains significant allophane. Its allophane might appear to be more siliceous from the higher silica : alumina ratios, but on the other hand some of the silica may have been associated with amorphous iron oxide.

The iron oxide contents are in agreement with expectations. They are highest in the surface horizons, low in the Dunlop subsoils, and have their greatest concentration in Amlaird $C_1$G where field survey showed ferrous iron to be present to the greatest extent.

## 5. Preliminary field work: allophane in forest soils.

The writer had hoped to visit the tertiary basalt areas of Mull and Fiunary on whose brown forest soils and podzols the problems of spruce check have been most widely encountered. Lack of time has precluded this until a later date. However, it was possible to examine briefly some tertiary basalt soils on the Kilpatrick and Campsie hills, using the sodium fluoride test as a guide to their allophane content. Previous expeditions had already shown that their grassland soils contained allophane. It was their forest soils of planted spruce and semi-natural hardwood which were of interest.

### (i) Carron Forest spruce and pine plantations, Campsies.

Soils were examined at sites in Carron Forest by the north west corner of the reservoir (OS 675855).

(a) Quarry outcrop. Freely drained shallow soil (Darleith series). Heather/grassland.

| | |
|---|---|
| A mor. | No reaction |
| B | Very strong reaction |

(b) Under healthy spruce on edge of quarry.

| | |
|---|---|
| $A_L$ | Thick needle litter |
| A | No reaction |
| B | Medium reaction |

(c) A flat area of gleyed soils was not sampled. The spruce appeared to be doing well, although their age was unknown.

(d) Steep grassy slope on freely drained shallow soil (Darleith series) planted with Scots Pine. These were 15 - 25 ft. high and dying except at the tops, their lower branches dead and lichen covered.

| | |
|---|---|
| A | No reaction |
| B | Medium strong reaction. Roots penetrated this horizon. |

Further information and survey would be needed to draw any conclusions on these sites.

(ii) Kilpatrick hills, oak woodland.

The south side of the hills above Bowling are comprised of rough pasture intercut by gullies and steep slopes supporting oak woodland. Woodland sites and sites on the adjoining grassland were examined.

(a) Road cutting through basalt outcrop; grass verge at adjoining wood above road to Bowling (OS 452737).

| | |
|---|---|
| A | Weak reaction |
| B | Strong reaction |

(b) Oakwood below layby.

| | |
|---|---|
| $A_L$ | Oak litter |
| $A_H$ | Mainly leafmould. No reaction |
| B | Strong reaction. |

(c) Oakwood on steep slope east of Milton (OS 433745).

| | |
|---|---|
| A/B | No reaction |
| B (9) | No reaction. Massive rooting system. |

(d) Oakwood as above

| | |
|---|---|
| $A_0$ | Oak litter |
| $A_1$ | Mull. No reaction |
| B | No reaction. Massive rooting system. |

(e) Grassland on edge of woodland. On rock outcrop.

| | |
|---|---|
| $A_H$ (2") | No reaction |
| B (6") | Medium-strong reaction . |
| C (10") | Very strong reaction. |

(f) Semi-grassed woodland plantation (OS 437745).

Exposed soil of uprooted larch: medium reaction.

(g) Adjoining grassland.

Recent mole hill: no reaction.

(h) Gully woodland of mixed species making splendid growth. (OS 441742). Oak dominant, with larch, Scots pine, abies spp., hawthorn. Sample taken from under massive Scots pine with grass on verge of wood.

| | |
|---|---|
| A (3") | No reaction |
| B (10") | No reaction |

(i) Gully woodland as above. Sample taken from under oak and moss.

| | |
|---|---|
| A (2") | No reaction |
| B (6") | No reaction |
| C (12") | No reaction |

(j) Grassland a few yards above wood.

| | |
|---|---|
| A (2") | No reaction |
| B (9") | Medium strong reaction |
| C (16") | Weak reaction. |

The results, together with pH measurements on NaF treatment for some of the soils are collected in Table

## Discussion.

Discussion is admittedly based on the results of very few samples. Nevertheless they suggest that long established hardwood soils do not respond to the sodium fluoride test ie. they either contain negligible allophane or the allophane is strongly masked from fluoride interaction. There is not enough evidence to indicate how far the character of the hardwood itself or its long establishment has this effect. However, the

Table 99 Sodium fluoride reactivity of grassland and woodland soils on Kilpatrick hills.

| Ref. | Site | Vegetation | Horizon | NaF reaction | rise in pH on NaF treatment | |
|---|---|---|---|---|---|---|
| | | | | | 5 min. | 1 day |
| (a) | verge of road cutting | grass | A | weak | | |
| | | | B | strong | | |
| (b) | adjoining oakwood | oak | $A_H$ | none | | |
| | | | B | strong | | |
| (c) | oakwood | oak | A/B | none | | |
| | | | B | none | | |
| (d) | oakwood | oak | $A_1$ | none | 6.8 | 7.6 |
| | | | B | none | 7.1 | 8.0 |
| (e) | adjoining grassland | grass | $A_H$ | none | | |
| | | | B | med. str. | | |
| | | | C | v. strong | | |
| (f) | grassland-plantation | larch | B | medium | | |
| (g) | grassland/molehill | grass | ? | none | | |
| (h) | mixed woodland | Scots pine | A | none | 8.3 | 8.75 |
| | | | B | none | 8.3 | 8.95 |
| (i) | mixed woodland | oak | A | none | 7.8 | 8.75 |
| | | | B | none | 7.55 | 9.25 |
| | | | C | none | 8.4 | 9.38 |
| (j) | adjoining grassland | grass | A | none | | |
| | | | B | med. str. | | |
| | | | C | weak | | |

only oakwood sample that contained allophane was from the wood by the road cutting (b) and the disturbance to the site when the road was constructed may conceivably account for its presence there.

The occurrence of allophane under grass in close proximity to its absence under oak suggests that perhaps the allophane is 'tanned' by the organic matter derived from oak litter and leachates. It may be relevant to recall that Mehta et al. (1960) and Clapp and Emerson (1962) found forest soil aggregates, unlike grassland aggregates were stabilised by some unknown material resistant to periodate and pyrophosphate but sensitive to $ClO_2$ oxidation. This was described in Chapter V 4 pp.247, 252. Hence one could postulate that the forest 'humate' is bound more tightly to the aluminium than the grassland 'humate', or one could propose that it increases the acidoid : basoid ratio more effectively. A high base saturation from the litter may also play a part. The same result would not be expected from a long established coniferous forest, because there the soil processes are dominated by podzolisation and lead to accumulation of allophane in the C horizon.

The effect of the hardwood on the soils now leads one to question the 'cultivation effect' noted by Bibby on Mull and by Patterson in Fiunary Forest, in which absence of phosphate deficiency and good spruce growth seemed to correlate with previously cultivated inbye land. (Chapter VIII 6 p.346). It appears to the writer that this may be due to a much older influence: ie. to the influence of the native mixed forest, rather than to crofting cultivations in more recent times. In pre-crofting times, one may suppose that stock would be grazed in the open woodland and that when this disappeared as a result of burning, clearing and loss of regenerative capacity, the head dyke more or less co-incided with the poor pasture beyond the tree line. The 'spruce cathedrals' described to the writer by Bibby could be inheriting soils ameliorated by the forest influence.

## Conclusion.

The experimental results strongly suggest that aluminium toxicity, giving rise to phosphate deficiency is the cause of failure of spruce on Darleith brown forest soils and Darleith podzols. They add weight to the predictions made in Chapter VIII on the basis of field evidence and chemical considerations. There are several aspects to be further investigated if this diagnosis proves correct.

(a) Are 'normal' podzols ie. podzols with allophane accumulated in the C horizon, inimical to deep rooting? If they are not, is this because their allophane is different, eg. more siliceous than Darleith allophane, or is it because the phosphate obtained from upper horizons enables the healthy tree to cope with the more difficult conditions at depth?

(b) Assuming long established hardwoods are indeed able to mask or change soil allophane, how long does it take for such trees to become established, how long for them to remove the allophane effects, and is this removal permenant?

(c) How can such soils best be improved or utilised?

Some recommendations on this last point were put forward at the end of Chapter VIII and can only be repeated. If aluminium toxicity exists, the soil may be amended by liming and by additions of organic matter. Liming would immobilise the aluminium but may not be suitable treatment for spruce. Additions of organic matter would be preferred. In chemical terms, one could say that this would change the amphoteric properties of the allophane by increasing its acidoid : basoid ratio, or one could say the aluminium would be masked; but in either case the result will be to make the alumina less soluble and toxic. This treatment might be difficult to apply to crops already in the ground, and it is uncertain whether the spruce litter in the course of time might have the same effect as has been observed with hardwood litter. Unplanted areas could be so treated but the expense might be prohibitive in view of transport costs. The ability of other forest species to withstand high alumina or to create for themselves ameliorating conditions should be examined. Knowledge of this would be useful even if no economic crop were envisaged at the time. It should also be borne in mind that the Darleith brown forest soils support an excellent grassland.

# CHAPTER XVI: ARTEFACTS.

## 1. Artefacts from plastic bags.

Soils were normally collected in plastic bags, and since those on the Drumboy hydrologic sequence were originally used for an introductory soils course, it was the practice to store them moist by putting a test tube of water in the bag before sealing it, so that they were in a 'natural' condition when they came to be examined. Certain chemical changes in ion availability are said to take place under moist storage (Jackson 1962), but since at that time the main interest was mineralogical, soils were kept in this way for research purposes also, often for many months before being sieved and dried. The consequences of this were found in a round-about manner.

### Exp. 109 Recovery of a water-insoluble substance from soil distilled under vacuum.

An anomaly was discovered in that 10 ml aliquots of an aged and therefore very dilute Dunlop $B_{2g}$ sol gained weight on peroxidation. This was later established as due to impurities in the $H_2O_2$ which precipitated as a white salt on evaporation and indicated the importance of using analar $H_2O_2$. At the time however, it was also wondered if the weight increase could be caused by the loss of organic matter volatile at $100^{\circ}$, and to test this possibility the clay was distilled under vacuum. To the writer's surprise, small oily flakes were indeed found floating on the surface of the water in the receiver. Distillation of 200 ml newly dispersed Amlaird $B_{2g}$ suspension produced the same oily flakes on the distillate; and when coarse sand from an Amlaird $C_1G$ dispersion was lightly ground, vibrated for 5 minutes in 30 ml water and then distilled, the surface of the distillate was again covered with insoluble material. Thus the material was either all-pervasive in soil, or it was an artefact.

The distillate was shaken with ether and the ether fraction examined under an ultraviolet lamp. The evaporating solution gave out a yellow fluorescent glow. It was tried shaking up the clay suspension with ether to avoid the distillation step. This was unsuccessful, suggesting that the solubility of the material in ether could not overcome the energy of its adsorption on the clay. An infra-red spectrum was obtained for the etherial evaporate, and was identified as di-n-butyl phthallate. This was inconclusive however, because it was stated to be a common contaminant in ether extracts.

### Exp.110 Recovery of a water-insoluble substance from organic matter extract.

A similar substance was found in the organic matter extract of Dunlop $B_{2g}$. The extract was fractionated by pouring it into ethanol so that the bulk of it precipitated, and it was planned to examine the supernatant for the presence of small polysaccharides and sugars following the removal of salt with a cation (IR 120 $H^+$) and anion (IRA 400 $OH^-$) exchange resin. The volume of the ethanol was evaporated down and then made to 100 ml with water, whereupon a white turbidity developed which intensified as the solution was added to the water at the top of the column. The turbidity persisted into the eluate. It was tested by the following methods:

(a) Chromatography:- the extract was spotted on an alumina plate and run in an n-propanol:ethyl acetate: water 8:1:2 solvent with glucose and mannose standards; the colour developer reagent $A_gNO_3$/EtOH/$OH^-$ revealed intense spots that were thought too far travelled to correlate with a sugar.

(b) The $\alpha$-napthol/$H_2SO_4$ test for polysaccharide (ie. for reducing substances) gave an intense lilac pink. This was thought too intense to be entirely due to sugars.

(c) The substance was fluorescent under UV light.

(d) IR spectrum: the substance was extracted from alcohol into ether, and the alcohol removed by evaporating it over $CaCl_2$ in a desiccator. The residue was taken up in $CCl_4$ and gave an IR spectrum (fig. 43 p.748) of an unidentified hydrocarbon.

Exp. 111 Investigation of plastic bags.

At this stage it was essential that there should be no artefacts causing interference with the investigation of soil polysaccharide. All plastic material was becoming suspect. The plastic bags used for collecting soul were examined by filling three of them either with a little water, ether or carbon tetrachloride and leaving them to soak for a few days. All three solutions were found fluorescent under ultraviolet light. An infra-red spectrum was obtained for the $CCl_4$ extract (fig. 44 p.749) and showed a very simple hydrocarbon pattern.

Fresh soil was collected in (a) plastic bags and (b) glass jars. Their distilled clay suspensions produced no insoluble material in the distillate. It was concluded that under the conditions of storage, hydrocarbons had seeped from the moist plastic bags and

Fig. 43 Infra-red absorption spectrogram of substance precipitated in water from the Dunlop $B_{2g}$ organic matter extract : due to plastic bag material.

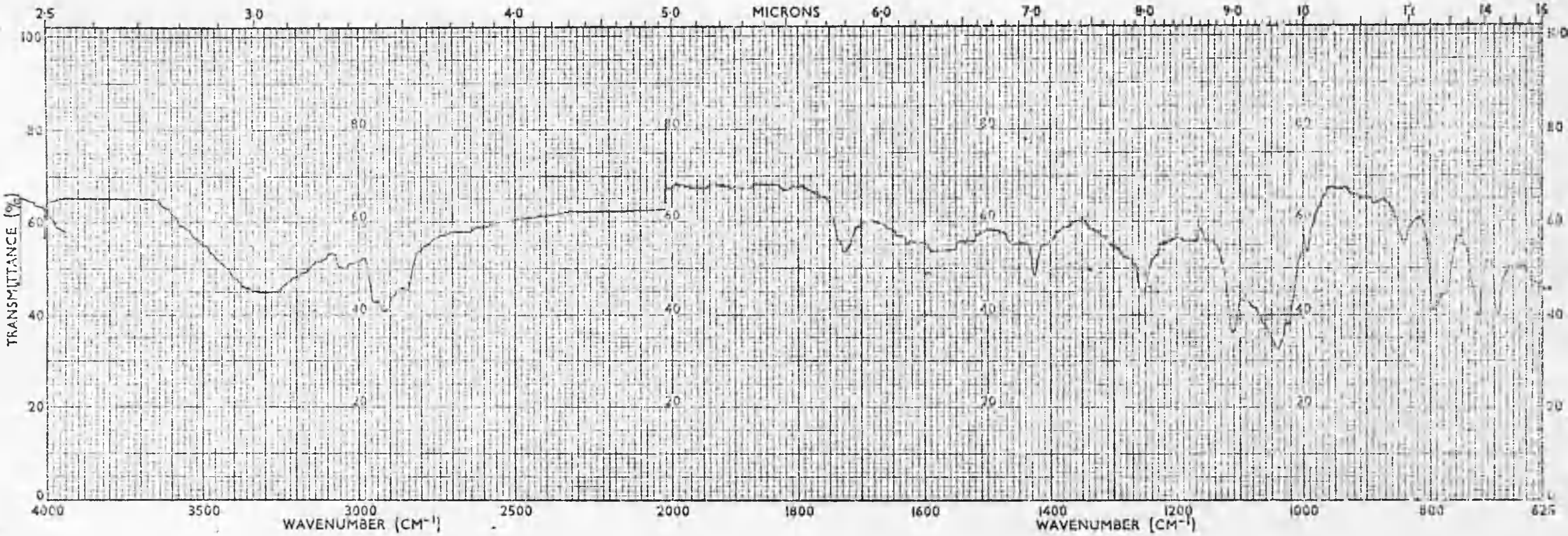
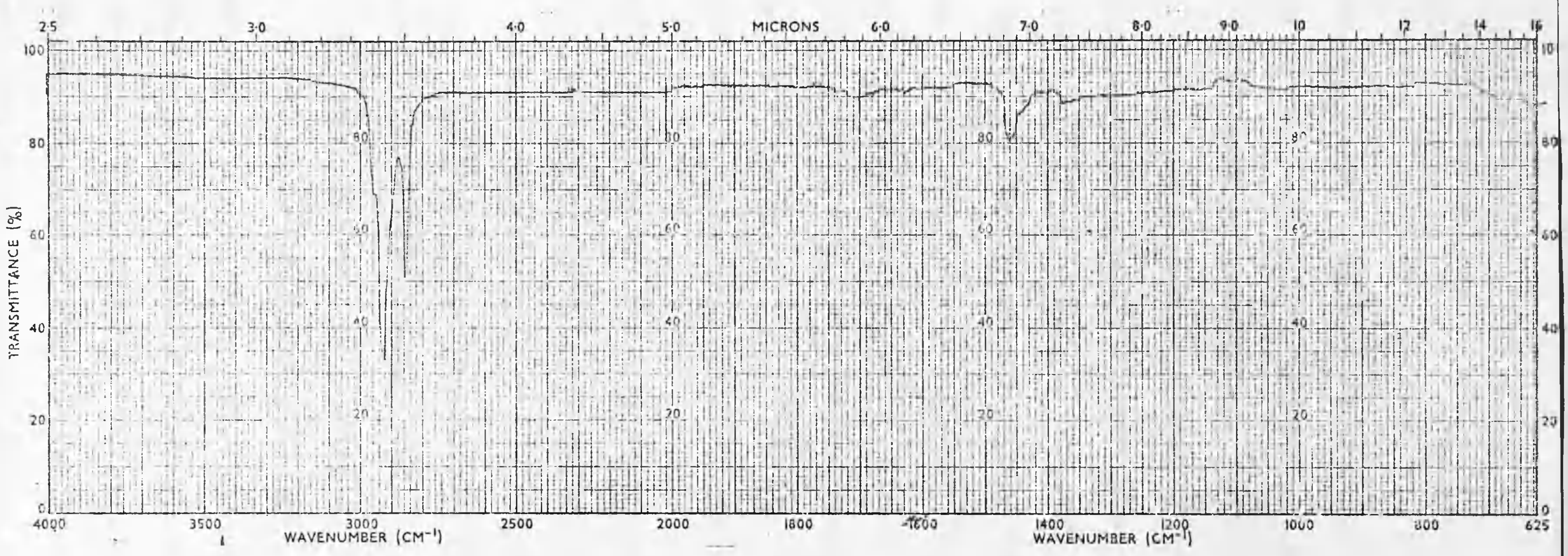


Fig. 44 Infra-red absorption spectrogram of $CCl_4$ extract of plastic bag.



were sufficiently mobile to diffuse and penetrate the whole soil mass, even into those coarse sand aggregates which resisted sonic vibration. In the writer's view, soil should never be collected in plastic when the organic matter fraction is to be examined and plastic vessels and tubing should be avoided; and as a corollary to this it seems important to know the conditions of collection and storage when organic matter extraction is being discussed, since estimates of both the hydrocarbon content and the polysaccharide content may be interfered with by plastic artefacts. This will be demonstrated even more conclusively in the next section.

It was thought the plastic bag behaviour should be further investigated. 200 ml aliquots of deionised water, tap water, sea water, water acidified to pH 4.4 and water made alkaline to pH 8.8 were added to plastic bags. The bags were sealed and kept for over a year but have not yet been opened for analysis. The idea was to see to what extent plastics release their components into water under common conditions. It was wondered for example, whether the use of plastics in food storage, or in the lining of fish ponds might have deleterious effects. The dangers of plastic pollution through the agency of such toxic products as PCB are now well-known. But there was also the possibility that the slow but widespread release of other hydrocarbons might be harmful, since their insolubility would encourage their adsorption or uptake by aquatic organisms. It is suggested that biological experiments should be conducted on these lines.

## 2. Artefacts from visking tubing.

During the work on the extraction of organic matter, it was thought that the simplest method of getting rid of the large amounts of sodium fluoride and other salts was to dialyse the extracts. The dialysate was to be recovered and analysed also, in view of the reported loss of carbohydrates by this method, discussed in Chapter VI 3 p.273. It is indeed worth reiterating Swincer et al. (1968) who stated: "About 40% of the carbohydrates in the fulvic acid fraction were lost during dialysis in visking tubing against distilled water. Half of this carbohydrate was recovered in the dialysis water, presumably as low molecular weight fragments, but not as monosaccharides. The other half was sorbed on the tubing and could not be recovered by washing (Clapp 1957; Muller, Mehta and Deuel 1960)."

Exp. 112 Dialysis of organic matter extracts.

The organic matter extracted from Dunlop and Amlaird soils in sodium fluoride solution was separated into a purified fraction and a high-salt fraction by placing it in visking tubing and dialysing against distilled water over a period of 2 to 3 days. The water was changed until no further chloride or sodium was detected in the dialysate, and the bulk washings were rotary evaporated down to approx. 1 litre. The undialysable residue and the dialysate were analysed for polysaccharide content by the phenol-sulphuric method, and the results compared with the values obtained for the whole soil and also the undialysed extract.

Exp. 113 Distillation products of the dialysate.

Insoluble droplets collected on the surface of the distillate during rotary evaporation in the same way as they collected from the distilled soil. Since these experiments were made over the same period of time, the droplets were at first thought to come from the same source ie. from soil organic matter. They were strongly fluorescent when extracted into ether or carbon tetrachloride and gave a much more pronounced but apparently identical spectrum to that obtained earlier from the 'white turbidity' (p.746) This discovery was further confused by the fact that a colleague (H.J. Duncan) who was examining an extract from potatoes, and had taken it up in chloroform, obtained an identical IR spectrum for his substance.

### Exp. 114 Interference with phenol-sulphuric polysaccharide measurements after dialysis.

The dialysate gave strong reactions with the phenol-sulphuric solution used to estimate polysaccharide content. This was partially expected in view of the quotation from Swincer et al. (1968) above. Examination of several dialysates however, showed that this method of purifying organic extracts was highly undesirable. In the first place, strong concentrations were expressed in a red tinged colour which was different to the golden colour produced by the reaction of phenol-sulphuric with standard polysaccharides. Secondly, on standing the dialysate samples appeared to increase their reactivity with phenol-sulphuric. Measurements that averaged 40 μg/ml were increased to 60 μg/ml after the dialysate had stood for 16 days before retesting. Thirdly, correlation of the phenol-sulphuric measurements with polysaccharide content was plainly invalid, as shown by the figures in Table 100 p. 755. The dialysate and undialysable residue each apparently contained 2 to 3 times the polysaccharide content of the undialysed extract, and together they represented between 46% and > 100% soil polysaccharide extraction. Clearly, other reducing substances were present, but it was not certain at that time whether they were produced from the visking tubing or from salt interference, although the high "polysaccharide" content of the undialysable fraction suggested it was visking tubing. Salt interference was discounted by adding a few crystals of (a) sodium fluoride (b) potassium aluminium sulphate to aliquots prior to a phenol-sulphuric test. These additions made no difference to the colorimeter readings. Visking tubing interference was examined crudely by soaking it in a little water. The resultant liquid gave a slight yellow colouring with phenol-sulphuric. More definitive tests were then made and are described after the account of the next experiment.

Table 100 The effect of dialysis on the estimation of polysaccharide content in organic extracts.

| | mg polysaccharide/g soil, estimated from colorimetric measurements. (phenol-sulphuric method). | | | |
|---|---|---|---|---|
| Soil | whole soil | undialysed extract | undialysable extract | dialysate. |
| Dunlop $B_{2g}$ 1st extract | 6.8 | 2.3 | 6.6 | 6.8 |
| 2nd - 5th extract | - | 0.2 | 0.35 | 0.58 |
| Amlaird $B_{2g}$ 1st extract | 5.9 | 1.15 | 2.2 | 2.7 |

### Exp. 115 Interference with chromatograms of sugars.

When paper chromatograms of the dialysate and undialysable organic extract were made with sugar standards, the $A_gNO_3//EtOH/OH^-$ developing reagent revealed all the dialysate and most of the undialysable material as large blotches whose size and position on the paper was reminiscent of glycerol (plate 5 p.757). It was thought that these were produced by the same material as was interfering with the polysaccharide determinations. Artefacts due to silicone grease or vaseline picked up during rotary evaporation were discounted since the whole soils showed no 'glycerol' patches.

### Exp. 116 Tests to ascertain visking tubing interference in chromatograms.

12 inch lengths of visking tubing were soaked in 250 ml aliquots of water and solutions were made up as follows:-

(a) Tubing in water.

(b) Tubing in NaF solution.

(c) Tubing in potassium aluminium sulphate solution.

(d) Tubing in potassium aluminium sulphate solution. $Al(OH)_3$ was precipitated on addition of NaOH (pH 4.05). Addition of NaF raised the pH to 9.5

Plate 5

Chromatogram of glycerol artefact from visking tubing and this was lowered to 7.2 with HCl. It was expected this solution would contain cryolite and $Al(OH)_3$.

(e) Solution as (d), but with no tubing.

The tubing was soaked for 7 days and the solutions evaporated down on a rotary evaporator to leave a considerable amount of fatty-looking substance in the tubing samples. A chromatogram was run in butanol/HOAc/water against glucose and glycerol standards. The developing reagent showed a glycerol-like blotch for all the visking tubing samples, and purple spots for the synthetic 'cryolite' (d) and (e) samples, suggesting that the 'cryolite' had perhaps formed some complex with the silver.(plate 5).

Exp. 117 Test to ascertain reducing power of visking tubing.

Instead of the phenol-sulphuric measurement normally used, a Fehling's test was employed to determine whether solubilised visking tubing had reducing power. The evaporated samples (d) and (e) above were made to 10 ml. Duplicates of 1 ml each were taken and 1 ml Fehling's solution added. The colorimeter readings were as follows:-

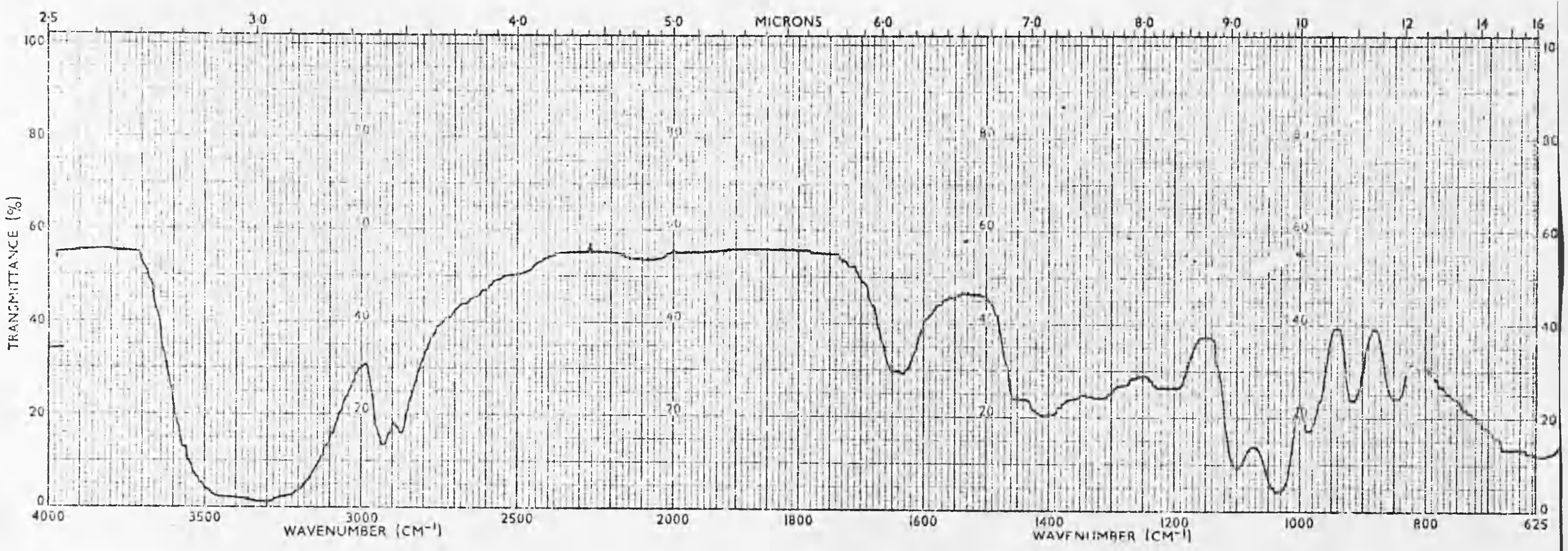
| Sample | % Trans. |
|---|---|
| (d) 'cryolite' tubing | 29<br>25 |
| (e) 'cryolite' only | 7.5<br>12.0 |
| Fehlings control | 6.5 |

Exp. 118 <u>Infra-red spectrum of leached tubing material</u>.

Finally, an infra-red spectrum was made on the material recovered after evaporating down sample (a) ie. the liquid obtained from soaking visking tubing in water. The oil was smeared between salt plates and its spectrum is reproduced in fig. 45 p.760. Again it showed a hydrocarbon trace, slightly different to earlier ones, and yet to be identified.

Thus the problem was solved, and a number of anomalous findings and observations made during attempts to fractionate the organic extracts were explained. Visking tubing was henceforth avoided when dealing with organic matter. The appearance of precipitates during dialysis of clay in a much later experiment could be similarly explained as due to tubing artefacts, and removed on this basis. It is difficult to understand however, why the interference should not have been

Fig. 45 Infra-red absorption spectrogram of material dissolved from visking tubing in water.



noted before. Swincer et al. (1968, 1969) and those whose work they reviewed, appear to have thought that the dialysate substances came from the soil. This now seems unlikely. Moreover, the finding that it was impossible to remove the 'polysaccharides' from the tubing completely must have been due to the fact that the tubing continued to leach out its reactive material.

# APPENDIX A

## Lattice spacings of soil minerals.

A1 Basalt rock outcrop. Whole rock powdered.

Analysis: Labradorite and augite, with antigorite and magnetite.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| w | 14.84 | | |
| w,df | 9.74 | | |
| w,df | 7.25 | antigorite | 7.30 |
| m | 6.46 | labradorite | 6.48 |
| w | 4.86 | magnetite | 4.85 |
| mw | 4.69 | labradorite | 4.68 |
| vw | 4.56 | | |
| m | 4.44 | | |
| w | 4.15 | | |
| ms | 4.05 | labradorite | 4.04 |
| ms | 3.9 | labradorite | 3.89 |
| s | 3.75 | labradorite | 3.75 |
| m | 3.63 | labradorite | 3.64 |
| | | antigorite | 3.63 |
| mw | 3.47 | labradorite | 3.47 |
| mw | 3.36 | labradorite | 3.37 |
| vs,bd | 3.21 | labradorite | 3.20 |
| | | augite | 3.20 |
| w | 3.13 | labradorite | 3.13 |
| vs | 3.03 | labradorite | 3.02 |
| | | augite | 2.99 |
| s | 2.95 | magnetite | 2.97 |
| | | labradorite | 2.95 |
| s | 2.90 | | |
| s | 2.538 | labradorite | 2.53 |
| | | magnetite | 2.53 |
| m | 2.50 | labradorite | 2.51 |
| | | augite | 2.51 |
| | | antigorite | 2.52 |
| w | 2.222 | | |
| w | 2.205 | augite | 2.20 |
| w | 2.147 | | |
| m | 2.13 | augite | 2.13 |
| m | 2.105 | magnetite | 2.10 |
| m | 2.037 | augite | 2.04 |
| w,df | 2.022 | augite | 2.00 |
| w | 1.972 | augite | 1.97 |
| w | 1.877 | | |
| m | 1.833 | augite | 1.82 |
| w | 1.815 | antigorite | 1.815 |
| mw | 1.796 | | |
| mw | 1.77 | | |

Contd/

A1. Contd.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| m | 1.748 | augite | 1.74 |
| mw,df | 1.717 | augite | 1.71 |
| mw,df | 1.672 | augite | 1.68 |
| df | 1.622 | augite | 1.62 |
| w | 1.584 | | |
| w | 1.562 | | |
| w | 1.547 | | |
| w | 1.526 | | |
| m | 1.509 | augite | 1.51 |
| s,db | 1.487 | augite | 1.49 |
| m | 1.422 | augite | 1.42 |

A2 Description: opaque white coarse sand grains

Analysis: Labradorite and quartz, with accessory hematite.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| w | 6.46 | labradorite | 6.48 |
| s | 4.26 | quartz | 4.26 |
| m | 4.05 | labradorite | 4.04 |
| s | 3.77 | labradorite | 3.75 |
| m | 3.46 | labradorite | 3.47 |
| s | 3.35 | quartz | 3.343 |
| s | 3.23 | labradorite | 3.23 |
| s | 3.2 | labradorite | 3.20 |
| w | 3.13 | labradorite | 3.13 |
| w | 3.05 | labradorite | 3.02 |
| v | 2.99 | | |
| w | 2.94 | labradorite | 2.95 |
| v | 2.90 | | |
| w | 2.69 | hematite | 2.69 |
| m | 2.57 | | |
| w | 2.522 | labradorite | 2.53 |
| m | 2.452 | quartz | 2.458 |
| w | 2.282 | quartz | 2.282 |
| w | 2.337 | quartz | 2.337 |
| m | 2.124 | quartz | 2.128 |
| m | 1.978 | quartz | 1.98 |
| s | 1.818 | quartz | 1.817 |
| w | 1.791 | | |
| w | 1.69 | hematite | 1.69 |
| s | 1.659 | quartz | 1.659 |
| m | 1.542 | quartz | 1.541 |
| s | 1.375 | quartz | 1.375 |
| s | 1.371 | quartz | 1.372 |

A3 Description: "Conglomerate" coarse sand aggregates, dark brown and blackish. Magnetic to bar magnetite. Releases silt-size blackish magnetic grains on sonic treatment.

Analysis: Labradorite and augite, with magnetite and hematite.

| Intensity | dÅ | Mineral | ASTM |
|---|---|---|---|
| vw | 6.45 | labradorite | 6.48 |
| vw | 5.8 | | |
| vvw | 4.82 | magnetite | 4.85 |
| w | 4.43 | | |
| w | 3.97 | labradorite | 4.04 |
| w | 3.87 | labradorite | 3.87 |
| vw | 3.74 | labradorite | 3.75 |
| w | 3.45 | labradorite | 3.47 |
| m | 3.32 | augite | 3.31 |
| s | 3.21 | augite | 3.20 |
| s | 3.00 | augite | 2.99 |
| s | 2.95 | augite | 2.94 |
| | | magnetite | 2.97 |
| | | labradorite | 2.95 |
| m | 2.90 | | |
| vw | 2.8 | | |
| vw | 2.69 | hematite | 2.69 |
| m | 2.56 | augite | 2.56 |
| | | magnetite | 2.53 |
| vs | 2.512 | augite | 2.51 |
| m | 2.299 | augite | 2.29 |
| vw | 2.244 | | |
| vw | 2.203 | augite | 2.20 |
| w | 2.148 | | |
| m | 2.129 | augite | 2.13 |
| m | 2.103 | magnetite | 2.10 |
| m | 2.083 | | |
| m | 2.036 | augite | 2.04 |
| mw | 1.969 | augite | 1.97 |
| s | 1.833 | augite | 1.82 |
| s | 1.749 | augite | 1.74 |
| vw | 1.704 | hematite | 1.69 |
| w | 1.671 | | |
| s | 1.624 | augite | 1.62 |
| s | 1.609 | magnetite | 1.617 |
| s | 1.477 | magnetite | 1.477 |
| s | 1.423 | augite | 1.43 |

A4 Description: brown tablets which flake, coarse sand fraction.

Analysis: Hematite with goethite, possibly accessory talc.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| vw, spotty | 9.36 | talc | 9.30 |
| vw | 9.28 | | |
| vw | 4.56 | talc | 4.58 |
| s | 4.17 | goethite | 4.18 |
| s | 3.67 | hematite | 3.67 |
| w, spotty | 3.34 | quartz | 3.34 |
| vw, spotty | 3.11 | talc | 3.10 |
| s | 2.69 | hematite | 2.69 |
| w | 2.58 | goethite | 2.58 |
| s | 2.516 | hematite | 2.514 |
| m | 2.442 | goethite | 2.44 |
| w | 2.246 | goethite | 2.25 |
| s | 2.204 | hematite | 2.204 |
| s | 1.838 | hematite | 1.838 |
| vw | 1.798 | goethite | 1.799 |
| s | 1.692 | hematite | 1.692 |
| s | 1.97 | hematite | 1.597 |
| m | 1.563 | goethite | 1.564 |
| mw | 1.505 | goethite | 1.509 |
| s | 1.486 | hematite | 1.486 |
| s | 1.453 | hematite | 1.453 |
| vw | 1.347 | goethite | 1.35 |

A5 Description: bottle-glass green crystals from coarse sand fraction. Green varies from pale to deep green.

Analysis: Augite. Remote possibility of crandallite as accessory.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| s | 5.69 | crandallite | 5.70 |
| ms | 4.41 | | |
| m | 3.29 | augite | 3.26 |
| m | 3.22 | augite | 3.20 |
| s | 2.99 | augite | 2.99 |
| s | 2.95 | augite | 2.94 |
| m | 2.90 | | |
| m | 2.56 | augite | 2.56 |
| w | 2.535 | | |
| ms | 2.512 | augite | 2.51 |
| m | 2.296 | augite | 2.29 |
| m | 2.204 | augite | 2.20 |
| w | 2.153 | crandallite | 2.16 |
| m | 2.132 | augite | 2.13 |
| w | 2.112 | | |
| m | 2.066 | | |
| m | 2.034 | augite | 2.04 |
| m | 1.819 | augite | 1.82 |
| m | 1.749 | augite | 1.74 |
| m | 1.626 | augite | 1.62 |
| w | 1.545 | augite | 1.55 |
| m | 1.419 | augite | 1.43 |

A6 Description: clear orange crystals in coarse sand fraction of Dunlop and Amlaird soils.

Analysis: Heulandite, with accessory quartz.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| s | 8.94 | heulandite | 8.90 |
| w | 7.89 | heulandite | 7.91 |
| vw | 5.08 | heulandite | 5.10 |
| m | 4.63 | heulandite | 4.65 |
| w | 4.25 | quartz | 4.26 |
| s,d | 3.945 | heulandite | 3.96 |
| w | 3.42 | heulandite | 3.42 |
| s | 3.34 | quartz | 3.35 |
| s | 2.96 | heulandite | 2.97 |
| w | 2.79 | heulandite | 2.80 |

A7 Description: Amorphous yellow material in coarse sand fraction.

Analysis: Anatase, possibly with accessory talc.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| vvw | 9.36 | talc | 9.36 |
| vvw | 4.55 | talc | 4.58 |
| ms | 3.51 | anatase | 3.51 |
| m | 2.38 | anatase | 2.379 |
| m | 1.891 | anatase | 1.891 |
| w | 1.701 | anatase | 1.699 |
| vw | 1.48 | anatase | 1.480 |

A8 Description: yellow-orange grains, clear to translucent, ground to pale yellow powder.

Analysis: Calcite.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| w | 1.523 | calcite | 1.525 |
| w | 1.601 | calcite | 1.604 |
| w | 1.625 | calcite | 1.626 |
| s | 1.873 | calcite | 1.875 |
| s | 1.903 | calcite | 1.913 |
| s | 2.094 | calcite | 2.095 |
| s | 2.283 | calcite | 2.285 |
| m | 2.493 | calcite | 2.495 |
| vs | 3.03 | calcite | 3.035 |
| spotty | 3.86 | calcite | 3.86 |

A9 Dunlop $B_{2g}$ $<1.4\mu$ clay

Analysis: Expanding clay mineral, kaolinite, quartz, hematite, anatase. Illite? very faint and occasional.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| s | 14.15 | expanding clay | 14-14.5 |
| vvw,df | 10.0 | illite | 9.9 |
| vs | 7.15 | kaolinite | 7.16 |
| s | 4.48 | kaolinite | 4.46 |
| vw | 4.26 | quartz | 4.26 |
| vw | 4.17 | kaolinite | 4.172 |
| w | 3.58 | kaolinite | 3.573 |
|  |  | vermiculite | 3.56 |
| m | 3.51 | vermiculite | 3.53 |
|  |  | anatase | 3.51 |
| s | 3.34 | quartz | 3.34 |
| vw,df | 3.245 |  |  |
| vw,df | 3.22 |  |  |
| m | 2.7 | hematite | 2.69 |
| m,bd | 2.575 | vermiculite | 2.57 |
| w,bd | 2.519 | kaolinite | 2.526 |
|  |  | vermiculite | 2.525 |
|  |  | hematite | 2.514 |
| m | 2.387 | vermiculite | 2.38 |
| m | 2.336 | kaolinite | 2.338 |
| m | 1.696 | hematite | 1.692 |
| m | 1.668 | kaolinite | 1.662 |
| mw | 1.54 | kaolinite | 1.54 |
|  |  | vermiculite | 1.53 |
| m | 1.50 | illite | 1.50 |
| m | 1.489 | kaolinite | 1.489 |

A10 Dunlop $B_{2g}$ $<1.4\mu$ clay treated with HF for 2 minutes.

Analysis: illite, kaolinite, anatase, hematite, possibly with quartz.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| mw | 10.04 | illite | 9.9 |
| mw | 7.12 | kaolinite | 7.16 |
| w,d | 4.96 | illite | 4.97 |
| | | kaolinite | 4.46 |
| ms | 4.47 | illite | 4.45 |
| m,d | 4.14 | kaolinite | 4.18 |
| mw | 3.87 | illite | 3.87 |
| s | 3.67 | hematite | 3.67 |
| s | 3.51 | anatase | 3.51 |
| ms | 3.34 | illite | 3.35 |
| | | quartz | 3.34 |
| w | 3.24 | | |
| w | 3.19 | | |
| w | 2.99 | illite | 3.09 |
| w | 2.85 | illite | 2.85 |
| vs | 2.69 | hematite | 2.69 |
| w | 2.56 | illite | 2.56 |
| s | 2.52 | hematite | 2.52 |
| w | 2.433 | anatase | 2.435 |
| s | 2.375 | anatase | 2.379 |
| w | 2.327 | anatase | 2.336 |
| s | 2.21 | hematite | 2.204 |
| s | 1.89 | anatase | 1.891 |
| s | 1.838 | hematite | 1.838 |
| vs | 1.691 | hematite | 1.692 |
| s | 1.667 | anatase | 1.665 |
| s | 1.597 | hematite | 1.597 |
| vd | 1.498 | anatase | 1.494 |
| s | 1.484 | hematite | 1.484 |
| s | 1.452 | hematite | 1.452 |
| m | 1.362 | anatase | 1.367 |
| m | 1.338 | anatase | 1.338 |
| m | 1.310 | hematite | 1.310 |

All Trachyte (tuff) from outcrop on Darleith series.

Optical Description p.417.

Analysis: Oligoclase, quartz, kaolinite, hematite.

| Intensity | dÅ | Mineral | dÅ ASTM |
|---|---|---|---|
| mw | 7.12 | kaolinite | 7.15 |
| ms | 6.38 | oligoclase | 6.38 |
| w | 5.9 | oligoclase | 5.93 |
| rw | 5.6 | oligoclase | 5.62 |
| vw | 4.44 | kaolinite | 4.46 |
| s | 4.24 | quartz | 4.26 |
| s | 4.03 | oligoclase | 4.03 |
| w | 3.96 | | |
| w | 3.86 | oligoclase | 3.86 |
| s | 3.77 | oligoclase | 3.76 |
| s | 3.68 | oligoclase | 3.69 |
| w | 3.57 | kaolinite | 3.573 |
| m | 3.47 | oligoclase | 3.49 |
| vs | 3.35 | quartz | 3.35 |
| vs,bd | 3.19 | oligoclase | 3.18 |
| m | 2.99 | oligoclase | 2.98 |
| m | 2.94 | oligoclase | 2.93 |
| m | 2.91 | | |
| mw | 2.84 | oligoclase | 2.84 |
| mw | 2.76 | kaolinite | 2.748 |
| m | 2.70 | hematite | 2.69 |
| w | 2.64 | oligoclase | 2.65 |
| m,vbd | 2.54 | oligoclase | 2.55 |
| ms | 2.46 | quartz | 2.458 |
| w | 2.416 | | |
| w | 2.334 | kaolinite | 2.335 |
| | 2.386 | kaolinite | 2.383 |
| | 2.342 | kaolinite | 2.342 |
| w | 2.29 | quartz | 2.282 |
| w | 2.202 | hematite | 2.204 |
| m | 2.162 | | |
| s | 2.13 | quartz | 2.128 |
| m,df | 2.032 | | |
| s | 1.98 | quartz | 1.980 |
| w | 1.933 | kaolinite | 1.936 |
| w | 1.906 | | |
| w | 1.879 | | |
| m,df | 1.849 | kaolinite | 1.845 |
| ms | 1.819 | quartz | 1.817 |
| m | 1.798 | | |

All Contd.

| Intensity | dÅ | Mineral | dÅ ASTM |
|---|---|---|---|
| m | 1.781 | kaolinite | 1.781 |
| ms | 1.70 | quartz | 1.672 |
|  | 1.69 | hematite | 1.692 |
| mw | 1.596 | hematite | 1.597 |
| m | 1.571 | quartz | 1.541 |
| m,vbd | 1.495 | kaolinite | 1.49 |
|  | 1.45 | kaolinite | 1.45 |
| mw,bd | 1.437 | kaolinite | 1.430 |
| w | 1.409 |  |  |
| ms | 1.375 | quartz | 1.375 |
| ms | 1.372 | quartz | 1.372 |
| w,df | 1.355 |  |  |

A12 Brown veined trachyte (tuff?) from outcrops on Darleith and Baidland series. Optical description p.417.

Analysis: orthoclase?, quartz, kaolinite, hematite.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| w | 7.15 | kaolinite | 7.16 |
| m | 6.43 | orthoclase | 6.44 |
| w | 5.83 | orthoclase | 5.86 |
| w | 4.48 | kaolinite | 4.46 |
| | | orthoclase | 4.25 |
| s | 4.24 | quartz | 4.26 |
| ms | 4.04 | orthoclase | 4.02 |
| s | 3.76 | orthoclase | 3.80 |
| w | 3.67 | hematite | 3.66 |
| vw | 3.58 | kaolinite | 3.573 |
| mw | 3.46 | orthoclase | 3.49 |
| vs | 3.34 | quartz | 3.343 |
| vs,bd | 3.22 | orthoclase | 3.18 |
| m | 2.90 | orthoclase? | 2.93 |
| m | 2.89 | orthoclase? | 2.83 |
| mw | 2.76 | kaolinite | 2.753 |
| m | 2.70 | hematite | 2.69 |
| w | 2.57 | kaolinite | 2.558 |
| m | 2.517 | kaolinite | 2.526 |
| | | orthoclase | 2.47 |
| s | 2.45 | quartz | 2.458 |
| vw,df | 2.414 | | |
| vw | 2.385 | kaolinite | |
| s | 2.282 | quartz | 2.282 |
| | 2.23 | quartz | 2.237 |
| | 2.201 | hematite | 2.201 |
| | 2.162 | | |
| s | 2.157 | | |
| s | 2.128 | quartz | 2.128 |
| vw | 2.006 | | |
| s | 1.98 | quartz | 1.98 |
| w | 1.915 | | |
| vw,df | 1.885 | | |
| vw | 1.843 | kaolinite | 1.845 |
| s | 1.817 | quartz | 1.817 |
| w,bd | 1.793 | | |
| s | 1.789 | kaolinite | 1.781 |
| m | 1.696 | hematite | 1.69 |
| m | 1.672 | quartz | 1.672 |
| vw | 1.66 | kaolinite | 1.662 |
| w,df | 1.568 | | |
| s | 1.54 | quartz | 1.541 |
| mw,df | 1.489 | kaolinite | 1.489 |

A13 Colloidal supernatant of Dunlop $B_{2g}$ after NaF treatment of soil with pH maintained at 6 to 7 and removal of suluble salts.

Analysis: cryolite and κ - $Al_2O_3$

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| s | 4.53 | cryolite | 4.51 |
| s | 4.43 | κ- $Al_2O_3$ | 4.47 |
| w | 4.14 | κ- $Al_2O_3$ | 4.14 |
| s | 3.88 | cryolite | 3.88 |
| w | 3.46 | cryolite | 3.49 |
| w | 2.79 | κ- $Al_2O_3$ | 2.79 |
| s | 2.74 | cryolite | 2.75 |
| w | 2.71 | κ- $Al_2O_3$ | 2.73 |
| vw | 2.58 | κ- $Al_2O_3$ | 2.572 |
| w | 2.478 | | |
| m | 2.431 | cryolite | 2.43 |
| | | κ- $Al_2O_3$ | 2.418 |
| w | 2.356 | | |
| vs,b | 2.328 | cryolite | 2.33 |
| | 2.312 | κ- $Al_2O_3$ | 2.323 |
| | | NaF | 2.319 |
| m | 2.263 | cryolite | 2.27 |
| w | 2.219 | cryolite | 2.22 |
| m | 2.148 | cryolite | 2.15 |
| m | 2.116 | κ-$Al_2O_3$ | 2.114 |
| w | 2.06 | cryolite | 2.08 |
| | | κ- $Al_2O_3$ | 2.06 |
| vs | 1.942 | cryolite | 1.94 |
| w | 1.89 | cryolite | 1.89 |
| w | 1.782 | | |
| m | 1.736 | κ-$Al_2O_3$ | 1.740 |
| m | 1.717 | cryolite | 1.72 |
| s | 1.637 | κ- $Al_2O_3$ | 1.636 |
| m | 1.615 | | |
| m | 1.595 | cryolite | 1.60 |
| s | 1.57 | cryolite | 1.57 |
| m | 1.373 | κ- $Al_2O_3$ | 1.39 |

A14 Positive fraction of colloidal supernatant of Dunlop $C_g$ after NaF treatment of soil with pH maintained below 8.8 and removal of soluble salts.

Analysis: $\kappa$- $Al_2O_3$ with kaolinite, quartz and hematite.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| w | 7.09 | kaolinite | 7.16 |
| s,bd | 4.47 | $\kappa$- $Al_2O_3$ | 4.47 |
| | | kaolinite | 4.46 |
| vw | 4.13 | $\kappa$- $Al_2O_3$ | 4.14 |
| vw | 3.83 | kaolinite | 3.84 |
| w, spotty | 3.34 | quartz | 3.34 |
| s | 3.03 | $\kappa$- $Al_2O_3$ | 3.04 |
| spotty | 2.91 | | |
| w | 2.69 | hematite | 2.69 |
| m,bd | 2.565 | $\kappa$- $Al_2O_3$ | 2.572 |
| s | 2.032 | | |
| w | 1.913 | | |
| w | 1.866 | $\kappa$- $Al_2O_3$ | 1.871 |
| w,vb | 1.539 | | |

A15 Amlaird $B_{2g}$ soil treated with NaF, pH allowed to rise to its maximum ie. ~ 8.9, salts removed and < 1.4μ clay peroxidised.

Analysis: kaolinite, $\kappa$- $Al_2O_3$, hematite and anatase.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| ms | 7.15 | kaolinite | 7.16 |
| vs | 4.47 | $\kappa$- $Al_2O_3$ | 4.47 |
| | | kaolinite | 4.46 |
| | | illite | 4.45 |
| s | 4.14 | $\kappa$- $Al_2O_3$ | 4.14 |
| mw | 3.56 | kaolinite | 3.57 |
| mw | 3.51 | anatase | 3.51 |
| s | 3.34 | quartz | 3.34 |
| m | 2.69 | hematite | 2.69 |
| s | 2.57 | $\kappa$- $Al_2O_3$ | 2.57 |
| | | kaolinite | 2.56 |
| | | illite | |
| s | 2.436 | $\kappa$- $Al_2O_3$ | 2.418 |
| w | 2.378 | kaolinite | 2.379 |
| | | anatase | |
| w | 2.33 | kaolinite | 2.338 |
| | | anatase | 2.336 |
| w | 2.213 | | |
| vb | 1.69 | hematite | 1.69 |
| w | 1.547 | kaolinite | 1.542 |
| w | 1.517 | | |
| ms,bd | 1.504 | | |
| ms,bd | 1.489 | kaolinite | 1.489 |
| mw | 1.455 | hematite | 1.452 |

A16 Colloidal supernatant of Dunlop $B_{2g}$ after NaF treatment of soil with pH allowed to rise to ~11.4.

Analysis: Sodium fluoride, sodium aluminate?

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| m | 3.36 | | |
| w | 3.22 | | |
| m | 3.025 | | |
| m | 2.68 | NaF<br>$NaAlO_2$ | 2.68<br>2.67 |
| m | 2.554 | $NaAlO_2$ | 2.56 |
| m | 2.361 | $NaAlO_2$ | 2.37 |
| vs | 2.319 | NaF<br>$NaAlO_2$ | 2.319<br>2.31 |
| m | 2.142 | $NaAlO_2$ | 2.14 |
| m | 1.943 | $NaAlO_2$ | 1.95 |
| m | 1.825 | | |
| mw | 1.671 | | |
| vs | 1.639 | NaF | 1.639 |
| m | 1.513 | | |
| ms | 1.399 | NaF | 1.399 |
| s | 1.334 | NaF | 1.338 |

A17 Dunlop $C_g$ $< 1.4 \mu$ clay, treated with NaF and pH allowed to rise in order to destroy cryolite and $\kappa - Al_2O_3$, then washed free of salt.

Analysis: expanding clay mineral, kaolinite, illite hematite, anatase, possible accessory quartz.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| vs | 14.96 | expanding clay | 14-15 |
| vw,d | 10.00 | illite | 9.9 |
| s | 7.15 | kaolinite | 7.16 |
| vs | 4.48 | kaolinite | 4.46 |
| | | illite | 4.45 |
| s | 3.57 | kaolinite | 3.57 |
| s | 3.51 | anatase | 3.51 |
| | | illite | 3.35 |
| ms | 3.35 | quartz | 3.34 |
| w | 3.25 | | |
| m | 2.7 | hematite | 2.69 |
| vs,b | 2.61 | kaolinite | |
| | | illite | 2.56 |
| m | 2.513 | hematite | 2.52 |
| vw | 2.428 | anatase | 2.435 |
| | | kaolinite | 2.379 |
| m | 2.378 | anatase | 2.379 |
| | | kaolinite | 2.338 |
| w | 2.333 | anatase | 2.336 |
| w | 2.205 | hematite | 2.21 |
| w | 1.889 | anatase | 1.891 |
| w | 1.838 | hematite | 1.838 |
| s,d | 1.692 | hematite | 1.692 |
| m | 1.666 | anatase | 1.665 |
| | | kaolinite | 1.662 |
| s,d | 1.535 | | |
| s,d | 1.488 | kaolinite | 1.489 |
| m | 1.454 | hematite | 1.452 |

A18 Evaporate from n'th washed NaF extract of Dunlop $B_{2g}$.

Analysis: sodium aluminate? and sodium fluoride.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| m | 2.81 | $NaAlO_2 \cdot 3H_2O$ | 2.82 |
| m | 2.665 | NaF | 2.68 |
| m | 2.553 | $NaAlO_2 \cdot 3H_2O$ | 2.55 |
| w | 2.351 | | |
| vs,bd | 2.311 | NaF | 2.319 |
| | | $NaAlO_2 \cdot 3H_2O$ | 2.30 |
| m | 2.134 | $NaAlO_2 \cdot 3H_2O$ | 2.15 |
| w | 1.989 | | |
| w | 1.806 | $NaAlO_2 \cdot 3H_2O$ | 1.80 |
| s | 1.635 | NaF | 1.639 |
| w | 1.509 | $NaAlO_2 \cdot 3H_2O$ | 1.49 |
| m | 1.398 | NaF | 1.399 |
| ms | 1.334 | NaF | 1.338 |

A19 White precipitate recovered from dialysate of NaF organic matter extract.

| Intensity | dÅ |
|---|---|
| halo | ~ 4.4 |
| bd | 3.10 |
| bd | 1.917 |
| bd | 1.638 |

A20 Gibbsite (La Porte Industries).

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| vw | 5.38 | | |
| vs | 4.85 | gibbsite | 4.83 |
| us | 4.34 | gibbsite | 4.37 |
| | | | 4.32 |
| m | 3.36 | | |
| m | 3.32 | gibbsite | 3.306 |
| m | 3.19 | gibbsite | 3.187 |
| m | 3.105 | | |
| s | 2.453 | gibbsite | 2.454 |
| mw | 2.421 | gibbsite | 2.420 |
| s | 2.387 | gibbsite | 2.388 |
| m | 2.288 | gibbsite | 2.285 |
| m | 2.247 | gibbsite | 2.444 |
| ms | 2.163 | gibbsite | 2.168 |
| s | 2.049 | gibbsite | 2.043 |
| s | 1.998 | gibbsite | 1.993 |
| ms | 1.917 | gibbsite | 1.921 |
| s | 1.807 | gibbsite | 1.799 |
| s | 1.751 | gibbsite | 1.750 |
| s | 1.684 | gibbsite | 1.689 |
| m | 1.457 | gibbsite | 1.457 |
| m | 1.441 | gibbsite | 1.441 |
| m | 1.412 | gibbsite | 1.409 |
| m | 1.403 | | |

### A21 Evaporated zirconium nitrate solution.

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| s,bd | 8.91 | | |
| w | 7.36 | | |
| s,bd | 6.79 | $Zr(NO_3)5H_2O$ | 6.9 |
| mw | 5.18 | $Zr(NO_3)5H_2O$ | 5.2 |
| s | 4.7 | $Zr(NO_3)5H_2O$ | 4.73 |
| mw | 4.45 | | |
| s | 4.18 | $Zr(NO_3)5H_2O$? | 4.21 |
| s | 3.61 | $Zr(NO_3)5H_2O$ | 3.64 |
| s | 3.485 | $Zr(NO_3)5H_2O$ | 3.49 |
| s | 3.43 | | |
| s | 3.25 | $Zr(NO_3)5H_2O$ | 3.25 |

A22 Tirau B v.v. fine clay from an HCl dispersion.

Analysis Kaolinite ?

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| w,df | 7.1 | kaolinite | 7.16 |
| df halo | 4.4 | | |
| s | 3.375 | | |
| s | 3.37 | | |
| w | 2.021 | | |
| w | 1.671 | | |

A23 Tirau B residual 20 material after cold 5% $Na_2CO_3$ extractions.

Analysis kaolinite, andesine, quartz ?

| Intensity | dÅ | Mineral | ASTM dÅ |
|---|---|---|---|
| s | 7.18 | kaolinite | 7.16 |
| s | 4.44 | | |
| spotty | 4.38 | quartz | 4.34 |
| s | 4.03 | andesine | 4.02 |
| m | 3.74 | andesine | 3.739 |
| spotty | 3.34 | quartz | 3.34 |
| df | 3.21 | andesine? | 3.199 |
| w | 2.72 | | 3.174 |
| spotty | 2.278 | quartz | 2.28 |
| spotty | 1.696 | | |
| spotty | 1.376 | | |

## APPENDIX B: Variations in the values of Stokes' Law parameters and their effect on the accuracy of pipette analysis.

Stokes' Law $v = \frac{2}{9} \frac{gr^2}{\eta} (\rho_P - \rho_L)$.

$g$ = gravitational g ........Edinburgh 981.5 cm/sec$^2$
.......Greenwich 981.2 cm/sec$^2$ .

$\rho_P$ = density of particle, taken as 2.6, the average density of silicates.

$\rho_L$ = density of water 0.9997, 0.9982, 0.9957 at 10°, 20°, 30°C respectively.

$\eta$ = viscosity see Table 101 p.786 for $\eta$ values of water over a range of temperature.

$r$ = equivalent settling radius of particle.

Differences in the value of g in Britain and differences in $\rho_L$ due to changes in temperature have no effect on the calculation. Particle density values are an approximation especially in the silt fraction of Darleith soils which contain considerable pyroxene-magnite (density of magnetite = 5.2). The major source of error is in the variation of $\eta$, the viscosity, with temperature. Table 102 shows the calculated sampling times for clays of $< 1.4\,\mu$, $< 1.41\,\mu$ and $< 2\,\mu$ esd for the temperature range 18° to 22°C. Particle size normally analysed was $< 1.41\,\mu$. Silt + clay ( $< 20\,\mu$ ) sampling times are also shown.

APPENDIX B Table 101 <u>Values of Stokes' Law parameters and variation of sampling time with temperature</u>.

(depth of sampling 10 cm).

| temp. | viscosity | particle esd . . . . . . . | | | |
|---|---|---|---|---|---|
| $^{o}C$ | poise x $10^{-2}$ | $< 1.4\mu$ | $< 1.41\mu$ | $< 2\mu$ | $< 20\mu$ |
| 18 | 1.053 | 17 hr 5' | 16 hr 47' | 8 hr 22' | 5' 03" |
| 19 | 1.027 | 16 hr 39' | 16 hr 21' | 8 hr 10' | 4' 55" |
| 20 | 1.002 | 16 hr 15' | 15 hr 57' | 7 hr 57' | 4' 48" |
| 21 | 0.9779 | 15 hr 51' | 15 hr 33' | 7 hr 46' | 4' 41" |
| 22 | 0.9544 | 15 hr 29' | 15 hr 11' | 7 hr 35' | 4' 34" |

## APPENDIX C SRC Report on Colloid Science.

The report of a multidisciplinary panel on the science of colloidal dispersions given in a newly published pamphlet "Colloid Science" by the Science Research Council (January 1972) is apposite to the conclusions put forward in Chapters IVB and XIII. The panel referred for example, to the shortcomings of the DLVO theory when used by itself to discuss charged colloids; to the need for further study of hydrodynamic forces and coagulation under a variety of hydrodynamic conditions; and to the need for the study of floc structures. They stated: "Analysis of interparticle energies in terms of long range attractive and repulsive forces draws attention to the possibility of the existence of the secondary minimum in the interaction curve. This provides an explanation of the existence of floc structures, but a much more detailed study is needed of the significance of the secondary minimum."

The interaction curve is shown in fig. 46. Curve I shows a primary maximum P in the potential energy barrier which has to be surmounted before two particles can adhere, and a primary minimum $M_1$ which will lead to association of the particles by van der Waals attractive forces (defined as 'coagulation' by the SRC and as 'aggregation' in this work). Curve II shows a secondary minimum $M_2$ corresponding to association of particles in floc structures. This qualitative description is identical to that deduced by Mattson (1929b) and described in Chapter IVB (p.194). It reinforces the writer's view that colloid scientists should rediscover and appraise his work.

Fig. 46 Mutual potential energy of two colloidal particles as a function of the distance of separation between their surfaces.

(SRC 1972)