THE STUDY OF ULTRA-CLEAN COAL

BY

THIRUKUDANTHAI P. SOUNDARA RAJAN B.Sc; M.Sc.

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Dept. of Technical Chemistry,
Royal Technical College,
Glasgow C1.
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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
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T.P.S.Rajan

Technical Chemistry Dept.,
Royal Technical College,
GLASGOW.

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THE STUDY OF ULTRA-CLEAN COAL

INTRODUCTION

THE STUDY OF ULTRA-CLEAN

COAL

INTRODUCTION

The dawn of the machine age, with the introduction first of steam power and then of electricity, focused attention on the importance of coal as a primary source of power. The march of events since the beginning of this century has more than confirmed man's dependence on coal, not only as a primary fuel but also as a major source of organic chemicals. It is but logical, that the increasing importance of this raw material should have resulted in numerous investigations as to its proper conservation and utilisation.

Coal --- its origin.

Ordinary coal is a compact, stratified mass of the remains of plants, which have undergone partial decay, varying in character and arrested at different stages. With the exception of cannels, in the accretion of which the micro-organisms of plankton and marine fauna played a part, the practically, exclusive vegetable origin of coal requires no further proof (1)

/Coal............

Coal and its associated impurities.

It is well known, that coal is invariably associated with a certain amount of mineral matter apart from the pure coal substance. Thus from the earliest days of fuel research, investigators have been concerned with the nature of the "non-coal" associated with coal.

De Marsilly (1848) was perhaps the first to point out that "however pure a piece of coal may be, however homogeneous it may appear to the eye, its different parts do not yield the same proportions of fixed residue on incineration". Thus the fact that the mineral matter is not distributed uniformly in coal led subsequent workers to recognise two different types of mineral matter --- the inherent and the extraneous --- in coal. Their origin has been described by Stopes and Wheeler (2) as follows:- "In nearly all cell walls of plants (forming coal) at least a minute portion of the mineral matter is incorporated with the organic molecules and in some plants widely and in some locally, mineral matter is secreted and deposited in or on the walls. Such for instance are the silicate-impregnated walls in the gramineae, the calcerous sheaths of characeae, the aluminium in the lycopodiaceae. Such mineral matter would be an inherent part of the coal formed from any such species of plants". The ash corresponding to the inherent mineral matter of coal is

often ....

often referred to as the true, fixed or normal ash content of the coal. Little is known about the inherent mineral matter, because it cannot be detected by the microscope.

The extraneous mineral matter in coal is that part of the mineral matter, which is foreign to the plant material forming coal. This arises either from sedimentary material, which was deposited contemporaneously with the accumulation of plant debris, or from mineral salts (like gypsum, pyrite and marcasite, and carbonates of lime, magnesium and iron) introduced by the infiltration of various solutions after the coal seams were "laid down". In X-ray photographs, this may be seen in thin layers on several of the bedding planes and is often referred to as the adventitious mineral matter in coal.

The last source from which the ash in mined coal originates is in the fragments of rock from roof and floor of the mine, and, in some instances, from ribs of inorganic material occurring in the seam itself, which are mixed with the coal during mining operations. Quantitatively the rock debris accounts for the bulk of the ash in commercial coal.

The inherent mineral matter of coal varies in quantity and quality according to the constituent of coal with which it is

/associated................

associated. Thus according to Lessing (3)

(a) clarain and vitrain contain the inherent mineral matter of the plants (or what remains of it) yielding on incineration 1·1 to 1·3 percent of ash, which consists largely of water soluble matter together with a small proportion of clay material, which did not arise from mineral salts in the parent plants.

(b) Durain yields from 6 to 7 percent of ash mostly derived from clay and silt.

(c) The ash from fusain may vary from 4 to 30 percent and it shows evidence of having been introduced as carbonates of lime and iron in solution in hard waters and partly in suspension in the form of clay.

Coal preparation.

The nature of the associated impurities in coal has a direct bearing on the preparation of coal for the market. The inherent mineral matter in coal sets a limit up to which a coal could be cleaned by mechanical means alone, in the best possible circumstances.

The most important single characteristic of both coal and the associated impurities from the stand point of cleaning is the specific gravity. Thus coal ranges in apparent specific gravity from 1·2 to 1·7 depending on rank, moisture and ash content; shale, clay and sandstone range between 2·0 to 2·6 depending on the degree of purity; pyrite ranges from 2·4 to 4·9; and calcite and gypsum have a specific gravity of 2·7 and 2·3 respectively. Most coal cleaning processes use gravity concentration methods; but methods based upon surface and magnetic properties and upon electrical conductivity, sliding friction and strength are also sometimes used.

Modern coal cleaning practice and its limitations.

The impurities with which coal is associated as it comes from the mine are removable only to the extent that they are present in the form of discrete particles physically detached from the coal and of particle size amenable to cleaning. The common impurities coming under this head are shale, sand-stone, clay etc., which get admixed with coal during mining. Finely divided impurities disseminated throughout the coal substance (the "adventitious mineral matter") are not liberated to any appreciable extent at sizes suitable for cleaning.

The aim of an ideal coal cleaning process should be to produce not only clean coal but also clean refuse i.e. refuse relatively free of coal. But imperfect separation of materials of density intermediate between coal and "dirt" is a characteristic of all gravity concentration processes. Thus most plants produce a clean coal with a considerable loss in refuse, a loss partly off-set by recovery of the "middlings". But it is evident, that in all such processes, complete or near complete elimination of impurities could be achieved only at the expense of the yield. Besides this, physical methods of cleaning are of little or no avail in the cases of coals of high adventitious ash like bone coal and most cannels.

Clean coal --- an explanation.

In recent literature,one comes across expressions like clean coal, pure coal, very clean coal, clean fine coal etc., which frequently do not refer to the same product,when used by two different investigators. Most authors label as clean coal the product of comparatively low ash content, often 5 percent and below, prepared by any one of the usual coal cleaning processes. Bertrand (5) calls as pure coal, the product which is almost pure Vitrain (ash less than 1 percent) prepared by a special process as distinct from the clean coal prepared by the usual cleaning processes. Grumell and Dunningham (6) define pure coal as the material floating at specific gravity 1·35 and as clean coal the material floating at 1·6 specific gravity. This is liable to cause confusion, since the authors themselves give examples of pure coals (1·35 floats) of ash over 6 percent and of clean coals (1·6 floats) of ash 1·1 percent.

/It ....

It is more or less accepted now that the ash content should be the guiding factor in labelling coals and Wilkins (7) accordingly makes the following suggestions:-

(a) Very clean coal (2 to 3 percent ash content).

(b) Super clean coal (or ultra clean coal; usually less than 1 percent ash; coal which has been cleaned to its inherent ash content and beyond).

(c) Clean fine coal (In general, a low grade product of fine size and of relatively high ash).

This nomenclature has much to commend it and may command wider acceptance in due course.

The term pure coal (and in the United States, unit coal) is generally used to refer to the dry, mineral matter free coal substance and it is now seldom used in the same sense as by Bertrand.

Preparation of ultra-clean coals.

For producing coals of the lowest possible ash content, there are some advantages in using small sizes of coals; it is seen from radiographs made at the Fuel Research Station that even 'clean' lumps of coal of the lowest specific gravity contain some hundreds of visible patches or striations of "adventitious ash" per cubic inch (7). Heavy medium cleaning processes are generally found useful for the production of very clean coals.

It would be clear, that no single stage process could be expected to give reasonable yields of ultra clean coals in industrial practice.

The Ougree Marihaye Process (5): This Belgian process is claimed to be useful for the production of coal of less than 1 percent ash. In this case crushed coal (5 to 1 mm. size), previously de-dusted and desludged, passes over jigging tables on which the coal is sprayed successively with calcium chloride solutions of about 1·05, 1·18 and 1·25 specific gravity before it is admitted to the separating bath; on emerging from the bath, the products are sprayed with the same solutions in the reverse order and finally with hot water. This procedure is claimed to eliminate the difficult and costly step of reconcentrating large volumes of weak liquor. The process includes a separate treatment for the removal of fusain. In this process, purification is done at the expense of the yield, the limit for the ash content of the clean product being the inherent ash of pure vitrain; this process is reported to yield ultra-clean coal with ash content well below 1 percent.

Some German two-stage processes: Many important two-stage processes were developed by the Germans during the war for the production of ultra-clean coal; of these, those involving acid extraction of impurities are described later.

/(1)Heavy ....

(1) Heavy medium washing followed by froth floatation (8) (10):

The Konigin Elizabeth colliery near Essen produced about 12,000 tons annually of super clean coal by treating fusain free, de-dusted coal (8-1 mm) first in the Vogel laminar flow washer and then after recrushing in a froth floatation unit, using a tar oil fraction as the floatation agent. The final sample had an ash content of 0·6 percent.

(2) Electrostatic cleaning followed by froth-floatation:

The application of electrostatic methods to the treatment of coal is of very recent origin. In its simplest form (7) the separator consists of two rollers, which are oppositely charged to between 10,000 and 40,000 volts, with an arrangement for feeding fine graded particles to one of the rollers as a thin layer, and then collecting the products, which during falling, would have been deflected to different extents from their normal trajectory by the electrostatic field. Moisture content of the raw coal has to be within 1 percent. In Germany, the dry coal (1·0 to 0·1 mm size and 8 to 10 percent ash) was cleaned electrostatically to between 1·5 to 4 percent ash and after crushing recleaned by froth floatation (10).

The Pott-Broche Process: Pott and Broche were the first to produce on a large scale "ashless" coal (ash less than 0·1 percent) by dissolving the coal in oil under pressure.

/They ....

They found that the ternary mixture of tetralin, phenol, and naphthalene in a weight ratio of 2:1:2 was the most satisfactory solvent for bituminous coals. Continued work on the pressure extraction of coal (11) at 400°C has proved, that high boiling aromatic solvents such as naphthalene extract 20 to 30 percent of the coal; a readily dehydrogenated, hydroaromatic solvent such as tetralin dissolves about 50 percent of the coal and hydroaromatic compounds containing a phenolic group such as o-cyclohexylphenol or 1,2,3,4 tetra hydro-5-hydroxy naphthalene dissolves more than 80 percent of the coal. The last two are the best known solvents for coal.

While the industrial significance of the Pott-Broche process could be scarcely underrated, it is evident, its importance would not be as a producer of clean coal for industrial purposes. An ideal process for such purposes would be what one might call the reverse of the Pott-Broche process --- namely, one, which instead of attempting a solution of the organic coal substance, attempts to eliminate the mineral impurities of coal by solution. Thus Lessing (12) remarks ---

"The tendency of modern methods of coal refining is undoubtedly aiming at a complete elimination of the removable ash. In order to bring about this object, far going disintegration is essential and this can be brought about or at least assisted by acid treatment".

/Ultra-clean......

Ultra-clean coals by acid treatment - a historical survey.

Treatment with varying concentrations of hydrofluoric and hydrochloric acid has long been an important method in the determination of combustible matter in silicate and carbonate rocks. Lissner suggested that the silicious matter in such rocks could be extracted by evaporating the sample to dryness with a mixture of two parts of 40 percent hydrofluoric acid and one part of hydrochloric acid of specific gravity 1·18, after which, the residual combustible matter containing small quantities of inorganic materials could be analysed in the usual way. Fieldner, Selvig and Taylor (14) attempted to evolve an experimental procedure based on the above suggestions and found that there was a loss of organic hydrogen and carbon due to the use of hot acids; for reducing such losses to a minimum, they advised against the use of hot concentrated acids.

By applying the Lissner method to coals, Gallard (13) successfully reduced the ash content of bituminous coal samples from an initial value of 8-12 percent to one percent and below. He also noted that the elimination of the mineral impurities in coal, either by the Lissner method or by modifications of it, was always accompanied by a loss of organic carbon, hydrogen and volatile matter.

/Turner ....

Turner (15) modified the above procedure of acid treatment of coals, by first refluxing the sample (60 mesh) with concentrated hydrochloric acid for half an hour, washing it free of the acid and then treating it with 49 percent hydrofluoric acid at a temperature of 95°C, care being taken to prevent evaporation to dryness. The sample, after this treatment was again boiled with concentrated hydrochloric acid for one hour and washed free of acids. Thus he reduced the ash content of samples of bituminous coal, charcoal, anthracite and graphite with an initial value between 0·93 and 30·63 percent to between 0·09 and 1·1 percent. The ultimate analysis showed a loss of about 1·5 percent carbon, and 0·1 percent hydrogen for anthracite, and about 0·6 percent carbon and 1·0 percent hydrogen for bituminous coals.

Karavaev and Rapoport (16) were the first to point out that the use of cold dilute (10:1) hydrofluoric acid to dissolve the silicious impurities in coal before the usual combustion experiment, would avoid errors due to water of hydration of the silicates in the ultimate analysis. Nicolls and Swartzman (17) too realised the importance of coals freed from inorganic material by acid treatment for purposes of classification.

In Britain, Lessing (12) was the first to draw attention to the potentialities of acid treatment of coal;

/he..........

he further developed a process (18) for breaking down coal during mining by the use of acid vapours. In 1932, Pawlikowski (19) secured a British patent covering the removal of the more easily removable constituents of the mineral matter in coal by washing with acid as a preliminary to its use in internal combustion engines.

Down (20) developed a procedure for the elimination of the mineral matter in oil shales using hot dilute hydrochloric acid (5 N for 2 hrs. at 100°C), nitric acid (of 1·18 sp.gr for 100 hrs. at room temperature for the oxidation of the pyrites) and finally hydrofluoric acid. Nitric acid was substituted by a mixture of zinc dust and hydrochloric acid by Himus. Himus and Basak (22) tried this improved method on bituminous coals and found that the sample became oxidised during such treatment resulting in a loss of carbon and hydrogen.

The removal of the mineral impurities in brown coals by acid treatment has engaged the attention of investigators in G ermany since the early twenties. Follman (23) investigated the action of hydrochloric and hydrofluoric acids on the mineral impurities in brown coal. Hankiss (24)(4) studied the effect of varying concentrations of hydrochloric acid (2 to 10 percent) on various particle sizes of coal.

Sustmann and Lehnert (25) were the first to carry out a systematic study of the preparation of super clean coals by acid treatment of brown and bituminous coals. Apart from studying the effect of acid treatment on high and low ash coals with varying concentrations of dilute hydrochloric and hydrofluoric acids, they compared the ignition temperature, melting point of the ash etc. of the original and acid treated samples. They also pointed out the loss of coking properties due to acid treatment.

The outbreak of the war and the consequent search for an alternate source of ultra clean coal for the production of electrode coke required in the aluminium industry, saw the development in Germany of two processes, one based on the removal of mineral matter in coal by acids and the other by alkali.

(1) <u>The Deashing of Coal by Froth Floatation and Acid Extraction</u>. Carl Alexander Mine, Ruhr (26).

The froth from the froth floatation unit (1·1 percent ash) is led into the acid extraction (carbon) pot and the acid mixture (2 kgm of 40 percent HF and 4 kgm of 70 percent HCl in 200 kgm water) led in, in the ratio of 2 parts of acid to one of coal by weight. The pot is kept at 100°C for one hour by blowing in live steam, after which the coal is filtered through rubber lined acid resistant disc filters prepared from synthetic plastic material known as spalatite. The advantage of acid treatment is that the

/yield.........

yield of the final product with 0·5 percent ash is almost the same as the effective yield of the product with 1·1 percent ash from the floatation unit. It is needless to add that the yield of 0·5 percent ash coal by float and sink methods alone is negligible.

(2) The Deashing of Coal by Combined Jig Washing, Froth Floatation and Extraction with Alkali. (27) (I.G.Farbenindustrie A.G.Hochst). Raw coal of 4 to 5 percent ash is cleaned by two successive jig washings to 1·8 percent ash, finely ground and froth floated to a product of 0·8 percent ash. This product is extracted with a 2·5 percent solution of caustic soda for twenty minutes at 120 atmosphere pressure and 250°C. The product is subsequently acid and water washed and contains 0·28 percent ash.

In the United States too, an apprehension regarding the possible shortage of carbon suitable for electrode manufacture led Selvig, Ode and Gibson (28) to examine the possibilities of production of ultra-clean coals by the acid treatment of clean low ash Appalachian coals. As a result of the investigation they found that three out of the seven coals examined by them could be made to meet the specification for the manufacture of electrode carbon by acid treatment.

/Thus..........

Thus a survey of the available literature on the "cleaning" of coal by acid treatment points to the necessity for a further study of the various factors influencing this process. Complete and comprehensive data on the optimum concentration, of the acids to be used, the sizes of coal to be treated, the temperature of such treatment, and a suitable vessel for the reaction with hydrofluoric acid would be of some importance in the wider development of "deashing" of coals by acids as an industrial process.

Unlike the physical methods of coal cleaning, the removal of impurities by acid treatment depends on the chemical nature of the impurities concerned. It has been pointed out earlier that the quality and quantity of the inherent mineral matter in coal varies with the nature of the banded constituents of coal with which it is associated. So a study of the effect of acids on separate samples of each of these petrographic components of coal might throw some light on the nature of the inherent mineral matter in coal.

In the few cases, where acid extraction of the mineral impurities of coal is practiced industrially, the general tendency seems to be to apply acid treatment to coals, which have already been cleaned to a fairly low ash content by one or the other of the physical methods. Thus the production of ultra-clean coals by the present methods is a two or a three stage

/process............

process; but the chances of industrial application of acid-treatment of coals would be considerably improved, if a study could be made of the possibility of producing ultra-clean coals or very clean coals from coals high in adventitious ash or cannels (which cannot be cleaned to any appreciable extent by the prevalent physical methods) by acid extraction alone.

It will be noted that most of the earlier workers in this field have referred to the loss of organic carbon and hydrogen in the coal (with a consequent loss of volatile matter, and unit coal calorific value) in the course of treatment with acids. So it becomes necessary to examine whether the conditions of experiment could be so devised as to avoid any oxidation of the pure coal substance; for, a sample of coal with little or no "ash", produced by acid treatment, without in any way oxidising the coal substance, would be of considerable theoretical significance. It is well-known that what is usually referred to as the ash in coal originates from the mineral matter in coal, which undergoes many changes during incineration, the principal ones being:

(i) dehydration of hydrated materials, like silicates, gypsum etc.

(ii) the decomposition of carbonates (of calcium, magnesium and iron);

(iii) the decomposition of sulphides (mostly pyrite and marcasite) and

/(iv)the.........

(iv) the volatilisation of the chlorides of alkali metals. At present the general methods followed for the determination of the true content of the mineral matter in coal, fall into three categories (a) those taking into account the reactions occurring in the mineral matter during incineration (b) Brinsmaid's method (later modified by Stansfield and Sutherland) in which the calorific value is determined as a function of the ash content after separating the coal by float and sink methods into fractions varying in ash content and (c) methods depending on the extraction of all or part of the mineral matter of coal with acids.

The general literature available under these three heads is summarised in the introduction to Part Two of this thesis. Among the various formulae proposed under (a), from the point of view of scientific justification, the most accurate yet advanced for the calculation of mineral matter of coal from its ash content, is that due to King, Maries and Crosslay (29), although another one due to Parr (30) has gained widespread acceptance in the United States. If the extraction of the mineral impurities in coal could be effected, without oxidising the coal substance, this would provide an important means of studying the limits of applicability of the various formulae in the field.

These were some of the main considerations with which the present investigation was undertaken.

Given below are some of the major probable uses of ultra-clean coal. It need hardly be emphasised that if a successful industrial process could be worked out, the demand for ultra-clean coals would also increase considerably.

Some uses for specially cleaned coals (5) (7).

(a) Hydrogenation: In the hydrogenation of coal, the ash complicates the problem by accumulating in the plant and causing abrasion, while the ash constituents dilute and even poison the catalyst. The increasing purity of the raw material would provide better control over the reaction.

(b) Diesel fuel: For several years, experiments have been carried out at the fuel research station and elsewhere, to replace the mineral oil used in Diesel motors by a less expensive fuel --- namely pulverised fuel. The main problem is one of preventing the coal from scouring the cylinders and the moving parts. Generally this action leads to a rapid fall in efficiency, stoppages and excessive maintenance costs. Ultra-clean coal, the ash content of which has been reduced below its inherent ash, would permit motors to be run continuously on pulverised fuel. Recently attempts have been made by Pawlikowsky (5a) and

/Wahl.............

Wahl (5b) to burn the fuel in the pre-combustion chamber of the internal combustion engine. The successful adoption of such a device would facilitate the use of ultra-clean coal as a diesel fuel.

(c) Colloidal fuel is known to be a mixture of heavy mineral oil or anthracene oil and pulverised coal. The mixture is stabilised by various reagents, which even if they stabilise the coal particle, have only very slight effect on the inert matter which is intimately mixed with it. This results in sedimentation in pipe lines leading to uncertain performance. The substitution of ultra-clean coal would therefore widen the field for the use of colloidal fuel.

(d) The electrometallurgy of aluminium, magnesium and other light metals requires anodes containing less than one percent of ash or more exactly less than 0·5 percent of iron/and silica. At present in the aluminium industry three

/quarters ....

quarters of a pound of carbon electrode is consumed for each pound of aluminium produced. Calcined petroleum coke, the residue from crude oil distillation, has till recently been the starting point in the production of such electrodes. The war gave an impetus to the search for an alternative process and the results achieved by the German war machine have been enumerated above. Electrode carbon has, for years, been prepared from coke manufactured within ten miles of Glasgow. It might safely be claimed, that the use of low ash coke prepared from ultra-clean coals would completely replace the use of petroleum coke in the near future.

THE STUDY OF ULTRA-CLEAN COAL

PART I

THE PREPARATION OF ULTRA-CLEAN COALS BY ACID TREATMENT.

PART I

THE PREPARATION OF ULTRA-CLEAN COALS BY ACID TREATMENT.

A. GENERAL CONDITIONS OF ACID TREATMENT OF COALS.

In the methods described in the literature cited earlier, use has been made both of hydrofluoric acid and hydrochloric acid, under different conditions for the extraction of the mineral impurities in coal. The different practices followed by previous workers are discussed below.

(1) Concentration of the acids used: The earlier workers like Lissner, Gallard (13), Fieldner (14) and Turner, more or less confined themselves to the use of fairly high concentrations (generally 40 percent and above) of hydrofluoric acid. Karavaev and Rapoport (16) and later Nicolls and Swartzman (17) recommended the use of 10 percent hydrofluoric acid. Sustmann and Lehnert (25) used 15 percent hydrofluoric acid for brown coals and presumably the same strength for bituminous coals; they varied the concentration of hydrochloric acid from 1 to 6 percent. The German Carl Alexander Mine process (26) employed an acid mixture of 0·4 percent hydrofluoric

acid and 1·4 percent hydrochloric acid. Fieldner and co-workers (28) used varying concentrations (5 to 10 percent) of the two acids along with wetting agents.

The use of organic acids, particularly formic and acetic acids, for the removal of impurities in brown coals has been reported (25), but their use is presumably limited to special cases like lignites and brown coal.

(2) Temperature of acid treatment: The earlier practice was to treat coals with varying concentrations of hydrofluoric acid for definite periods, evaporate it to dryness over a water-bath and then leach it with water. Later workers preferred to keep the acid mixture simmering below the boiling point, while some others advised definitely against the use of hot acids. In the Carl Alexander Mine process, the coal was boiled in a mixture of the two acids at 100°C.

(3) Size of coal used: There is general agreement that finer sizes should be used; but Sustmann and Lehnert (loc. cit) conducted their experiments with coals just under 4 mm. in size. In the German Carl Alexander Mine process (loc.cit) the main feed for the froth floatation unit, (the product from which was later acid treated) was 0·75 mm. in size.

Fieldner and co-workers used coals crushed to pass a 60 mesh sieve (0·250 mm. opening). Hankiss (4) (24) studied the effect of acid treatment on coals of sizes 0·5 to 0·1 mm.

(4) Ratio of coal to acid mixture (by weight): Sustmann and Lehnert used two parts by weight of acid to one of coal; the proportions between coal and the acid mixture were the same in the German industrial process. Fieldner and co-workers (loc cit) varied this ratio from one part of coal to one part of acid mixture to one part of coal per 17 parts of the acid mixture.

(5) Vessel for hydrofluoric acid treatment of coal: Reference to the nature of the reaction vessel, apart from cases where a platinum dish had been employed, was absent in most of the papers mentioned. The use of the platinum dish was obviously limited to experiments dealing with a few grams of coal only.

In the Carl Alexander Mine process, the acid extraction pots were made of moulded carbon blocks, cemented by pitch.

/B. ....

B. CONDITIONS OF ACID TREATMENT IN THE PRESENT INVESTIGATION.

(1) Concentration of acids used: The success of any process for the preparation of ultra-clean coals by acid-treatment would largely depend on keeping the concentration of the acids used, as low as possible. According to the above survey, apart from the German industrial process, the lowest concentration of hydrofluoric acid used was 5 percent and that of hydrochloric acid 1·1 percent but Sustmann and Lehnert, who used the 1·1 percent acid, indicated that better results were obtained with 3·3 percent hydrochloric acid. In view of this, it was decided to carry out the present investigation with 5 percent hydrofluoric and 5 percent hydrochloric acids.

(2) The search for a suitable reaction vessel: The first few experiments on the hydrofluoric acid treatment of coal was carried out at the laboratory temperature in a rock jar, the inside of which had been coated with a hydrofluoric acid resistant bitumin paint. The contents of the jar were kept stirred by a motor driven stirrer with wooden arms. Prolonged treatment of a sample of coal (bituminous coal sample from the Lugar works, ash (dry) 2·6 percent) for 24-48 hours under these conditions seldom reduced the initial ash content by more than half. Thus quite early

/in ....

in the course of the present investigation, it was realised that the hydrofluoric acid treatment to be effective must be carried out at higher temperatures.

The choice of a suitable vessel for HF treatment at or near the boiling point of the acid presented considerable difficulties. Attempts to use a glass vessel coated with the hydrofluoric acid resistant paint, had to be given up, since the paint did not withstand temperatures higher than 85°C.

The first series of experimemts on the hydrofluoric acid treatment at 90°C and above was carried out in a lead lined cast iron vessel. This too could not be used for long, since the lining was not quite resistant to hot hydrofluoric acid.

The first successful set of experiments on hydrofluoric acid treatment near the boiling point of the acid was carried out in a keebush beaker (capacity two litres). After a few trials with water and brine baths, an air bath was considered to be the most suitable for heating this bakelite vessel. An air oven was devised out of a suitably insulated bucket, supported on a ring burner; an inverted tripod, suspended inside the bucket supported the bakelite vessel, the base of the vessel being a few inches above the bottom of the bucket. The contents of the beaker were kept stirred by a motor driven stirrer, with a vulcanite stem and wooden arms.

The stem stood the acid well, but the arms being of soft wood had to be replaced every week. A wooden cover was provided for the vessel and the bucket. This arrangement enabled acid treatment to be carried out at 90-95°C and was in use for a considerable period during the present investigation.

The main defects in this set-up were:-

(i) Bakelite being a very poor conductor of heat, it took ninety minutes for the contents of the beaker (one litre) to reach the maximum temperature of 90-95°C.

(ii) The maximum temperature obtainable under this arrangement was below the boiling point of the acid and experiments on acid treatment at the boiling point could not be carried out.

(iii) The bakelite developed cracks due to quick heating and cooling and the average life of the vessel was only three months of continuous use. (There was no evidence to suggest that the bakelite itself had been affected by the hot hydrofluoric acid).

(iv) In this case there was no provision for condensing the hot acid vapours and so the concentration of the acid was continually changing during the experiment.

(v) Examination of the results of the ultimate analyses of the original and the acid treated samples of the coals, led one to suspect the possibility of oxidation of the coal when treated

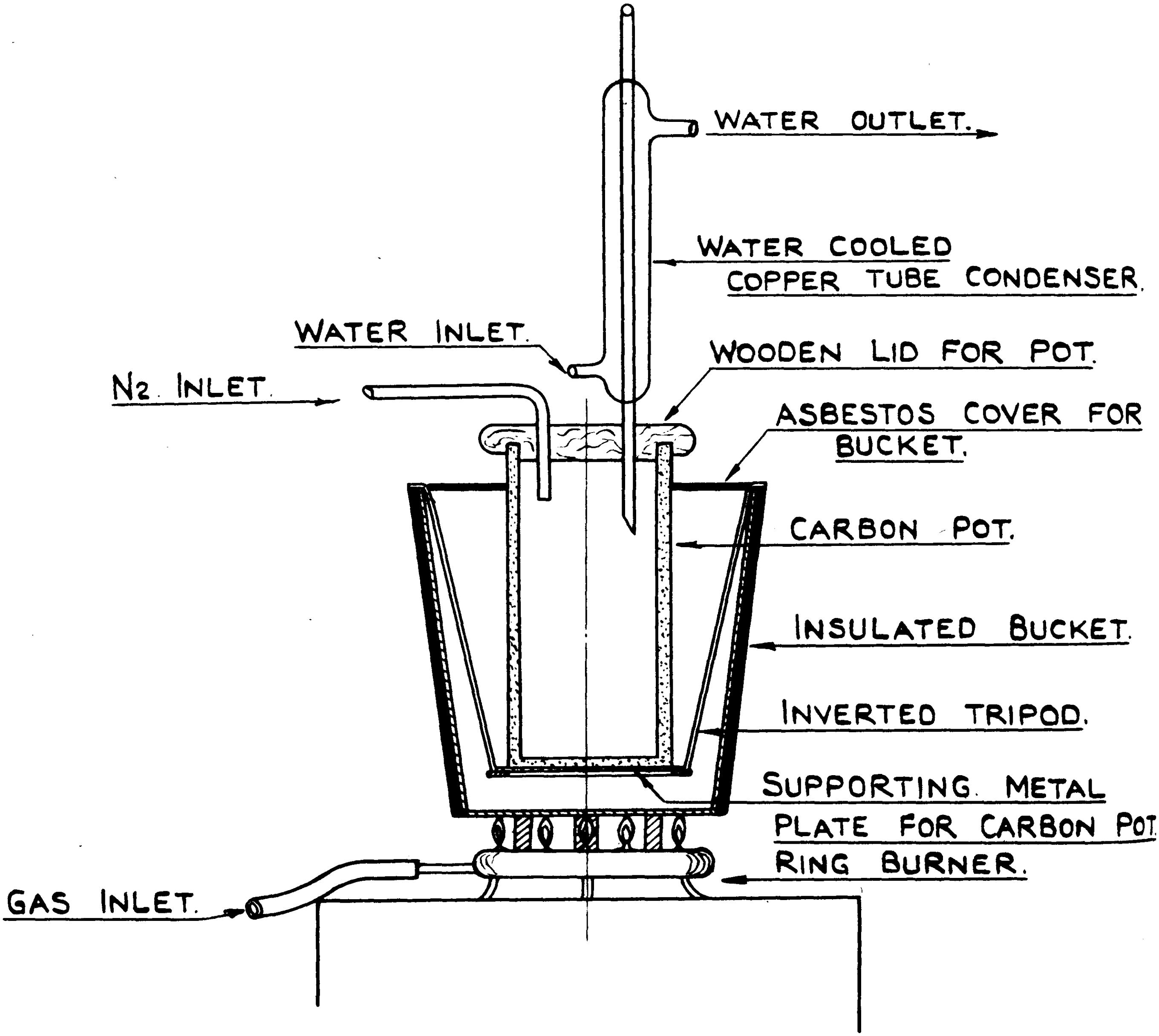
WATER OUTLET.
WATER COOLED COPPER TUBE CONDENSER.
WATER INLET.
WOODEN LID FOR POT.
N_2. INLET.
ASBESTOS COVER FOR BUCKET.
CARBON POT.
INSULATED BUCKET.
INVERTED TRIPOD.
SUPPORTING METAL PLATE FOR CARBON POT.
RING BURNER.
GAS INLET.

FIG. 1.

under these conditions. Hence it was desired to carry out the acid treatment in an inert atmosphere, for the maintenance of which this set-up was hardly suitable.

(3) Use of a carbon pot for the hydrofluoric acid treatment of coal:

It was noted that most of the defects mentioned above could be overcome by substituting a carbon pot in place of the bakelite vessel, and this was done, as soon as one was available.

The final set-up is shewn in Fig. 1. The arrangement of the air bath was the same as before. The cylindrical carbon vessel was fitted with a separate tight fitting, two holed wooden lid (made of hard wood and coated with the acid resistant paint). Through one of the holes in the lid was fixed a water-cooled, copper tube condenser and the other served as inlet for nitrogen. In this arrangement, the contents of the carbon pot (1 litre) reached the boiling point (100°C) in less than 45 minutes, after which boiling could be maintained with reduced flame.

The above arrangement was found quite satisfactory; but it must be mentioned that a cylindrical vessel was by no means the ideal one for refluxing. A spherical vessel, with a reasonably wide opening, which could have been closed with a

/tight ....

tight fitting cork, would have been more suitable. But carbon vessels in special shapes were difficult to get.

In the experiments with the cylindrical carbon pot, it was found necessary to seal the crevices between the wooden lid and the pot, with clay in order to prevent the leakage of acid vapours. Thus there was always the possibility, that while removing the hardened clay at the end of an experiment, a few particles might fall into the extraction pot and thereby spoil the experiment. This problem could have been solved by using a more suitable sealing substance than clay, but no such substance could be readily found and the experiments were carried out in the cylindrical carbon pot, using clay to seal the crevices between the lid and the pot.

(4) The coal samples used in the investigation: Table No.1 gives the proximate analyses of the coal samples used in this investigation.

Sample No.1 was clarain from the main seam, Barony colliery and this was found to be remarkably free from durain. Sample No.2 was obtained originally for preparing a sample of clarain, but had to be examined as received, since it was not quite easy to separate it from the other banded constituents present. Sample No.3 of durain was

/prepared ....

PARTICULARS OF COAL AND CANNEL SAMPLES EXAMINED

Number	Details
1.	Clarain, Main Seam, Barony colliery.
2.	Bituminous coal sample, Lugar Works.
3.	Durain, Thankerton colliery.
4.	Durain containing bright coal, (Lugar Works).
5.	Fusain, Diamond Seam, Ayr colliery.
6.	Fusain, Warrix colliery.
7.	Cannel, Loanbead colliery.
8.	Cannel, Cowdenbeath colliery
9.	Cannel, Randolph colliery
10.	Cannel, Virtuewell Seam, Royal George colliery
11.	Cannel, Kiltongue Seam.
12.	Inferior cannel, Whitehill colliery.

In the subsequent tables, these samples are referred to by the numbers cited above.

TABLE NO. I

PROXIMATE ANALYSIS
(Air dried basis)

Sample No.	Moisture %	Ash %	Volatile matter (dry CO_2 free) %	"Fixed carbon" %
1.	3·0	1·3	50·6	45·1
2.	3·9	2·5	45·0	48·6
3.	2·5	3·5	34·0	60·0
4.	2·0	4·8	38·6	54·6
5.	8·2	5·4	19·6	66·8
6.	2·5	23·4	21·5	52·6
7.	5·2	2·9	50·0	41·9
8.	3·4	3·9	51·2	41·5
9.	4·4	6·5	63·3	25·8
10.	3·9	26·5	40·1	29·5
11.	3·9	33·8	48·8	13·5
12.	4·5	43·5	40·8	11·2

prepared from a coal sample from Thankerton colliery; the band of dull coal was fairly thick and it was easy to separate the durain from the rest. Sample No. 4, contained reasonable amounts of durain, but in view of the very thin layers of bright coal interspersed in the layer of dull coal, it was considered advisable to examine it as such. Samples 5 and 6, of fusain were collected over a period of time, at the collieries mentioned, specially for the sake of this investigation.

All the cannel samples were examined as received; of these samples 7, 10, 11 and 12 had been stored in the laboratory for some time. Two samples, differing widely in ash content, of the cannel from Randolph colliery were available.

The wide variations in ash content (noted in Table No.1) made these samples specially suited for experiments on acid treatment of coals; besides none of these samples could be cleaned to any appreciable extent by any of the usual physical methods. By the very nature of the mineral matter in cannels, the density separation methods were inapplicable to them; but of the six other samples, only one gave any separation in the course of an examination of their washability characteristics by float and sink determinations using mixtures of carbon tetra chloride and benzene. This was sample No.2 (the coal sample from Lugar works;

ash 2·6 percent (dry)) which gave a 1 percent yield of a sample of 0·98 percent ash and a 38·5 percent yield of a sample of 1·58 percent ash, with solutions of specific gravity 1·255 and 1·263 respectively.

(5) A procedure for acid treatment: In all the following experiments the treatment with the two acids was carried out separately with 5 percent hydrofluoric acid and 5 percent hydrochloric acid. 40 percent commercial hydrofluoric acid and 35 percent pure concentrated hydrochloric acid were available in the laboratory and the required quantities of the two 5 percent acids were prepared by dilution.

At first hydrofluoric acid treatment was continued till there was no further reduction in ash content of the coal and this was followed by treatment with hydrochloric acid again, till no further reduction in ash content was noticeable. This normally meant the continuation of the treatment with each acid for ten to fifteen hours; subsequently it was found that better results could be obtained by treating the sample with hydrofluoric acid for a short period, followed by hydrochloric acid treatment for the same duration and then by repeating the treatment over again. This procedure, apart from the saving in time involved,

/almost ....

almost invariably gave a product with lower ash content. The period of treatment with hydrofluoric acid was five hours when the bakelite vessel was used but with the carbon vessel, it was reduced to four hours.

(6) Experimental details for hydrofluoric acid treatment of coal:

250 gms. of the sample (100 percent through 72 mesh B.S.sieve) were mixed with 1000 ml. of 5 percent hydrofluoric acid in the carbon pot; the pot was closed with the lid, sealed with clay and placed inside the air oven as shown in Fig. 1; the water-cooled copper tube condenser was fitted in and the air inside the vessel flushed out with nitrogen, after which the heating was started. A full flame was maintained at the start till the contents were raised to boiling, after which a reduced flame was maintained. A very slow stream of nitrogen was passed through the pot during this treatment. At the end of four hours, heating was discontinued, the apparatus allowed to cool, the clay used for sealing carefully removed, and the contents of the carbon pot filtered in a suction filter.

(7) Experimental details for hydrochloric acid treatment of coal:

250 gms. of the sample were taken in a two litre round bottomed flask containing 1000 ml. of 5 percent hydrochloric acid; the flask was fitted with a water-cooled

/reflux ....

reflux condenser and heated over a bunsen flame; refluxing was continued for four hours, at the end of which, the contents were cooled and filtered.

(8) Washing of acid treated coals: Washing the coal samples thus treated completely free of the acids was not quite easy. Normally by washing the product with hot tap water, three to four times the quantity of acid used, followed by a final wash with hot distilled water gave a sample which was neutral and free of chlorides; but on keeping the same sample in distilled water for a few minutes, the chloride reaction reappeared; and the sample could be completely freed from chlorides only by repeated boiling with hot distilled water. No difference in ash content was noted between the samples which had been freed from chloride and the ones which had been washed with tap water three to four times and finally with distilled water. So in all cases, the acid treated samples were washed with hot tap and distilled water only, and whenever necessary, completely chloride free samples were prepared from this main sample.

Sustmann and Lehnert (25) noted this difficulty in freeing the coals completely of the acids and they recommended that for ash determinations, it was not necessary to use a completely chloride free sample.

/9. ....

(9) Drying:

Drying of the acid treated samples was carried out in an electrically heated moisture oven at 50-55°C.

/C. ....

C. EXAMINATION OF THE FACTORS INFLUENCING ACID TREATMENT:

(1) The results of the general procedure:

The results of the acid treatment of the twelve samples are summarised in Table No.2. The samples were subjected to alternate treatments with 5 percent hydrofluoric and 5 percent hydrochloric acid, each treatment being for four hours. The quantity of acid used in each case was four times the weight of coal taken.

The ash determinations were made on air dried samples and in Table 2 they are given on a moisture free basis for purposes of comparison. The percentage yield of ultra-clean coals has been calculated on the dry weight of the original sample.

In cases where the sample even after two alternate acid treatments had an ash content over 1 percent, the acid treatment was repeated a third time under the same conditions to see whether any further reduction in ash content was possible. But in no case was there any further reduction in ash content. So it was considered necessary to examine the effect, of treatment with stronger reagents on such samples.

/(2) ....

TABLE NO. 2

ACID TREATMENT OF COAL

Size of coal = 100% through 72 mesh. (B.S. Sieve).
Quantity of acid = 4 times the wt. of coal taken.
HF treatment done in Nitrogen atmosphere.

	Ash content - dry basis					
Sample No.	Original Sample (a) %	(a) boiled with 5% HF, 4 hours. (b) %	(b) refluxed with 5% HCl, 4 hours. (c) %	(c) boiled with 5% HF, 4 hours. (d) %	(d) refluxed with 5% HCl, 4 hrs. (e) %	Yield of ultra clean coal (% of dry coal taken) %
(1)	1.34	1.10	0.88	0.72	0.53	98.0
(2)	2.60	1.10	0.80	0.70	0.52	96.0
(3)	3.59	2.10	1.80	1.10	0.82	95.0
(4)	4.90	2.40	1.60	0.70	0.42	93.0
(5)	5.88	3.80	1.70	1.40	1.34	91.5
(6)	24.00	12.60	6.50	4.50	3.03	66.0
(7)	3.06	1.90	1.20	0.80	0.73	94.5
(8)	4.04	2.10	1.20	0.70	0.52	95.0
(9)	6.80	3.90	2.60	2.10	2.01	91.5
(10)	27.57	20.00	15.42	4.60	1.37	70.5
(11)	35.18	18.60	10.62	3.60	1.25	60.0
(12)	45.55	25.60	14.70	1.50	0.63	50.0

NOTE: In the case of samples (Nos. 5, 6, 9, 10 and 11) the HF and HCl treatments were repeated a third time under the same conditions without any further reduction in ash content.

(2) Use of stronger acids (Cf: Table No. 3).

Five samples already acid treated under conditions referred to in Table No. 2 were chosen for these experiments. Three had ash contents above and two below 1 percent. These experiments could not be carried out with the two samples of acid treated fusain, since they were not available in sufficient quantities.

50 gms. of sample were used for these experiments, the quantity of acids used being twice the weight of the sample taken. The hydrofluoric acid treatment was carried out in an open nickel vessel by boiling; since in this case, fresh acid was added during the experiment to make up the loss due to evaporation, the concentration was not constant throughout each experiment. The treatment with HCl was carried out as usual.

(3) Variation of the order of treatment with acids:

In Table No. 4 are given the results of experiments, which were undertaken to see how the extraction of the mineral impurities in coal was affected by treating the samples first with 5 percent hydrochloric acid instead of with 5 percent hydrofluoric acid; alternate treatment with the two acids was repeated till the minimum possible ash content was reached.

/(4) ....

TABLE NO. 3

ACID TREATMENT OF COALS - USE OF STRONGER REAGENTS
(all ash values on a dry basis)

DETAILS	Sample No.7 Ash %	Sample No.9 Ash %	Sample No.10 Ash %	Sample No.11 Ash %	Sample No.12 Ash %
(i) original sample ----------------(a)	3.06	6.80	27.57	35.18	45.55
(ii) (a)treated with acids as in Table No.2.------------(b)	0.73	2.01	1.37	1.25	0.63
(iii) (b)boiled with 10% HF for 2 hrs. & 10% HCl for 2 hrs.-----------(c)	0.70	1.90	1.30	1.20	0.60
(iv) (c)boiled with 20% HF for 2 hrs. & 20% HCl for 2 hours. ---------(d)	0.70	1.90	1.30	1.00	0.60
(v) (d) boiled with 30% HF for 1 hr. & 30% HCl for 1 hour. ----------(e)	0.70	1.90	1.00	1.00	0.50
(vi) (e)boiled with 40% HF for 1 hr. & conc. HCl (35%) for 1 hour. ------(f)	0.70	1.90	0.96	1.00	0.46

TABLE NO. 4

ACID TREATMENT OF COALS : VARIATION OF THE ORDER OF TREATMENT WITH ACIDS

Size of coal : 100% through 72 mesh B.S.Sieve.
Quantity of acid : 4 times the weight of coal.

Expt. No.	Details	Sample No. 2 Ash % (dry)	Sample No. 7 Ash % (dry)
I			
(i)	Initial ash content, sample....(a)	2.60	3.06
(ii)	(a) refluxed with 5% HCl for 4 hours.................(b)	2.00	2.70
(iii)	(b) treated with 5% HF for 5 hours.................(c)	1.02	1.40
(iv)	(c) refluxed with 5% HCl for 4 hours.................(d)	0.80	1.00
(v)	(d) treated with 5% HF for 5 hours.................(e)	0.80	0.90
(vi)	(e) treated with 5% HCl for 4 hours.................(f)	0.50	0.70
II			
(i)	Sample (a) treated with 5% HF for 5 hours...............(g)	1.20	1.70
(ii)	(g) refluxed with 5% HCl for 4 hours.................(h)	0.80	1.30
(iii)	(h) treated with 5% HF, for 5 hours.................(i)	0.60	0.90
(iv)	(i) refluxed with 5% HCl for 4 hours.................(j)	0.50	0.70

HF treatment in the above experiments was carried out in the bakelite vessel at 95°C.

(4) Influence of particle size of coal on the extraction of the impurities in coal with acids:

It is well known that in chemical reactions finer particle sizes facilitate quicker reaction with the solvent; thus the effectiveness of acid treatment should be determined by the particle size to which the coal was crushed before treatment.

All the experiments that have been reported in the earlier tables were done with samples crushed to pass through a 72 mesh B.S. sieve; in this set of experiments, (Cf Table No.5) samples crushed to pass through 18,140, 200 and 300 mesh B.S. sieves were treated with the two acids under the same conditions as before. The various samples were prepared by carefully adjusting a coffee mill to give a product that would just pass through a particular sieve without an unduly high percentage of fines; ash determinations of the samples of various sizes of each coal showed that they were representative of the original sample.

(5) Acid treatment of coke: It is well known that coke is more porous than coal; it was thought that the higher porosity of the coke would facilitate better interaction between the impurities in coke and the acids than would the corresponding sample of coal. This was the main idea behind the experiments described in Table No.6.

TABLE NO. 5

ACID TREATMENT OF COAL - INFLUENCE OF PARTICLE SIZE.
Quantity of acids - 4 times the weight of coal.

Expt. No.	Sample No.	Size 100% Thro' B.S. Sieve	ASH CONTENT (DRY)				
			original sample (a) %	(a)4 hrs. 5% HF (b) %	(b)4 hrs. 5% HCl (c) %	(c)4 hrs. 5% HF (d) %	(d)4 hrs. 5% HCl (e) %
I	(1)	18	1.3	1.2	1.1	1.1	0.7
		72	1.3	1.1	0.9	0.7	0.5
		140	1.3	1.1	1.0	0.7	0.5
		200	1.3	1.0	1.0	-	0.5
		300	1.3	1.1	1.0	0.8	0.5
II	(2)	18	2.6	1.3	1.0	0.9	0.8
		72	2.6	1.1	0.8	0.7	0.5
		140	2.6	1.1	0.8	0.7	0.5
		200	2.6	-	-	0.7	0.5
		300	2.6	1.1	0.8	0.7	0.5
III	(9)	18	17.3	15.0	6.8	5.0	2.8
		72	17.3	12.4	7.5	3.7	2.1
		140	17.3	12.2	7.0	2.2	1.9
		200	17.3	11.5	6.7	3.9	1.8
		300	17.3	9.6	6.0	2.0	1.5

/IV. ....

TABLE NO. 5 (CONTD.).

Expt. No.	Sample No.	Size 100% thro' B.S. Sieve	ASH CONTENT (DRY BASIS) original sample (a) %	(a)4 hrs. 5% HF (b) %	(b)4 hrs. 5% HCl (c) %	(c)4 hrs. 5% HF (d) %	(d)4 hrs. 5% HCl (e) %
IV	(10)	18	27.6	23.4	16.3	6.5	2.5
		72	27.6	20.0	15.4	4.6	1.4
		140	27.6	17.9	8.3	3.1	1.4
		200	27.6	16.1	7.3	-	1.4
		300	27.6	15.9	6.4	3.2	1.4
V	(12)	18	45.6	28.7	14.0	4.8	2.0
		72	45.6	25.6	14.7	-	0.6
		140	45.6	25.4	12.0	3.3	0.6
		200	45.6	22.4	12.5	3.7	0.6
		300	45.6	20.4	8.7	2.5	0.5

TABLE NO. 6

ACID TREATMENT OF COAL AND COKE

Sizes of coal and coke used for acid treatment. } 100% through 72 mesh, B.S. Sieve.

Expt. No.	Details	Bituminous coal sample from Ingar Ash (dry) %	Cannel, Loanbead colliery. Ash % (dry).
I			
(i)	Original sample ....(a)	2.60	3.06
(ii)a.	carbonised at 800°C ....coke (b)	3.70	5.00
(iii)b.	treated with 5% HF, 5 hrs. ....(c)	1.25	2.46
(iv)c.	refluxed with 5% HCl, 4 hrs. ..(d)	1.00	1.90
(v) d.	treated with 5% HF, 5 hrs......(e)	1.00	1.20
(vi)e.	refluxed with 5% HCl, 4 hrs....(f)	1.00	1.20
II			
(i)	(a) acid treated as per Table No.2......................(g)	0.52	0.73
(ii)	(g) carbonised at 800°C,.....coke(h)	0.80	1.20
(iii)	(h) treated with 5% HF, 5 hours.......................(i)	0.80	1.20
(iv)	(i) refluxed with 5% HCl, 4 hours.......................(j)	0.80	1.20
(v)	(j) treated with 5% HF, 5 hours.......................(k)	0.80	1.20
(vi)	(k) refluxed with 5% HCl, 4 hours.......................(l)	0.80	1.20

NOTE: The HF treatment was carried out in the bakelite vessel at 95°C.

Two different sets of experiments were carried out (a) the coal and the cannel samples were carbonised (in an electric furnace at 800°C, the charge being contained in a silica tube) and the coke samples were acid treated under same conditions as before; (b) the same coal and cannel samples were first treated with the two acids under conditions described in Table No.2 and the resultant ultra-clean (coal) samples were carbonised at 800°C; the coke samples thus obtained were again acid treated under the same conditions.

The coal sample from Lugar works gave a good coke, which was crushed to pass through 72 mesh B.S.sieve before acid treatment; the coke from the cannel was powdery; so were the two samples obtained from the ultra-clean coal and cannel.

(6) Use of mixed acids: The main reason for carrying out the treatment with the two acids separately was the non-availability of a suitable condenser, that could be used with both acids. It was learnt that by using condensers, where the inner surface was coated with resins, which were resistant to both acids, the set up used for hydrofluoric acid treatment, could be used for a mixture of the two acids.

/One ....

One such resin was the Marco resin 61C, supplied by Messrs. Scott Bader and Co. Ltd., and this was described as a "versatile resin, with excellent fabricating properties and characterised by exceptional interlaminar adhesion, outstanding weather and chemical resistance", in their literature.

This resin was dissolved in monomer C (also supplied by the firm) in presence of the supplied catalyst (Benzoyl Peroxide) and the solution was used for coating the inside of a reflux condenser; care had to be taken to ensure that a light coating was obtained; for with a thick coating, because of the poor conductivity of the resin, there was little or no condensation of the acid vapours, even with maximum water circulation. But even with a thinly coated condenser, the use of this resin for combined acid treatment could not be described as an unqualified success; with thin coatings, it was difficult to get thorough adhesion on glass, with the result that the hydrofluoric acid vapours started attacking the uncovered spots. Three condensers had to be rejected during the experiments reported in Tables 7 and 10.

/In ....

TABLE NO. 7

ACID TREATMENT OF COALS - USE OF A MIXTURE OF ACIDS.

Acids used: 5% HF and 5% HCl, twice the weight of coal taken.

Size of coal used: 100% through 72 mesh B.S.Sieve.

Expt. No.	Sample No.	ASH CONTENT (DRY BASIS) original sample	Samples taken at the end of:- 5 hours	10 hours	15 hours	20 hours	Ash content of samples acid treated as per Table No.2.
I	(1)	1.34	0.70	0.50	0.50	-	0.53
II	(7)	3.06	1.10	0.70	0.70	-	0.73
III	(12)	45.55	14.20	-	1.50	0.60	0.60

In these experiments (Cf Table No. 7) three samples were treated with a mixture of 5 percent hydrofluoric and 5 percent hydrochloric acids in one operation; the only other modification in the procedure was that the total quantity of acids used was reduced to twice the weight of coal taken. The acid treatment was stopped at intervals of five hours for taking samples.

/D. ....

D. EXAMINATION OF THE EFFICIENCY OF ACID TREATMENT OF COALS.

(1) Examination of the ash: The aim of acid treatment of coal is the removal of the inorganic constituents of coal by solution. From the results tabulated earlier, it can be seen that there remains in all the samples of coals, a small percentage of mineral matter, which could not be removed by acid treatment. Thus for a proper determination of the efficiency of extraction of the mineral matter in coal by the two acids (in terms of the ash), it would be necessary to analyse the ash of the original and acid treated samples; but in the case of the ultra-clean coals prepared by acid treatment, because of the very low ash content, it would be tedious to obtain sufficient quantities of the ash necessary for complete ash analysis.

In view of this difficulty, the following experiments were designed to examine how far the different constituents in the ash of the various coals, which were soluble in water, dilute hydrofluoric acid and dilute hydrochloric acid, had been extracted by acid treatment.

Experiment: About 0·1 to 0·2 gms of ash was weighed out in a platinum crucible and digested with water for half an hour over an air bath; the contents were then filtered, repeatedly washed with cold water, and the residue incinerated to constant weight; the difference in weight gave the water soluble portion in the ash.

TABLE NO.8

EXAMINATION OF THE ASH.

PARTICULARS	Ash (dry basis) % (1)	Water Soluble Portion % of ash (2)	SiO_2 % of Ash. (3)	Fe_2O_3 % of Ash. (4)	Balance % of Ash. (5)
SAMPLE NO. I					
(a) original sample	1.34	42.8	8.1	21.3	27.8
(b) acid treated sample	0.53	7.0	8.7	13.5	70.8
(c) Efficiency of extraction (% of original sample)	60.7	93.6	57.9	75.1	-(?)
SAMPLE NO. 2					
(a) original sample	2.60	38.0	31.1	16.5	14.4
(b) acid treated sample	0.52	3.7	22.5	22.9	50.9
(c) Efficiency of extraction (% of original sample)	80.4	98.1	85.8	72.8	30.8
SAMPLE NO. 3					
(a) original sample	3.59	9.0	48.6	6.8	35.6
(b) acid treated sample	0.82	trace	33.4	3.2	63.4
(c) Efficiency of extraction (% of original sample)	77.8	100.0	84.8	89.6	60.4
SAMPLE NO. 4					
(a) original sample	4.90	7.9	38.8	17.5	35.8
(b) acid treated sample	0.42	trace	5.0	14.0	81.0
(c) Efficiency of extraction (% of original sample)	91.8	100.0	98.9	93.5	81.5

/SAMPLE NO.5 ....

TABLE NO. 8 (Contd.).

PARTICULARS	Ash (dry basis) % (1)	Water Soluble portion % of ash (2)	SiO_2 % of Ash. (3)	Fe_2O_3 % of Ash. (4)	Balance % of Ash. (5)
SAMPLE NO. 5					
(a) original sample	5.88	13.3	16.0	14.3	56.4
(b) acid treated sample	1.34	6.4	14.3	20.1	59.2
(c) Efficiency of extraction (% of original sample)	78.3	89.5	80.6	69.5	77.1
SAMPLE NO. 6					
(a) original sample	24.00	20.8	13.1	6.4	59.7
(b) acid treated sample	3.03	3.6	14.3	13.7	68.4
(c) Efficiency of extraction (% of original sample)	90.1	98.3	89.3	78.9	88.6
SAMPLE NO. 7					
(a) original sample	3.06	7.7	51.6	16.8	23.9
(b) acid treated sample	0.73	trace	9.0	31.3	59.7
(c) Efficiency of extraction (% of original sample)	76.8	100.0	95.9	56.6	41.8
SAMPLE NO. 8					
(a) original sample	4.04	6.3	48.6	17.3	27.8
(b) acid treated sample	0.52	trace	13.7	16.5	69.8
(c) Efficiency of extraction (% of original sample)	87.6	100.0	96.5	88.1	68.8

/SAMPLE NO. 9 ....

TABLE NO.8
(Continued).

PARTICULARS	Ash (dry basis) % (1)	Water Soluble Portion % of ash (2)	SiO_2 % of Ash. (3)	Fe_2O_3 % of Ash. (4)	Balance % of Ash. (5)
SAMPLE NO.9					
(a) original sample	6.80	7.8	60.5	28.5	3.2
(b) acid treated sample	2.01	trace	38.5	52.5	9.0
(c) Efficiency of extraction (% of original sample)	72.0	100.0	82.1	48.2	21.3
SAMPLE NO.10					
(a) original sample	27.57	4.9	61.6	2.8	30.7
(b) acid treated sample	1.37	trace	37.5	28.2	34.3
(c) Efficiency of Extraction (% of original sample)	96.3	100.0	97.7	63.3	95.9
SAMPLE NO.11					
(a) original sample	35.18	8.5	57.8	13.3	20.4
(b) Acid treated sample	1.25	trace	44.2	43.5	12.3
(c) Efficiency of extraction (% of original sample)	97.7	100.0	98.3	92.4	98.4
SAMPLE NO.12					
(a) original sample	45.55	9.1	72.7	16.3	1.9
(b) acid treated sample	0.63	trace	12.7	22.7	64.6
(c) Efficiency of extraction (% of original sample)	99.2	100.0	99.9	99.0	74.2

The water insoluble portion was carefully digested in the platinum crucible with 40 percent hydrofluoric acid over an air bath for forty minutes at the end of which it was allowed to evaporate to dryness; the residue in the crucible was then heated over a strong flame and weighed; the digestion and incineration were repeated till concordant values were obtained. The loss in weight gave the hydrofluoric acid soluble portion.

These experiments were repeated with the original and acid treated samples of all coals and cannels (Cf Table No.8).

The efficiency of extraction of each component could be expressed only on the basis of the ash or the corresponding portion of the ash of the original sample. Since each gram of the acid treated sample would have been derived from more than one gram of the original sample, all the values for the ash (and the different fractions) of the acid treated sample given in Table No.8 were corrected to the same basis as the ash content of the original sample before calculating the efficiency of extraction.

For purposes of comparison the values for iron (as Fe_2O_3), which were obtained by separate determinations, are also given in Table No.8.

(2) Examination of the distribution of iron in coal and the efficiency of its extraction by acid treatment.

Iron is known to occur in the mineral matter of coal in the form of carbonate and sulphate (soluble in dilute hydrochloric acid), pyrite (partly soluble in hot dilute hydrochloric acid) and also as silicates and oxides.

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So no data of the efficiency of extraction of iron in coal by acids would be complete without a knowledge of the form in which the iron was present. In the following experiments separate determinations were made for (1) the dilute hydrochloric acid soluble iron, (2) the pyritic iron and (3) total iron in coal. In the results tabulated in Table No.9 the difference between the total iron and the sum of pyritic and dilute acid soluble iron has been reported as iron present in other forms.

Determination of the total iron in coal: This was determined from a sample of the ash; the silica in the ash was removed by voltalisation with hydrofluoric acid; the residue was gently heated with sodium pyrosulphate and finally extracted with dilute sulphuric acid; made up to a known volume and titrated against standard titanous chloride using thiocyanate indicator in a carbon dioxide atmosphere.

The values for the total iron present are given as ferric oxide in Table No.8 and as iron in Table No.9.

Dilute hydrochloric acid soluble iron and pyritic iron in coal: These two determinations were originally made in connection with the evaluation of the correct value for the mineral matter in coal and the experimental details are given in Part II of this thesis.

/E. ....

TABLE NO. 9

DISTRIBUTION OF IRON IN THE MINERAL MATTER OF COAL AND THE EFFICIENCY OF ITS EXTRACTION BY ACID TREATMENT.

PARTICULARS	Ash dry basis %	Total iron % of ash	PERCENT OF TOTAL IRON			Percentage extraction per part of iron in the original sample by acid treatment			
			dil. HCl soluble iron %	Pyritic iron %	iron in other forms (diff) %	Dil. HCl soluble iron %	Pyritic iron %	Iron in other forms %	Total iron %
SAMPLE NO.1									
(a) original sample	1.34	14.9	10.0	85.0	5.0				
(b) acid treated sample	0.53	9.4	-	100.0	-	100.0	70.8	100.0	75.1
SAMPLE NO.2									
(a) original sample	2.60	11.5	20.0	66.3	13.7				
(b) acid treated sample	0.52	16.0	-	100.0	-	100.0	59.8	100.0	72.8
SAMPLE NO.3									
(a) original sample	3.59	4.7	17.7	68.3	14.0				
(b) acid treated sample	0.82	2.2	-	100.0	-	100.0	84.9	100.0	89.6
SAMPLE NO.4									
(a) original sample	4.90	12.3	20.0	73.7	6.3				
(b) acid treated sample	0.42	9.8	-	100.0	-	100.0	91.2	100.0	93.5

/SAMPLE NO.5 ....

TABLE NO. 9 (Contd.)

DISTRIBUTION OF IRON IN THE MINERAL MATTER OF COAL AND THE EFFICIENCY OF ITS EXTRACTION BY ACID TREATMENT.

PARTICULARS	Ash dry basis %	Total iron % of ash	PERCENT OF TOTAL IRON			Percentage extraction per part of iron in the original sample by acid treatment.			
			dil. HCl soluble iron %	Pyritic iron %	Iron in other forms (diff) %	Dil. HCl soluble iron %	Pyritic iron %	Iron in other forms %	Total iron %
SAMPLE NO.5									
(a) original sample	5.88	10.0	14.9	85.1	-				
(b) acid treated sample	1.34	14.0	-	100.0	-	100.0	64.3	-	69.5
SAMPLE NO.6									
(a) original sample	24.00	4.5	14.9	85.1	-				
(b) acid treated sample	3.03	9.6	-	100.0	-	100.0	75.2	-	78.9
SAMPLE NO.7									
(a) original sample	3.06	11.8	11.1	84.2	4.7				
(b) acid treated sample	0.73	21.9	-	96.9	3.1	100.0	50.2	70.8	56.7
SAMPLE NO.8									
(a) original sample	4.04	12.1	4.1	86.3	9.6				
(b) acid treated sample	0.52	11.5	-	76.7	23.3	100.0	89.6	71.3	88.1

/SAMPLE NO.9 ....

TABLE NO. 9 (Contd.)

DISTRIBUTION OF IRON IN THE MINERAL MATTER OF COAL AND THE EFFICIENCY OF ITS EXTRACTION BY ACID TREATMENT.

PARTICULARS	Ash dry basis %	Total iron % of ash	PERCENT OF TOTAL IRON			Percentage extraction per part of iron in the original sample by acid treatment.			
			dil.HCl soluble iron %	Pyritic iron %	Iron in other forms (diff)	dil.HCl soluble iron %	Pyritic iron %	Iron in other forms %	Total iron %
SAMPLE NO.9									
(a) original sample	6.80	19.9	0.9	98.1	1.0				
(b) acid treated sample	2.01	33.9	-	100.0	-	100.0	51.1	100.0	48.2
SAMPLE NO.10									
(a) original sample	27.57	1.9	7.5	68.3	24.2				
(b) acid treated sample	1.37	19.7	-	81.5	18.5	100.0	55.4	71.3	63.5
SAMPLE NO.11									
(a) original sample	35.18	9.3	12.2	54.6	33.2				
(b) acid treated sample	1.25	30.4	-	47.9	52.1	100.0	93.3	88.0	92.4
SAMPLE NO.12									
(a) original sample	45.55	1.1	11.5	66.5	22.0				
(b) acid treated sample	0.63	15.9	-	63.0	37.0	100.0	90.0	82.2	99.0

E. SOME VARIATIONS IN THE GENERAL PROCEDURE FOR THE ACID TREATMENT OF COALS.

(1) The use of bromine water with a mixture of acids: It would be seen from the results mentioned in Section D, that iron was not completely removed by the method of acid treatment followed earlier, due mainly to the presence of pyrites in the mineral matter of coal. The normal procedure for the extraction of pyrite in coal was by the use of dilute nitric acid and bromine water, a treatment, which would oxidise the coal sample as well. So the use of nitric acid or any other oxidising agent was not considered advisable. It would be noted from the experiments detailed in table No.9, that the pyritic iron in coal had been partially extracted by hot dilute hydrochloric acid; in the experiments summarised in Table No.10, it has been examined whether the presence of bromine water along with the dilute acid would improve the efficiency of extraction of the pyrite in coal.

The experimental set-up was the same as that for the use of mixed acids - the acid treatment being done in an atmosphere of nitrogen. Three samples, which were known to contain a fair amount of pyritic iron were chosen for these experiments; otherwise the general procedure was the same.

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TABLE NO. 10

ACID TREATMENT OF COALS HIGH IN PYRITIC IRON.

Acids used : a mixture of 5% HF and 5% HCl with 50 ml. bromine water.

Quantity of acids : 4 times the weight of coal.

Size of coal : 100% through 72 mesh B.S. Sieve.

Nitrogen atmosphere used throughout.

Expt. No.	Sample No.	ASH CONTENT (DRY BASIS) original sample %	Samples taken at the end of:- 5 hours %	10 hours %	15 hours %	20 hours %	Ash content of samples, acid treated as in Table No. 2 %
I	(9)	17.30	8.40	3.50	2.00	2.00	2.10
II	(10)	27.57	12.40	5.80	2.00	1.30	1.37
III	(11)	35.18	12.20	3.70	1.30	1.30	1.25

(2) Treatment of coal with dilute alkali: A comparison of the data in Tables 8 and 9, showed that the percentage extraction of iron was in most cases higher than percentage extraction of the hydrofluoric acid insoluble portion in ash; this might be due to poor extraction of the alumina present by acid treatment; if the primary object were to extract the alumina in the mineral matter, dilute alkali should be a better reagent than any other used till now.

Extraction of specially treated coals with alkali at high pressures was done in Germany during war time (27).

In the first experiment, the acid treated bituminous coal sample from Lugar works (ash: 0.52 percent) was refluxed with 5 percent potassium hydroxide solution for four hours; the resultant product had an ash content of 0.35 percent, but the yield was only 82 percent of the weight of acid treated sample. Since the main object of this investigation was to evolve a procedure for the extraction of the mineral impurities in coal without in any way affecting the coal substance, in the next set of experiments, the alkali treatment was done at the laboratory temperature by mixing the acid treated coal sample with alkali in a bottle and then

/continuing ....

TABLE NO. 11.

EFFECT OF DILUTE ALKALI ON ACID TREATED COALS.

Quantity of alkali (5% potassium hydroxide): 4 times the weight of coal.

Each sample kept in an electrical shaker for 18 hours at laboratory temperature.

Experiment No.	Sample No.	Ash in acid treated coal %(dry basis) (Cf. Table 2)	Ash after alkali treatment % (dry)
I	(1)	0.53	0.50
II	(2)	0.52	0.50
III	(3)	0.82	0.80
IV	(4)	0.42	0.40
V	(5)	1.34	1.35
VI	(6)	3.03	3.00
VII	(7)	0.73	0.75
VIII	(8)	0.52	0.50
IX	(9)	2.01	2.00
X	(10)	1.37	1.40
XI	(11)	1.25	0.90
XII	(12)	0.63	0.65

continuing the treatment by vigorous agitation for eighteen hours in an electrical shaker. The results are given in Table No.11; the coal, after the alkali treatment was washed first with dilute acetic acid until free of alkali and then with hot water till free of acid. The initial filtrate was almost colourless and neutralisation with acid gave only a very faint trace of a precipitate in all the cases.

F. DISCUSSION OF RESULTS.

The aim of acid treatment of coals is the extraction of the mineral matter associated with it by solution; in this case, the mineral matter forms the 'solute' and the hydrofluoric and hydrochloric acid solutions, the solvent. The solubility of any given solid is known to depend upon (1) the temperature (2) the nature of the solvent and (3) the nature of the solid. So one of the means of examining the results submitted earlier would be to study the influence of these factors on this process.

(1) The temperature of acid-treatment of coals: Generally the solubility of a solid in a liquid increases with rising temperature, but the rate of increase differs widely for the different solids, and in some cases, the solubility is diminished by increasing the temperature in some ranges.

In the present investigation, the extraction with the acids was carried out at the boiling point of the acids; but it was mentioned that in the case of the coal sample from Lugar works (sample No.2; ash 2·6 percent) even prolonged treatment with 5 percent hydrofluoric acid for 24-48 hours at room temperature did not reduce the ash content below half that of the initial value. The comparatively lesser solubility of the inorganic matter in coals at ordinary

/temperatures ....

temperatures has been noted by the earlier workers.

Gallard (13) found that 1 gm. of kaolin (one of the common silicate minerals associated with coal), when treated with 120 cc. of 10 percent hydrofluoric acid for 24 hours with and without heating dissolved to the extent of 97·86 and 77·88 percent respectively.

Selvig, Ode and Gibson (28), who carried out the treatment with the two acids (5 to 10 percent) and wetting agents, at the room temperature had to continue digestion of the samples (initial ash content between 0·56 and 2·13 percent) for 24 hours to obtain a final product with ash contents between 0·35 and 0·60 percent (dry basis).

Turner and co-workers (15) treated the coal samples with hydrofluoric acid at a temperature just below the boiling point of the acid; so did Sustmann and Lehnert (25). In the present investigation also, when a bakelite vessel was used for the hydrofluoric acid treatment, the temperature was below the boiling point of the acid; but in such cases for effecting the same reduction in ash content as given in Table No.2, it was found necessary to continue the treatment for five hours, instead of the normal four hours, while using the carbon pot. (The longer period of treatment was partly due to the poor conductivity of the vessel).

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So, it could be stated that the solubility (and hence the rate of extraction) of the mineral matter of coal in the two acids, increased with rising temperature.

(2) The nature of the solvent.

(i) Concentration: The "solvents" employed in this case were five percent solutions of hydrochloric and hydrofluoric acids. The results of acid treatment following the general procedure outlined in Section C, can be seen in Table No.2. The ash contents of the final samples after two alternate treatment with the two acids (with the exception of samples No.6 and No.9) varied between 0·42 to 1·37 percent, while the initial ash contents were between 1·34 and 45·55 percent (dry basis). These values compare very favourably with the ash contents of samples obtained by previous workers, who had used much higher concentrations of the same two acids.

Gallard (loc cit) used two parts of 40 percent hydrofluoric acid and one part of hydrochloric acid of Sp. gr. 1·18 to reduce the ash content of two coal samples from 12·24 and 8·74 percent to 0·94 and 0·58 percent respectively.

Turner (loc cit), who boiled the samples with concentrated hydrochloric acid before and after the treatment with hydrofluoric acid, used 49 percent hydrofluoric acid at 95°C; thus from samples of anthracite, graphite, bituminous coal and charcoal with ash contents varying between 0·90 and 30·63 percent, he obtained ultra-clean samples, the ash contents of which were below 1·17 percent, the lowest value being 0·30 percent.

Sustmann and Lehnert (loc cit), boiled the brown and bituminous coal samples first with 1·5 percent hydrochloric acid and treated the product with 15 percent hydrofluoric acid for four hours at 90°C; the ash content of the final samples were between 0·06 to 2·0 percent while the initial values were between 2·4 and 16·2 percent.

Selvig, Gibson and Ode, (loc cit), who used a mixture of the two acids with wetting agents found, that for the seven samples of bituminous coal examined by them, a mixed acid solution containing 5 percent hydrofluoric acid and 5 percent hydrochloric acid was as effective in reducing the ash content as 10 percent hydrochloric acid and 5 percent hydrofluoric acid or 10 percent hydrochloric and 10 percent hydrofluoric acids.

The yield of ultra-clean coal given in the last column of Table No.2, as a weight percentage of the dry original sample indicated, that there was no appreciable loss of the coal substance due to acid treatment under these conditions; but any definite conclusion about such losses can be drawn only from the results of ultimate analyses of the samples, which have been reported in the second part of this work.

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The effect of stronger acids on the acid treated samples mentioned in Table No.2, can be seen in the results given in Table No.3. In this experiment, the concentration of the two acids was gradually increased to a maximum; but, out of the five cases examined, it could not be claimed, that there was any further appreciable reduction in ash content, due to the use of more concentrated acids. This was true also of one of the two exceptions noted earlier i.e. the cannel from Randolph colliery, whose ash content could not be reduced below 2·0 percent by repeated treatments with the two five percent acids.

So it could be stated that the treatment of coal samples with hydrofluoric and hydrochloric acids did not give completely "ash free" samples; the maximum possible extraction of the impurities associated with the samples listed in Table No.2 could be effected by the use of five percent hydrofluoric and five percent hydrochloric acids at their boiling points; and that the use of stronger acids, though it would influence the period of treatment, was unlikely to give a product of lower ash content.

Apart from other economic considerations, Sustmann and Lehnert (loc cit) were in favour of the use of dilute acids, since the quantity of wash water required to free the samples of the acids increased with increasing concentration of the acids.

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(ii) <u>The relative solvent action of the two acids:</u> Table No.2 gives the ash content of the samples after each treatment with the two acids. One gram of the sample after each treatment, because of its diminishing ash content, would have been derived from more than one gram of the original sample. So the results given in Table No.2 were not strictly comparable. To facilitate such comparison, values (given in Table No.12) for the reduction in ash content effected by successive treatments, were calculated, in terms of the ash content of the original sample.

A word of explanation might be necessary about the significance of these values; these were calculated from the values for ash in each case (Cf Table No.2) and hence did not represent the corresponding percentages of the mineral matter in coal; but these would be related the same. The values for "ash" content were determined only as a means of studying the rate of extraction of the corresponding portions of the mineral matter in coal.

In Table No.12, columns 4 and 6 give the reduction in "ash" content effected by the first and second treatment with hydrofluoric acid, as a percentage of the ash of the original sample; columns 5 and 7 give similar values for the two hydrochloric acid treatments. The values under column 8 are the sum of the corresponding values in columns 4 and 6 and represent the reduction in "ash" content due to

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TABLE NO. 12

A STUDY OF THE PROGRESS OF EXTRACTION OF THE MINERAL MATTER IN COAL BY ACID TREATMENT.
(Values calculated from Table No.2)

	ASH CONTENT (dry basis)		REDUCTION IN ASH CONTENT (AS PERCENTAGE OF THE ASH OF ORIGINAL SAMPLE).							Percentage extraction of mineral matter	SiO_2 extracted as % of ash of original sample
Sample No.	Original sample	Final Sample	I HF treatment	I HCl treatment	II HF treatment	II HCl treatment	Total I & II HF treatment	Total I & II HCl treatment	Total Entire Process		
(1)	(2) %	(3) %	(4) %	(5) %	(6) %	(7) %	(8) %	(9) %	(10) %	(11) %	(12) %
1	1.34	0.53	17.9	16.7	12.0	14.2	29.9	30.9	60.8	66.1	4.7
2	2.60	0.52	58.3	11.4	3.8	6.9	62.1	18.3	80.4	80.5	26.7
3	3.59	0.82	42.4	8.4	19.3	7.7	61.7	16.1	77.8	79.6	41.2
4	4.90	0.42	52.3	16.2	17.7	5.7	70.0	21.9	91.9	92.2	38.4
5	5.88	1.34	36.8	35.5	5.0	1.0	41.8	36.5	78.3	80.0	12.9
6	24.00	3.03	54.3	23.7	7.1	5.1	61.4	28.8	90.2	92.7	11.7
7	3.06	0.73	38.6	22.9	12.9	1.3	51.5	24.2	75.7	75.2	49.5
8	4.04	0.52	49.1	22.1	12.0	4.4	61.1	26.5	87.6	88.2	46.9
9	6.80	2.01	44.4	19.0	7.2	1.3	51.6	20.3	71.9	72.4	49.7
10	27.57	1.37	34.4	17.8	35.2	9.0	69.6	26.8	96.4	96.5	60.2
11	35.18	1.25	57.9	20.2	15.0	4.6	72.9	24.8	97.7	97.8	56.8
12	45.55	0.63	58.2	21.2	18.8	1.0	77.0	22.2	99.2	99.3	72.6

the two hydrofluoric acid treatments alone; column 9 gives the similar values for the two hydrochloric acid treatment; in column 10 are given the values for the total percentage of the "ash" of the original sample extracted during the entire process. To enable all the above values to be understood in their proper perspective, in col.11 are given the values for the total percentage extraction of the <u>mineral matter</u> of the original sample, by acid treatment. The mineral matter contents of the original and ultra-clean coal samples were calculated on the basis of the King, Maries and Crossley formula, the details of which, will be found in Part II of this work.

The results in Table No.12 indicate that the acid extraction of the mineral impurities in coal is similar to any normal extraction process. It is seen that in nearly all the cases between forty and sixty percent of the total extraction was effected by the first hydrofluoric acid treatment; after this during each treatment there was a gradually diminishing rate of extraction; in some cases the reduction in ash content effected by the final hydrochloric acid treatment was very slight, but in the case of the durain sample from Thankerton colliery, the two treatments with hydrochloric acid seemed to be almost equally effective. The clarain sample from Barony colliery was a major exception, since it had an almost uniform rate of extraction throughout the process, with either acid.

On comparing the values in columns 8 and 9, it will be seen that 5 percent hydrofluoric acid had definitely a greater solvent action than 5 percent hydrochloric acid. The percentage of total mineral matter extracted by either acid would depend on the nature of the impurities in coal in each case. Thus in the case of the clarain sample from Barony colliery (sample No.1), the total percentage extraction with 5 percent hydrochloric acid was actually higher than that with 5 percent hydrofluoric acid; again in the case of the fusain sample from Diamond Seam, Ayr colliery (Sample No.5), the total extraction with hydrochloric acid was comparable to, if not higher than that with the other acid. A high percentage of the mineral matter in these two cases must have consisted of salts soluble in water and dilute hydrochloric acid as distinct from the other cases, where the percentage extraction with hydrofluoric acid was higher.

Column 12 of the same Table gives the values of the quantity of silica (SiO_2) (as percent of the ash of the original sample) extracted by treatment with hydrofluoric acid; these values were calculated by multiplying the SiO_2 content of the ash (Cf Table No.8) by the corresponding value for the efficiency of its extraction. On comparing these values with the total percentage extraction effected by the two hydrofluoric acid treatments (column 8), the latter will always be found to be higher; so

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dilute hydrofluoric acid must have extracted other portions of the mineral matter as well, besides the silicate minerals. This was only to be expected; for, being the earlier acid to be used in the treatment, hydrofluoric acid, besides reacting vigorously with the silicate minerals, would have extracted all the normally dilute acid soluble components like carbonates and sulphates; moreover, of the other two major constituents of the mineral matter in coal, both iron and aluminium could form soluble fluorides. In the case of four, of the six cannels examined (samples 7-12) the two values agreed within reasonable limits; this might be due to the predominantly silicious nature of the mineral matter associated with the cannels.

Among the previous workers, Turner and co-workers, (loc cit) boiled the coal sample with concentrated hydrochloric acid before and after treatment with hydrofluoric acid. In the experiments of Sustmann and Lehnert (loc cit), also, a hydrochloric acid treatment preceded a hydrofluoric acid treatment. The results given in Table No.4 show that an initial hydrochloric acid treatment was not in any way an improvement over the suggested general procedure. When the sample was initially treated with hydrochloric acid, it required in all, three treatments with 5 percent hydrochloric acid and two treatments with 5 percent hydrofluoric acid, to effect the same reduction in ash content as done by the two alternate treatments with the two acids, starting with hydrofluoric acid.

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The difference in the rate of extraction of the impurities in the two cases could be explained by the results in Table No.12. It is seen that generally the initial hydrofluoric acid treatment effected between 40 and 60 percent of the total reduction in ash content; so during the subsequent treatment with dilute hydrochloric acid, the reaction between the acid and the remaining portions of the mineral matter would have been facilitated by the absence of impurities, the greater portion of which would normally have been insoluble in hydrochloric acid. So a hydrochloric acid treatment, preceded by hydrofluoric acid, should lead to better extraction.

The more recent workers in this field prefer an initial treatment with hydrofluoric acid. Demann and Schonmuller (according to Yancey and Geer (4)) concluded that the treatment with hydrochloric acid was more effective if preceded by hydrofluoric acid to decompose the silicious impurities. But Yancey and Geer (4), after a survey of the literature on the acid treatment of coals, reported that for brown coals, hydrochloric acid followed by hydrofluoric acid was the most effective; it was found that, with brown coals, each gram of hydrochloric acid dissolved about three grams of impurities irrespective of the concentration of the acid.

A study of columns 5 and 6 in Table No.12 elucidates the function of 5 percent hydrochloric acid in the present procedure.

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In most cases, the rate of extraction (as studied through ash determinations) was found to slacken considerably at the end of four hours of treatment with 5 percent hydrofluoric acid. This slackening might have been due to (1) the acid becoming spent and/or (2) the inaccessibility to the acid of further portions of mineral matter. The former was unlikely because in all these cases, the quantity of acid used was four times the weight of coal taken; and the ratio between the quantity of acid and mineral matter in coal must have been considerably higher. The latter reason seemed to be more probable, since a re-treatment of the same sample with 5 percent hydrofluoric acid, after an intervening treatment with 5 percent hydrochloric acid, effected a further extraction, in most cases of about 3 to 20 percent and in the case of one high ash sample (No.10) of 35 percent.

So the action of the two acids was complementary; it was advisable to start the initial extraction with dilute hydrofluoric acid; then by selectively extracting a portion of the mineral matter of the coal, each acid facilitated the further extraction by the following acid of additional portions of the mineral matter.

The percentage extraction of the mineral matter in coal (col. 11, Table No.12) varied between 65 and 99 percent; this would have been influenced solely by the nature of the mineral matter present in each case. It might be mentioned that such

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high efficiencies would be unattainable with any of the usual physical methods for cleaning coals.

(iii) <u>The use of a mixture of the two acids:</u> The general procedure for acid treatment followed in this investigation involved separate treatments with the two acids; each sample of coal or cannel was treated with the same quantities of the two acids, for the same periods, irrespective of its initial ash content. So no definite conclusions regarding the rate of extraction of the mineral matter could be drawn from the same.

Some conclusions on the rate of extraction of the mineral matter were possible from the results of experiments given in Table No.7, where each sample had been treated with a mixture of the two acids. For the first two samples, (the clarain sample from Barony colliery and the cannel from Loanbead colliery) a treatment for just over five hours was sufficient to effect a reduction in ash content from 1·34 and 3·06 percent to 0·50 and 0·70 percent (dry basis) respectively; the inferior cannel from Whitehill colliery required between 15 to 20 hours for a reduction in ash content from 45·55 to 0·60 percent.

Before attempting any comparison of the three cases, it should be noted that, the conditions of extraction being the same, the rate of extraction of the mineral matter would

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depend on (1) its chemical composition (2) its physical condition and (3) its quantity. The results in Table No.7, show that with decreasing quantities of the mineral matter, the rate of extraction also diminished. This must have been due to the fact, that, towards the later stages of extraction, the acids had to deal with those portions of the mineral matter, which were closely bound up with the coal substance and hence were less accessible to the acids than the other portions.

This was in accordance with the experience of the earlier workers, who found, that the extraction with hot acids of the mineral matter associated with bituminous coals, was essentially a slow process. Thus in the German Carl Alexander Mine process (26), the bituminous coal sample with 1·1 percent ash had to be boiled for one hour at 100°C with a mixture of the two acids, to yield a product with 0·5 percent ash. The results in Table No.7, indicated that along with bituminous coals, in the case of cannels also, the extraction was a slow process.

(iv) The variation of the total quantity of the acids: An important factor governing the solubility of solids in liquids is the ratio of the quantity of the solvent to that of the solute.

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In the general procedure outlined earlier, the quantity of acids used was four times the weight of coal taken; the ratio of the quantity of acids to that of the mineral matter would have varied roughly between 200:1 (in the case of the clarain sample from Barony) and 8:1 (in the case of the inferior cannel from Whitehill colliery). In the experiments listed in Table No.7, the quantity of acids used was twice the weight of coal taken and so the latter ratios would have been halved.

It will be seen that the ash contents of the final samples were nearly the same in both cases; this confirmed the finding of Selvig, Ode and Gibson (loc cit), that there was no difference in the ash contents of the treated coals, using either a ratio by weight of one part of coal and one part of acid or a ratio of one part of coal and 17 parts of acid solution.

(3) The influence of the nature of the mineral matter in coal on acid treatment.

The nature of the mineral matter in coal has been discussed by Crossley (36). The three main kinds of minerals associated with coals are shales or clay, sulphide minerals and carbonates.

The shaly matter consists mainly of kaolin, micas and feldspar with some quartz. The individual minerals in these classes have been identified by Ball (31) and Gauger, Barrett and Williams (32). According to Ball, the non-clay minerals, although always present are quantitatively of minor importance.

The most common sulphide minerals are pyrite and marcasite, the two distinct crystalline forms of iron disulphide, the former being cubic and the latter orthorhombic; small quantities of sulphate usually of iron and calcium occur with these minerals.

A wide range of carbonate minerals is known to be associated with the impurities in coal, the most common ones being those of calcium and iron and the less frequent ones being those of magnesium, manganese, sodium and Potassium.

(i) Influence of particle size: The solubility of solids in liquids is generally known to increase with decreasing particle size; according to this, finer grinding of the coal sample should lead to better extraction.

The effect of varying the particle sizes will be seen in Table No.5. In all the five cases examined, there was a distinct improvement in the quality of the final product, when the samples were crushed to pass 72 mesh B.S.Sieve;

coarser sizes than this yielded a product of higher ash content, while crushing to finer sizes had little or no influence on the quality of the product; but the rate of extraction of mineral matter increased with finer sizes.

Hankiss (24) (4) observed that the reduction in ash content possible with coal of 0.5 mm. size was doubled when coal was crushed to 0·1 mm. size.

The size of aperture in inches for the different sieves used is given below:-

B.S.S. No.	Size of aperture in inches.
18	0·0336
72	0·0083
150	0·0041
200	0·0030
300	0·0021

The 0·5 mm. size referred to by Hankiss would correspond approximately to a 30 mesh B.S.Sieve, while the 0·1 mm. would correspond to the 150 mesh B.S.Sieve.

The rank of the coal examined by Hankiss was not known (referred to as Maza coal); for the samples examined in this investigation, the limiting size for obtaining best results was between 18 and 72 mesh B.S.Sieves; as such there was agreement with the upper limit for sizes (0·02 in. or 30 mesh B.S.Sieve)

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recommended by Hankiss. The improvement, due to fine grinding in three samples (Nos. 9, 10 and 12) out of the five examined, could be described in the words of Hankiss "as a doubling of the possible reduction in ash content" compared with the coarser sizes.

Selvig, Ode and Gibson (loc cit) found that the crushing of one of the bituminous coal samples to pass a No.200 Sieve (U.S.Sieve) series (?) opening 0.0029 in.) gave the same reduction in ash content as a No.60 Sieve (opening 0.0098 in.). Though the coal was treated in the cold in this case, the size ranges mentioned agreed closely with the results presented.

This limiting value for sizes should have a bearing on the nature of the mineral impurities associated with coal. The silicate minerals occur as distinct bands, clay veins, sandstone intrusions and in many other forms; the sulphides too are present as bands, nodules and pyritised fossil; but both the silicate and the sulphide minerals are also known to be finely disseminated throughout the coal substance. Thus, Thiessen (37) found that there were microscopic particles of pyrite varying in diameter from a few microns to 100 microns and that the majority measured between 25 to 40 microns, with relatively few particles exceeding the latter diameter.

/Assuming ....

Assuming that the average diameter of finely disseminated pyrite and other minerals, to be 40 microns (1 micron = 0·00004 in), the diameter of each such particle would be 0·0016 in. and below. This diameter would compare favourably with that of a particle passing through a 300 mesh B.S. Sieve (opening 0·0021 in.), yet even at these sizes, complete extraction of mineral matter was not possible. This might be due partially to the fact that some of the minerals like pyrite could not be extracted completely by the two acids; but in the case of the other minerals, which were normally extracted by the two acids, it was possible that small amounts of inorganic matter were (as suggested by Fieldner in the discussion of Turner's paper (15)) adsorbed in the coal colloid and so resisted extraction with acids.

(ii) Influence of the chemical condition of the mineral matter (acid treatment of coal and coke).

These experiments (Table No.6) were undertaken to examine whether the physical changes undergone by the coal during carbonisation would in any way facilitate better extraction of the inorganic matter associated with it.

It was noted from the results, that,

(a) it was possible to obtain coke samples with lower ash content by carbonising ultra-clean coals (obtained by acid treatment) rather than by the acid treatment of coke samples obtained by the carbonisation of untreated samples of the same coal, and

/(b) ....

(b) the ash content of a sample of coke obtained by the carbonisation of ultra-clean coals (prepared by acid treatment) could not be reduced any further by repeating the acid treatment with the coke sample.

Oshima and Fukuda had shown (38) that the acid treatment of coke did not give a product with very low ash content. They treated finely ground samples of coke, with concentrated hydrochloric and hydrofluoric acid with the following results:-

	Before extraction Ash (dry) Percent.	After extraction Ash (dry) Percent.
(1) Metallurgical coke I	5·68	0·51
(2) Metallurgical coke II	14·15	3·91
(3) Gas coke I	13·73	2·79
(4) Special coke I	12·74	2·12
(5) Special coke II	15·05	4·88

The present results also confirm the same.

These results on the acid treatment of coal and coke offer an insight into the probable mechanism of extraction of the mineral matter in coal by acid treatment.

Fischer (according to Sustmann and Lehnert (loc cit) was the first to propose, that the capillary structure of brown coals facilitated the extraction of impurities, during acid treatment. The capillary structure is characteristic of the bituminous coals also, though perhaps not to the same extent as brown coals. King and Wilkins (47), after an examination of the free space within the coal substance, concluded, that in general, coal was interspersed by pores or capillaries of various sizes. The diameter and the extent of these capillaries would determine the extent of penetration of the acids and consequently the amount of mineral matter extracted. The difficulties experienced in washing the samples completely free of the acids after the acid treatment, indicated that the extent of such penetration was considerable.

In coke, the mineral matter is not present in the same condition as coal. It is known that carbonisation would be attended by two fundamental changes in the original structure of coal. The first one, which would follow the decomposition of the coal at temperatures, varying between 320 and 450°C, would result in the cementing of the fusing mass of coal to form a coherent coke; the cementing action is known to be facilitated by the presence of resinous compounds (the gamma compounds) in the original coal; secondly, almost simultaneously with the fusion, due to the evolution of the volatile matter, the coal would swell up resulting in a spongy mass, that is characteristic of the appearance of coke. It is this spongy mass, that accounts for the higher porosity of coke. The amount of extraction of the mineral matter in coke, would be determined solely by the ability of the

/acids ....

acids to react with the fused particle and this was bound to be low; hence the poorer extraction with coke as compared to coal.

(iii) The chemical nature of the mineral matter associated with coal.

Most studies on the nature of the mineral matter in coal are based on a chemical examination of the ash; ash is the residue, on ignition in air of the inorganic compounds in the mineral matter of coal that have not been volatilised; on incineration the silicate minerals usually contribute silica and alumina, while the rest contribute small quantities of the oxides of iron, calcium, sodium, potassium, magnesium, titanium and phosphorus.

Normally a complete chemical analysis of the ash from each sample would require about five grams of ash, which in the case of the acid treated samples, with their ash contents varying between 0·4 to 1·4 percent would involve the incineration of 350 to 1250 gms. of each of the samples. This consideration ruled out the idea of complete ash analysis.

After an examination of the numerous coal ash analysis, calculated to a sulphur trioxide free basis, Thiessen (33) found that over 95 percent of coal ash, with few, if any exceptions, was composed of alumina, silica, iron oxide, lime and magnesia, the magnesia content being frequently

/negligible.................

negligible; the remaining five percent consisted of such items as the oxides of sodium, potassium, phosphorus, and titanium and chlorine. Thiessen further commented that the values for these items making up the 5 percent became even less important, when the ash analysis was calculated back to the original mineral matter in coal.

So, it was thought, any indirect method that would give an idea of the silica, alumina, iron and lime content of the ash, might justifiably be adopted in place of complete ash analysis in this investigation.

In the final procedure adopted (experimental details are given in Section D), the ash was first extracted with water by digestion, washed repeatedly with cold water and incinerated; the procedure was repeated to constant weight; then the residue was digested with hydrofluoric acid twice, allowed to evaporate to dryness, raised to red heat, cooled and weighed. The loss of weight on digestion was assumed to be the silica content (SiO_2).

The correctness of the silica value would depend entirely on the complete elimination of calcium oxide at the first stage; for calcium oxide would form calcium fluoride in the subsequent treatment with hydrofluoric acid; since this fluoride is stable to red heat, the values for silica would be lowered.

/These............

These experiments were carried out with 0·2 gms. of the ash; so even if the calcium oxide content were to be as high as 50 percent, it was quite possible that it could be extracted by repeated washing with cold water. (The solubility of lime 0·131 gm/100 ml. at 10°C). Of the other two major constituents of the water insoluble residue i.e. iron oxide and alumina, according to Gore (in Mellor's treatise on 'Inorganic and Theoretical Chemistry' Vol. II, p.133), the higher oxides of iron would not be attacked by hydrofluoric acid; as for alumina, the formation of its fluoride would not affect the result, since it is not stable to heat. So, barring the chance formation of complex double fluorides with any of the trace alkali oxides, the values obtained for the silica content should be reliable. The results in Table No. 8, showed them to be of the right order.

The main justification for the adoption of this procedure was that it enabled certain general conclusions about the nature of the mineral matter in coal to be drawn, in the absence of complete ash analysis.

The results of the analysis are given in Table No. 8. Column 5 of this table gave the difference of the sum of the values in columns 2, 3 and 4 from 100 percent; since these three columns accounted for the water soluble, silica and iron content of the ash, from a general knowledge of the ash compositions, one could expect a high percentage of alumina in the remaining

/portions...............

portions (i.e. the values in Col. 5).

The ash of the clarain sample (No.1, Table No.8) contained a high proportion of water soluble salts and the silicate content was low; the latter according to Lessing (3) represented trapped detrital matter not strictly belonging to the group. The ash was of a light reddish brown colour, due perhaps to the iron in the sample.

The ash of the bituminous coal sample from Lugar works (No.2) had also a brownish tinge; the values more or less had the same significance as sample No.1; the distinctly higher percentage of silica was due to intrusions of durain in the original sample.

The ash of the durain sample from Thankerton colliery (No.3) was greyish; it was characterised by high silica and alumina content with a low value for iron. Lessing (loc cit) showed the ash of durain samples to consist predominantly of clay substance, since the alumina to silica ratio for kaolin agreed closely with the corresponding value for the ash of durain samples.

The values for the ash of the durain sample containing bright coal (No.4) followed the same trend as the earlier sample; the effect of the intrusion of bright coal was to lower the silica content and increase the iron content; the colour of

/the................

the ash was light brownish grey.

The two samples of fusain (No.5 and No.6) showed wide variations in ash content, that was typical of them. The ash in either case was dense and dark brown. The moderate amount of water soluble, low silica and the high values in column 5, indicated their derivation from the carbonates or the other salts of infiltrated water, retained by the highly absorptive surface of fusain.

The ash samples of most of the cannels (Nos.7-12) were white, with a brownish tint in some cases; but samples Nos.9 and 11 were deep brown in colour. The chief characteristic of all these was the high silica content; the iron content showed considerable variations.

(a) Efficiency of extraction of the water soluble portion of the ash. (Table No.8, Col.2).

The figures for the efficiency of extraction varied between 89 and 100 percent; the majority of the samples had an almost complete extraction. (In the ash of all acid treated coal samples, there was a small but negligible portion extracted with water).

The water soluble material in the ash would be the oxides of alkali metals and lime, the latter being the only one likely to occur in any quantity.

/The...............

The influence of temperature on the extraction of the impurities could be seen from the relative proportions of the water soluble portion of the ash in the following cases.

In the present investigation, where the extraction was carried out at the boiling point of the two acids, the water soluble portion of the ash of the acid treated sample rarely exceeded 7 percent of the ash; in most cases (eight out of the twelve cases) it was below one percent, which is recorded as trace.

The total lime and magnesia content (roughly corresponding to the water soluble portion in the present case) of the ash from the coke in the German Carl Alexander Mine process was 4·4 percent (alkali and SO_3 not determined). But in the ash analyses of samples, acid treated at room temperature by Selvig, Ode and Gibson (28), the total lime, magnesia and SO_3 content varied between 32 and 57 percent; this figure was partly due to the SO_3 content of the ash which varied between 12 and 32 percent. In the present investigation, due to the adoption of standard procedure of ashing, the SO_3 in ash never exceeded 5 percent of the ash of the original sample, while it was negligible in the ash of the acid treated sample. In the results of Selvig and co-workers for ash of the treated coals, the magnesia content was always below 4 percent while the lime varied between 8 and 23 percent. The low figures for the water soluble portion of the ash of the treated coals, in the present case, can therefore be attributed to the higher temperature of extraction.

Terres and Rost (39), after a complete examination of the mineral constituents of a number of coals, by analyses of the ash and of aqueous and acid extracts, showed that in brown coals a large proportion of these constituents might exist as salts of the humic acids or of resin or wax acids; they further pointed out that the percentage of such salts was negligible in the case of bituminous coals. In the latter case the possible presence of calcium humate was mentioned by Fieldner (in the discussion of Turner's paper (15)). Normally calcium humate should be decomposed by hydrochloric acid forming a soluble chloride and insoluble humic acid. The comparatively lower values for the percentage extraction of water soluble salts (89 and 93 percent) were obtained in samples (fusain from Diamond Seam and clarain from Barony colliery respectively) likely to contain a fair amount of lime.

So it might be assumed that at least in some cases, a small portion of the normally water soluble oxides in ash was originally present in the coal, combined with organic radicals in such a form as to resist attack by acids.

/(b) ....

(b) <u>Efficiency of extraction of silica. (Table No.8, Col.3)</u>.

The values in this case varied between 58 and 100 percent; the majority of the samples had over 80 percent of their silica content extracted by acid treatment. The very high percentage of extraction indicated that the silicate minerals associated with coal, besides being the most abundant, were in a form that reacted easily with hydrofluoric acid.

It was also significant that all the acid treated samples did contain small but definite amounts of silica i.e. the silicate minerals were not completely extracted by acid treatment. This might have been due to any one of the following reasons:-

(1) the minerals were not completely soluble in the acids. Gallard (13) (discussed earlier under the influence of temperature) has shown that a sample of kaolin was dissolved only to the extent of 97·86 percent by boiling with 10 percent hydrofluoric acid;

(2) small parts of the inorganic matter containing silicates might have been adsorbed in the coal colloid and resisted the attack by acids (suggestion by Fieldner referred to earlier); and

(3) Ball and Cady (40) attempted a study of the character and composition of the mineral matter in bituminous coals by recalculating the ash composition as kaolinite, calcite, pyrite and silica; in all the cases, they found that 94

/percent..........

percent or more of the mineral matter was accounted for. Silica was present at times in considerable excess above that necessary to combine with alumina to form kaolinite and was by far the largest component not readily associated with any other constituent in the ash. The two possible explanations suggested by them were (1) that the excess of silica represented finely divided quartz of detrital origin or (2) that silica of organic origin, though not necessarily in organic combination, was present in the coal.

The present results indicated that a small amount of the total silica was present in the coal, in a form that was either not readily attacked by the acids or was inaccessible to them. The one sample that gave the lowest percentage extraction of silica (clarain from Barony colliery) was also the one that had the lowest silica content. Lessing had shown that the silicates in the mineral matter of clarain were of detrital origin. This would suggest that the reason for incomplete extraction was mainly the inability of the acids to reach such fine particles.

(c) Efficiency of extraction of iron compounds.

The nature of the iron compound present: The iron compounds most commonly associated with the mineral matter in coal are pyrite and marcasite; besides these, Marson and Cobb (41) have mentioned the possible occurrence, in small

/quantities..........

quantities of the oxides and sulphates of ferrous and ferric iron, ferrous carbonate, iron silicates and iron in organic combination.

Iron, as pyrite in coal generally predominates, but exceptions are known. These are only to be expected, for the analyses of three different samples of pyrite by Sinnatt and Simpkin (44) revealed, that between 1·22 and 46·09 percent of the total iron was nonpyritic (FeO) in character.

Woolhouse (42), studying the distribution of iron in Parkgate coal, found that the pyritic iron constituted over 80 to 90 percent of the total iron in five out of the six cases examined; the last sample contained only 52·6 percent of pyritic iron.

Sinnatt, Grounds and Bayley (43) found, that in Lancashire Seams, the percentage of iron in ferrous condition varied between 15 and 35 percent of the total iron.

Sinnatt and Simpkin (loc cit) examined the distribution of the various forms of iron, in seven different Lancashire seams. They found (1) that the iron extracted by water (mostly the sulphates present) varied from nil to 24·79 percent of the total iron; but as a rule the amount of iron extracted by water was negligible, in some cases, the extract being merely acidic in reaction; (2) from 0·84 to 35·76 percent of the iron present went into solution in 10 percent hydrochloric acid (all the carbonates and sulphates); (3) the pyritic iron content (extracted with dilute nitric acid) varied between 55·55 and 98·05 percent and (4) that the silicate iron content was between nil to 9·52 percent.

In the present investigation separate determinations were made of the dilute hydrofluoric acid soluble iron, pyritic iron and total iron; the values reported under the column iron in other forms, were the difference of the sum of the first two, from the total iron. (Table No.9).

The values for the dilute acid soluble form of iron were between 0·89 and 20·00 percent of the total iron; for nine out of the twelve samples, the value varied between 10 and 20 percent.

The pyritic iron content varied between 55 (sample No.11) and 98 (sample No.9) percent of the total iron; five samples had values between 84 and 86 percent; four had between 66 and 68 percent; and one more had 74 percent of the total iron as pyritic iron.

The values for pyritic and dilute acid soluble iron obtained in these experiments were comparable to those of the other workers, mentioned above.

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Simpkin and Sinnatt (loc cit) showed that iron silicate was not extracted by dilute nitric acid, and so in this investigation, the nonpyritic, dilute hydrochloric acid insoluble form of iron should be the iron silicate.

The silicate iron content was found to vary between nil and 33 percent; the two fusain samples had the nil values; samples 1 to 4 had between 5 and 14 percent; but the values in the case of the cannels showed wider variations i.e. between 1 and 33 percent, the values for samples No.10, No.11, and No.12 being 24, 33 and 22 percent respectively. Thus three of the cannels examined had a higher silicate iron content than bituminous coals; such a result was quite likely, because of the predominantly silicious nature of the mineral matter in cannels.

The efficiency of extraction of the different forms of iron: The results indicated that, in all cases, the dilute hydrochloric acid soluble form of iron had been readily extracted during acid treatment; the extraction of iron silicate too was complete for six out of the ten samples, in which it was present; only in the case of the cannels it was incomplete; here again, the percentage of extraction was between 71 and 88 percent. So hydrofluoric acid was able to extract iron silicate, with comparative ease, the efficiency of extraction being governed mostly by the

/accessibility ....

accessibility of the compound to the acid.

The high percentage of extraction of these two forms of iron indicated, that their presence in any sample was unlikely to affect the overall efficiency for the extraction of the total iron adversely.

The values for the extraction of pyritic iron showed marked variations. In the case of three cannels (Nos.7,9,10) and the bituminous coal sample (No.2), it varied between 50 and 60 percent; the values for the two samples of fusain (Nos.5 and 6) and of clarain (No.1) were comparatively higher, being 64 and 75 percent and 11 percent respectively; for the other samples, the efficiency of extraction was comparable with that of the other forms of iron, the variations being only between 85 and 94 percent.

Normally pyritic iron was not completely extracted by dilute hydrochloric acid. So the efficiency for the extraction of total iron was influenced also by the fact that the pyrites was the predominant form of iron present in the mineral matter of coal. The comparatively high figures for the extraction of pyritic iron in some cases, suggested, that in presence of hydrofluoric acid, pyrite was extracted to a greater extent.

The values for the efficiency of extraction of iron were over 75 percent for seven samples, and over 63 percent for ten samples; only two samples had the relatively low figures of 57 and 48 percent (Nos.7 and 9 respectively). The highest efficiency, 99 percent, was obtained in the case of the inferior cannel sample (No.12) but two cannels (Nos.4 and 11) had 93 and 92 percent of the total iron extracted. The figure for the minimum extraction (52 percent for No.9) was also obtained with a cannel. This suggested, that the extraction was not influenced by the type of coal.

Bearing in mind, the difficulty of the elimination of pyrite in the prevalent methods of coal cleaning, the above figures might be regarded as satisfactory. This should be one of the important factors in deciding the future of acid treatment as an industrial process. This aspect has been considered in the chapter on general discussion.

Use of bromine water with a mixture of acids: Attempts have been made to effect a complete extraction of the iron in the mineral matter of coal by modifications of the treatment with acids. The normal procedure for the determination of the pyrite in coal was extraction with dilute nitric acid and bromine water. Himus (22) attempted the reduction of the sulphide with zinc and hydrochloric acid, whereby the iron could be removed as the chloride. But in the present investigation, the use of strongly oxidising or reducing agents was avoided, in view of their possible effect on the coal substance.

/Three.........

Three experiments (Table No.10) were conducted with coals high in pyritic iron using a mixture of the two five percent acids with 50 ml. of bromine water, to see whether the pyritic iron was extracted to any greater extent than before. The results indicated, that the reduction effected in ash content was the same as in the former case; consequently the efficiency of extraction of iron also was the same as before.

This was only to be expected, for the complete extraction of iron could be effected only by converting the sulphide into the easily soluble forms of sulphate or chloride of iron.

McCulloch and co-workers (45) in the course of a study of the halogenation of coal, found that when coal was chlorinated to the extent of 26·6 percent, the iron present could be removed as the chloride.

A 35 percent solution of iodine trichloride was the most satisfactory reagent (46) for removing the pyrite; but the use of such quantities of costly reagents was undesirable; besides this too might have an oxidising action on the coal substance.

So a complete elimination of pyritic iron was impossible in any process, where oxidising agents could not be used.

(d) Extraction of alumina: The values in col. 5 of Table No.8 show that the water insoluble, non silicate portion of the ash of the acid treated coal sample varied between nil and

81 percent of the ash. Since alumina was likely to be the major component of this portion of the ash, this could only indicate incomplete extraction of alumina.

The results of Selvig, Ode and Gibson (28) also showed that the extraction of aluminium compounds from the mineral matter of coal, by acid treatment (at room temperature) was not very efficient; they found that the alumina content of the ash of the seven acid treated bituminous coal samples varied between 18 and 41 percent.

Acid treatment at higher temperatures did not increase the efficiency of extraction appreciably. The ash of the coke, prepared from the ultra-clean coal of the Carl Alexander Mine Process (26), where the extraction was carried out at the boiling point of the acids, contained 23·65 percent alumina.

Aluminium is known to occur in the mineral matter of coal either as a component of the silicate minerals, or as alumina itself.

Gauger, Barrett and Williams (32) in the course of petrographic studies of ten coal samples, found kaolin minerals (Al_2O_3, 2 SiO_2, X H_2O) in all the samples, but detected diaspore (Al_2O_3,H_2O), the one mineral where alumina is not present in combination with silica, only in two samples; the occurrence of alumina by itself, in the mineral matter of coal samples, seems to be relatively infrequent.

Hydrofluoric acid reacts vigourously with the silicate minerals, which almost invariably contain alumina; on comparing the efficiency of extraction of silica (Col. 3) with the corresponding values for the water insoluble, non silicate portion of the ash (Col. 5; Table No.8), in five cases, the two values were comparable (samples 4, 5, 6, 10 and 11;)the values for silica varied between 80 and 99 percent, while those for the latter were between 81 and 98 percent); in three cases (samples 3, 8 and 12), the two values differed by about 30 percent and in the rest by about 50 percent, the values under column No.5, almost always being the lower ones. The very low value for sample No.1 might have been due partly to experimental errors. So, in seven out of the twelve samples, the silica portion of the mineral matter had been extracted to a much greater extent than the alumina one.

One possible explanation for this would be the formation of insoluble fluorides. This was hardly likely for (1) Selvig, Ode and Gibson confirmed the absence of any fluorine in the ash of the acid treated coal samples, by qualitative tests; and (2) when hydrofluoric acid reacts with the aluminium compounds to form aluminium fluoride (2 AlF_3, 7 H_2O), only under conditions of supersatuation, it could be deposited; such conditions could not

/have...............

have prevailed during the present experiments, where for every part of the mineral matter, the quantity of acid was between 8 and 200 times; so the fluoride would have dissolved in the excess of acid to form a salt of hydrofluoaluminic acid. (The existence of this acid is not confirmed but its salts are known, cryolite, Na_3AlF_6, being the most important).

In view of the large number of compounds of alumina and silica, which are known to exist in the mineral matter of coal, it would be difficult to predict the exact form in which alumina might be present in the mineral matter of acid treated samples; it is not unlikely that it might exist as alumina itself.

Demann and Schonmuller (35) were the first to suggest the use of alkali for extracting the alumina in the mineral matter of coal. This was applied industrially in Germany (27) when a sample of coal, after being cleaned by jig washing, was extracted with 3 percent potassium hydroxide at 120 atmospheres and 250°C for 20 minutes. The yield of the ultra-clean coal (ash 0·26 percent) was not known; but it must have been low, because of the action of the hot alkali on the coal substance.

Refluxing of the acid treated bituminous coal sample from Lugar works (No.2) with 5 percent potassium hydroxide, though it reduced the ash content from 0•5 to 0•35 percent (dry basis), affected the coal substance to the extent of 18 percent of the initial weight of the coal taken. So further experiments were carried out at room temperature; provision for the intimate contact of the alkali and coal particle was made by attaching the bottle containing the two to an electrical shaker for 18 hours. The alkali extract, on neutralisation gave only a faint precipitate; no loss of the coal sample could be detected by weighing.

The results (Table No.11) did not indicate that any further reduction in ash content could be effected by treatment with alkali at room temperature.

The use of acid treated coals for the manufacture of electrode coke.

It has been mentioned, that one of the important uses of ultra-clean coals produced by acid treatment would be in the field of electro-metallurgy of aluminium and other light metals. The aluminium industry requires anodes with less than 1 percent ash or more exactly with less than 0•5 percent of iron and silicon.

Of the twelve samples examined in the course of the present investigation, seven gave a final product with less than 1 percent ash. Table No.12 (A) gives the ash, silica and iron contents of these ultra-clean coal samples and also the corresponding values for the coke obtainable from them; the latter values were calculated on the basis of a coke yield of 65 percent. It will be noted that all the seven samples (including Nos. 3 and 7, the coke samples of which had more than 1 percent ash) complied with the specifications for iron and silicon required by the aluminium industry. The values compared very favourably with those obtained in German industrial practice by acid treatment; the Carl Alexander coke (26) contained 0.11 parts of ~~coke~~ silica (as Si) and 0.12 parts of iron per 100 parts of coke. A general feature to be noted in connection with all acid treated samples was that most of them were richer in iron than in silica.

Selvig and coworkers (28) refer to the specifications for the manufacture of some special electrodes (also for the aluminium industry) which require the maximum iron and silicon content to be below 0.06 and 0.08 percent respectively. Of the samples listed in Table No.38, three (No.1, 4 and 12) would meet even these requirements.

Table 12(A) gives the values for the "coke" from cannel samples also; these values, which are only of theoretical interest, were included, mainly because all the acid treated samples would be noncoking.

/The............

TABLE NO. 12 (A).

SILICON AND IRON CONTENTS OF THE MINERAL MATTER OF ACID TREATED COALS AND COKES.

Sample No.	COAL			COKE		
	Ash (dry) %	per 100 parts of coal Si	Fe	Ash (dry) %	per 100 parts of coke Si	Fe
1	0.53	0.02	0.05	0.82	0.03	0.08
2	0.52	0.06	0.08	0.80	0.09	0.12
3	0.82	0.13	0.02	1.26	0.20	0.03
4	0.42	0.01	0.04	0.65	0.015	0.06
7	0.73	0.03	0.16	1.12	0.05	0.25
8	0.52	0.03	0.06	0.80	0.05	0.09
12	0.63	0.04	0.01	0.97	0.06	0.015

The possibilities of manufacture of coke suitable for the aluminium industry by acid treatment of coals have been examined in somewhat greater detail in the general discussion.

PART I

The Preparation of Ultra-Clean Coals by Acid Treatment.

SUMMARY

The extraction of the mineral impurities in coal with acids is similar to the solution of solids in liquids.

(1) The nature of the "solvent".

The maximum possible extraction (between 66 and 99 percent) of the mineral matter associated with the coal and cannel samples examined, could be effected by the use of 5 percent hydrofluoric and hydrochloric acids at their boiling point in an inert atmosphere. The use of stronger acids, though it would influence the period of treatment was unlikely to give a final product of lower ash content.

If a mixture of the two acids was not used, it was advisable to start the initial extraction with dilute hydrofluoric acid; of the two acids, the latter was definitely the better 'solvent' for the mineral matter in bituminous coals and cannels.

The efficiency of extraction was the same when using a acid to coal ratio (by weight) of either two or four.

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(2) The nature of the "solute".

The quality of the final product was not improved by grinding the initial sample to sizes finer than 72 mesh B.S.Sieve. The critical size was likely to be between 30 and 72 mesh B.S.Sieve.

Better results could be obtained by the acid treatment of coals than of coke.

Acid treatment under the suggested conditions effected a complete or near complete extraction of the water soluble portions and the silica of the mineral matter in coal.

The efficiency of extraction of iron varied between 60 and 99 percent; of the different forms of iron present in the mineral matter, both the iron silicate and the dilute hydrochloric acid soluble iron were almost completely extracted; the overall efficiency of extraction of iron was determined mainly by the pyrite present. The mere addition of bromine water to the mixture of acids did not improve the percentage extraction of pyritic iron in the absence of an oxidising agent.

There were reasons to believe that the extraction of alumina by the two acids was far from complete in some cases. The use of cold alkali had no influence while hot alkali attacked the coal substance as well as the alumina.

THE STUDY OF ULTRA-CLEAN COAL

PART II

A STUDY OF THE INFLUENCE OF ACID-TREATMENT ON THE COAL SUBSTANCE.

P A R T II

A STUDY OF THE INFLUENCE OF ACID-TREATMENT ON THE COAL SUBSTANCE.

A. INTRODUCTION

Methods of determination of the mineral matter in coal:

An attempt to develop a method for the preparation of ultra-clean coals by acid treatment, has, quite naturally, to be followed by a comparative study of the properties of such coals with those of the original samples; but since both the original and acid treated samples contain associated inorganic impurities in varying amounts, it becomes necessary to decide upon the method of determination of the quantity of mineral matter present in each case.

From the early days of fuel research investigators have been conscious of the fact, that a proper comparison of the properties of different coals could be made only on the basis of "pure coal" i.e., coal free from associated mineral matter. Thus Reynault's classification (1837) used the analytical results on a dry, ash free basis. Till the beginning of the present century, the distinction between ash and mineral matter was not properly appreciated. The first critical study of the calculations to "pure coal" basis appears to have been made by Parr and Wheeler (1909). Since those days, a considerable volume of work has been done on the relation of the mineral matter in coal to its ash.

The general methods, now available, for determining the true content of the mineral matter of coal fall into three categories, namely (a) methods based upon a study of the chemical nature of the mineral matter and those based upon the reactions occurring in the mineral matter during "ashing"; (b) methods involving the separation of coal fractions of different density and ash content and (c) methods depending on the extraction of all or part of the mineral matter with acids. Among these, methods based on (a) being the most satisfactory for general use, have claimed by far the greatest attention from investigators.

(a) Methods based upon the chemical nature of mineral matter and the reactions during incineration:

The two most important formulae to be considered under this heading are those due to Parr and Wheeler (30) and King, Maries and Crossley (29).

The Parr formula: This formula follows certain assumptions regarding the chemical nature of the mineral matter. According to this formula,

$$\text{Mineral matter} = 1.08 \text{ ash} + 0.55 \text{ sulphur}$$

The factor 0.08 ash is the correction for the water of constitution of the shaly matter associated with coal. Parr was the first to point out the need for this correction and this figure

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(with slight modifications) is widely accepted. The main assumption of Parr's formula is that all the sulphur in coal is pyritic. Attempts have been made to give a proper correction for the pyritic sulphur in coal by Tideswell and Wheeler (49), Fieldner and Selvig (50), Fieldner, Selvig and Gibson (51) and Thiessen (52, 53). Cady (in the discussion of Fieldner's paper (51)) has listed the ten possible modifications of this formula. The theoretical errors involved in the Parr formula and its limits of applicability have been discussed at length by Ball and Cady (40).

Parr's formula is widely used in the United States. In the United Kingdom also, Seyler's classification of solid fuels employs the same basis. The considerable attention that this formula has received, is mainly due to its simplicity and to the fact that it enables values for the mineral matter to be derived from available commercial analysis. The one important feature of the King, Maries and Crossley's formula is that it is governed more by considerations of accuracy rather than of simplicity.

The King, Maries and Crossley formula: This formula is based on the fact that the ash from a coal differs from the mineral matter in coal by an amount depending on the changes undergone by the mineral matter during incineration. The following are the more important reactions that occur during ashing:-

(i) loss of water of constitution of the shaly matter;

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(ii) conversion of iron sulphide into ferric oxide and sulphur dioxide and the fixation of SO_3 in the lime and the alkali oxides of the ash;

(iii) loss of carbon-dioxide by carbonates resulting in oxides and

(iv) decomposition of the chlorides.

The corrections to be applied to the ash due to each of these reactions have been discussed in detail in the original paper. The final formula is as follows:

$$\text{Mineral matter} = 1{\cdot}09\ \text{ash} + 0{\cdot}5\ \text{pyritic sulphur} + 0{\cdot}8\ \text{carbon-dioxide} - 1{\cdot}1\ SO_3\ \text{in ash} + SO_3\ \text{coal} + 0{\cdot}5\ \text{chlorine.}$$

The two most probable sources of error in this formula would be due (1) to the probable variations in the combined water content of the shaly matter associated with coal and (2) to the proposed conversion factor for the decomposition of the chlorides in the mineral matter of coal.

The combined water content of clays associated with coals is known to vary widely and the only satisfactory convention would be to assume a mean value, that would be applicable to as wide an area as possible. The factor 0·09 represents such a value derived from an analysis of air dried clays from all over Britain and the authors have also recommended separate values for Scotland, Wales and England.

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As regards the conversion factor for the decomposition of the chlorides, the authors have pointed out that since at least half the chlorine in coal is known to be inorganic, the nett correction factor in terms of chlorine should be between 0·35 and 0·70. In the absence of complete knowledge a factor 0·5 chlorine has been adopted. When the chlorine content of the coal is between 0·1 and 0·2 percent, the error involved in the assumption cannot exceed +0.03 to - 0.04 percent of the coal.

An essential difference between the K.M.C. formula and the Parr one is that the latter is on a sulphur free basis. So the oxygen figure (including analytical errors) calculated in all methods by difference has a greater error in those formulae, which neglect organic sulphur than in that due to King and co-workers.

Since the formula was first proposed in 1936, apart from criticisms about the labour involved in carrying out the necessary determinations, the accuracy of the values obtained has never been questioned. This formula has been adopted in the more recent reports of the physical and chemical survey of the National Coal Resources. Edwards (54) after a review of the various formulae proposed for the evaluation of mineral matter up to 1944 (including a simplified form of the K.M.C. formula proposed by Mott and Spooner (48)) commented that from the point of view of scientific justification, the most accurate

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formula yet advanced is that due to King, Maries and Crossley. So it might be stated that this formula represents the most reliable basis available at present, for the evaluation of the pure coal substance i.e. coal free from mineral matter.

The K.M.C. formula and acid treatment of coals: Acid treatment provides a chemical means by which the coal substance could be essentially freed from the inorganic impurities. It has been pointed out earlier that Gallard (13), Turner (15), Nicolls and Swartzman (17) and others had referred to a loss of organic carbon and hydrogen during acid treatment. So a comparison of the analytical results of the original sample on the K.M.C. basis, with those of the acid treated samples would indicate, whether the coal substance had been affected during the treatment with acids. If, on the other hand, the procedure of acid treatment adopted in the present investigation, was successful in extracting the mineral matter without affecting the coal substance, the results would offer a means of studying the validity of the K.M.C. formula.

The experiments detailed in the following pages were carried out with this object in view.

(b) Methods based on the density separation of coal:

Brinsmaid (55) was the first to describe a graphical method to construct a calorific value/ash curve; he calculated from the curve, both the pure coal calorific value and the decrease in calorific value due to each percent ash.

Stansfield and Sutherland (56) modified the technique for the graphical determination of the pure coal calorific value and mineral matter content of coal. They fractionated samples of Alberta coals (size through 28 mesh Tyler) in a centrifuge using solutions of specific gravity 1·30, 1·33, 1·35 and 1·38. The calorific value and ash content of these samples, when calculated to a dry basis and plotted, were found to lie on a straight line. The extrapolation of the straight line to zero calorific value would give the ash equivalent of 100 percent mineral matter and the extrapolation to zero ash would give the calorific value of the pure coal substance. Since the calorific value at zero ash content was the same as the value at zero mineral matter, another straight line connecting the calorific value at zero ash with zero coal represented the variation of calorific value with mineral matter; thus the mineral matter corresponding to any particular ash content could be read directly from the graph.

Fieldner, Selvig and Gibson (51), on comparing the corrected B.Th.u. values obtained by the Stansfield and Sutherland graphical method with the results by the Parr, modified Parr and ordinary dry ash free calculations, found close agreement between the graphical method and the Parr basis.

Hertzog (57), after a study of the various methods for the evaluation of the pure coal calorific value, recommended as the most reliable method, the use of "the pure coal constant", which was the arithmetic equivalent of the graphic extrapolation method.

Thiessen and Reed (55) applied this graphic extrapolation method to a number of Illinois coals; they found the linear relation to hold good for values of ash content up to 40 percent; but according to Grudner (quoted by Thiessen and Reed) the linear relation did not hold good for ash values over 20 percent.

The critical assumption of the graphical method is that the curve provided by gravity separation is a true dilution curve, which can be extrapolated correctly as a straight line to zero ash and zero heat value. This rests upon two assumptions;- (1)that the pure coal and mineral matter component of the coal remain constant in composition and properties throughout the various fractions of the samples and (2) that the transformation of mineral matter to ash involves no appreciable production or absorption of heat. Available literature throws doubt on the validity of either.

It is well known that density separation methods effect a preferential separation of the petrographic components of coal. Lessing (3) used float and sink methods for the separation of clarain and vitrain. The Belgian process (5) for the preparation of ultra-clean coal exploits the same principle. The authors of the graphical method also (Stansfield and Sutherland, loc cit) refer to "a barely noticeable tendency for very clean coals to have slightly lower calorific values than anticipated."

As for the second assumption, the thermal decomposition of the mineral matter in coal has been studied by Stumper (56) and Purdon and Sapgirs (57).

Stumper found that the value of unit coal calorific value was not affected by the additions of gypsum to the coal up to 25 percent of the weight of the coal; similarly the values for unit coal remained unchanged with additions of silica up to 15 percent of the weight of coal. Increase of gypsum over 25 percent resulted in incomplete combustion. The decrease in unit coal calorific values with additions of silica over 15 percent must also be due to the same reason. Excess of inert material simply made the coal difficult to burn by preventing access of oxygen.

Purdon and Sapgirs (loc cit) found that the influence of calcium carbonate on the unit coal calorific values, when present in quantities up to 20 percent of the weight of coal taken was negligible. But with pyrite, the increase in unit coal calorific values was more or less proportional to the quantity of pyrites added. The exact increase noted was equal to two thirds of the theoretical value calculated for the oxidation of the pyrite and the formation of sulphuric acid with the water formed during combustion.

Besides a very small error is likely to be introduced if the ratio of organic sulphur to pure coal does not remain constant with a change in the ash content of the sample.

The main assumption of the graphical method is that a sample of coal could be regarded as a mixture of pure coal substance and inert material with no calorific value. Since gypsum, silica and calcium carbonate are unlikely to be present in such quantities as to affect the calorific value, this assumption, in the absence of appreciable amounts of pyrite in the mineral matter of the original sample, could be regarded as essentially correct.

This method has found only limited application till now; for Thiessen and Reed (loc cit), among others, have demonstrated that from the point of view of accuracy, the results obtained are in no way better than those from the Parr formula. Moreover as Thiessen comments "this procedure involved too great an amount of labour to make its use very common".

It will be appreciated, that unlike the gravity separation methods, acid treatment of coals does not involve a separation of the petrographic components of coal. When samples with differing ash contents are obtained from a particular coal by acid-treatment, the nature of the coal substance in all the samples would be the same, provided there has been no oxidation of the sample during the treatment. So one of the two major objections to the use of the graphical method would not arise in this case; as for the correction necessary for the heat of formation of ferric oxide from pyrite, it will be seen, that in the case of the samples examined, the values (discussed later) are not of such an order as to affect the calorific value to any appreciable extent.

In view of this, there is greater justification for applying the graphical method to the acid-treated coal samples than to those obtained by float and sink determinations; besides a comparison of the pure coal calorific values and ash to mineral matter ratios obtained by this improved graphical method with those from the King, Maries and Crossley formula would throw some light on their relative merits.

Experiments described in Tables 26-29 were carried out with this object in view.

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(c) Determination of the mineral matter by acid extraction:

This method of determination of mineral matter has received comparatively little attention. Follman (61) digested finely powdered coal with hot dilute hydrochloric acid, washed the sample free of acid and dried at 110°C; the loss in weight gave the moisture and mineral matter soluble in acid. The total mineral matter was determined by adding to the above value, the ash content of the hydrochloric acid treated coal.

Alternatively, the sample was evaporated to dryness with hydrofluoric acid and then digested with dilute hydrochloric acid; the loss in weight added to the ash content of the dry acid treated sample was taken as the mineral matter content of the coal. Adopting this method for various coals from China, Tiflis and Germany, Follman obtained mineral matter/ash ratios varying between 1·05 and 1·21, with an average of 1·12.

Mayer (62) slightly improved the above procedure by determining the iron content of the ash from the hydrochloric acid treated sample and corrected for pyrite not extracted by the acid. The average mineral matter to ash ratio obtained by him was 1·13.

/Neither..............

Neither Follman nor Mayer adopted precautions to prevent possible oxidation of the coal sample. To obtain correct values, it would be necessary to treat small quantities of the sample in an inert atmosphere. Even then, the accuracy of the values was unlikely to be greater than those obtained by the King, Maries and Crossley formula. In view of this, it was not considered advisable to carry out experiments along these lines.

B. EXPERIMENTAL PROCEDURE.

(1) Determination of the mineral matter content of coal by the King, Maries and Crossley formula.

The results of these experiments are set out in Tables 13-24. All the determinations for acid treated samples mentioned in this section were carried out with specially prepared chloride free samples. The procedure adopted for most of these determinations was the same as outlined in the 'British Standard Methods for the Analysis and Testing of Coal and Coke' (British Standards Institution No.1016 of 1942). But in the following cases, there were slight variations from the recommended procedure.

(i) Ultimate analysis - determination of carbon and hydrogen: The set up of the apparatus was the same as recommended; but in the last section of the combustion tube, instead of a 4 cm. roll of silver gauze, a reduced copper gauze of the same length was used; the reduction of the copper gauze was done at the beginning of each experiment.

(ii) Sulphate sulphur: 5 gm. of finely powdered coal (through 120 mesh B.S.S.) was extracted with 300 ml. of 3 percent hydrochloric acid for 40 hours at 60°C with frequent shaking. After filtering, the filtrate was boiled with bromine water and the iron precipitated with ammonium hydroxide and extracted with dilute hydrochloric acid. The iron present, determined by titration with titanous chloride using thiocyanate indicator in a CO_2 atmosphere, has been reported as dilute hydrochloric acid soluble iron in Table No.9 (Part I). The sulphur in the filtrate was determined as barium sulphate.

(iii) Pyritic sulphur: 5 gms. of finely powdered coal was extracted for 24 hours at room temperature with 300 ml. of dilute nitric acid (1 volume of acid of Sp.gr. 1·42 with 3 volumes of water) and 10 ml. of bromine water. After filtering and boiling off the bromine, the iron was precipitated by ammonium hydroxide; nitric acid was completely eliminated by double precipitation of iron, which was estimated as before. The difference between this value and the dilute hydrochloric acid soluble iron has been reported as pyritic iron in Table No.9. The percentage of pyritic sulphur in coal is 1·15 x the percentage of pyritic iron.

This procedure was adopted in preference to a direct determination of pyritic sulphur, because the treatment of coal with dilute nitric acid and bromine water is liable to cause oxidation and solution of part of the organic sulphur in some cases. Any error due to this would be avoided by calculating the quantity of pyritic sulphur from the pyritic iron present.

Application of the K.M.C. formula to analytical results.

The following formulae (as derived by the authors) were used:

The percentage of carbon in the coal substance (C_p) is given by the expression

$$C_p = (C - 3/11\ CO_2)\ 100/100 - (N+M)$$

where C is the experimental value for carbon including CO_2 and N and M are moisture and mineral matter respectively of the air dried coal.

In the case of hydrogen, it is necessary to deduct the proportion of hydrogen corresponding to the water of hydration of the clay. Thus

$$H_p = (H - 0{\cdot}01A + 0{\cdot}01\ S_{pyr} + 0{\cdot}01\ CO_2)\ 100/100 - (N+M)$$

/where.........

where H_p = hydrogen content of the pure coal substance, H, the experimentally obtained value, A = the ash, S_{pyr}, the pyritic sulphur content and CO_2 the carbon dioxide content of the air dried sample.

Since all the nitrogen in coal is taken to be organic, the expression for nitrogen in the coal substance (N_p) would be

$$N_p = N'100/100 - (N+M)$$

N' being the experimentally determined nitrogen content of the air dried sample.

For sulphur, it is necessary to determine the organic sulphur content of the coal. The difference between the total sulphur and the sum of the pyritic and sulphate sulphur (this being calculated from the SO_3 coal given in the Tables) in coal would be the organic sulphur content (Sorg). So sulphur in the coal substance (S_p) would be

$$S_p = \text{Sorg } 100/100 - (N+M)$$

The difference from 100 of the sum of the C_p, H_p, N_p and S_p figures has been reported as oxygen and errors.

Calorific value: In the determined figure for the calorific value of air dried coal, correction is made for the heat of formation and dissolution in water of sulphuric acid,

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assuming that all the sulphur in coal is converted to sulphuric acid. A further correction is necessary to take into account the heat of formation of ferric oxide from pyrite; the corrected value would then represent the heat of combustion of the pure coal assuming that the organic sulphur is burnt to sulphur dioxide only. The figure for the heat of formation of ferric oxide from FeS_2 is 3032 gm. cal. per gm. of pyritic sulphur. Since the formation Fe_3O_4 is possible in part, the authors of the formula recommended a figure of 3000 gm. cal. per gm. of pyritic sulphur. The expression for the calorific value of pure coal substance ($C.V_p$) in B.Th.u would then be

$$C.V_p = (C.V - 54\ Spyr)\ 100/100 - (N+M)$$

where C.V is the experimentally determined value.

Calculation of the mineral matter content of the acid treated sample.

For this the following formula was adopted.

$$\text{Mineral matter} = 1{\cdot}00\ \text{ash} + 0{\cdot}6\ \text{Spyr} + 0{\cdot}5\ \text{chlorine}$$

The derivation of this formula is given in the following section on the discussion of results.

(2) The determination of the mineral matter content of coal by the Parr formula.

Even though, the present investigation was concerned mainly with the K.M.C. formula, it was considered advisable to obtain values for the mineral matter content and calorific value of coal by the Parr method also for

/purposes................

purposes of comparison. The values are given in Table No.25.

(3) The improved graphical method.

The calorific value of the different samples obtained in the course of the acid treatment of the original samples (Nos. 9, 10, 11 and 12) were determined by the Bomb-calorimeter.

The results are given in Tables 26, 27, 28 and 29 and graphs Nos. 1, 2, 3, and 4. The figures for ash and calorific value obtained experimentally with air dried samples, were corrected to a dry basis and plotted as shown. The calorific value of dry, mineral matter free coal, and the ash equivalent of 100 percent mineral matter were obtained by extrapolation of the ash - calorific value line to zero ash and zero calorific value respectively. The calorific value - mineral matter line, obtained by connecting zero coal with the point representing the calorific value of dry mineral matter free coal, made it possible to obtain the mineral matter content corresponding to a given ash content of the coal, to be read from the graph.

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TABLE NO. 13

CLARAIN SAMPLE FROM BARONY COLLIERY (SAMPLE NO. I)

	Original Sample (air dried)%	Acid treated Sample (air dried)%
(i) Proximate analysis		
Moisture	3.0	6.0
Ash	1.3	0.5
Volatile Matter (dry, CO_2 free)	50.6	51.4
Fixed carbon	45.1	42.1
(ii) Ultimate analysis		
Carbon (excluding CO_2)	78.60	77.00
Carbon (present as CO_3'')	0.04	-
Hydrogen	5.60	5.50
Nitrogen	1.20	1.20
Sulphur (volatile)	1.06	0.90
Oxygen and errors (diff.)	9.20	8.90
Calorific value B.Th.u./lb.	14180	13870
(iii) Evaluation of Mineral Matter (K.M.C. formula).		
Total sulphur	1.08	0.90
Sulphate in coal (as SO_3)	0.03	-
Pyritic sulphur	0.19	0.05
Sulphur in ash (as % of ash)	1.60	-
Sulphur in ash (as % of coal)	0.02	-
SO_3 in ash (as % of coal	0.05	-
Carbonate in coal (as CO_2)	0.14	-
Chlorine	0.16	0.10
Mineral Matter	1.68	0.58

/(iv).............

TABLE NO.13
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal".				
Carbon	82.2	82.5	82.4	82.4
Hydrogen	5.9	5.9	5.9	5.9
Nitrogen	1.3	1.3	1.3	1.3
Sulphur	1.1	0.9	1.0	0.9
Oxygen and errors (diff.)	9.5	9.4	9.4	9.5
Calorific value B.Th.u./lb	14,840	14,880	14,840	14,840

TABLE NO. 14

BITUMINOUS COAL SAMPLE FROM LUGAR WORKS
(SAMPLE NO. 2)

		original sample (air dried) %	Acid treated sample (air dried) %
(i)	Proximate analysis		
	Moisture	3.9	4.2
	Ash	2.5	0.5
	Volatile Matter (dry, CO_2 free)	45.0	46.0
	Fixed carbon	48.6	49.3
(ii)	Ultimate analysis		
	Carbon (excluding CO_2)	81.00	82.70
	Carbon (present as CO_3'')	0.02	-
	Hydrogen	4.90	4.90
	Nitrogen	1.40	1.40
	Sulphur (volatile)	1.01	0.85
	Oxygen & errors (difference)	5.27	5.45
	Calorific value B.Th.u./lb.	14,880	15,110
(iii)	Evaluation of mineral matter (K.M.C. formula).		
	Total sulphur	1.06	0.85
	Sulphate in coal (as SO_3)	0.06	-
	Pyritic sulphur	0.22	0.09
	Sulphur in ash (as % of ash)	2.05	-
	Sulphur in ash (as % of coal)	0.05	-
	SO_3 in ash (as % of coal)	0.125	-
	Carbonate in coal (as CO_2)	0.07	-
	Chlorine	0.01	0.01
	Mineral matter	2.82	0.56

/(iv) ....

TABLE NO. 14
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	86.2	86.8	86.8	86.8
Hydrogen	5.2	5.2	5.1	5.1
Nitrogen	1.5	1.5	1.5	1.5
Sulphur	1.1	0.9	0.9	0.8
Oxygen and errors (diff.)	6.0	5.6	5.7	5.8
Calorific value B.Th.u./lb.	15,920	15,950	15,860	15,870

TABLE NO. 15.

DURAIN SAMPLE FROM THANKERTON COLLIERY
(SAMPLE NO. 3)

	Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i) Proximate analysis		
Moisture	2.5	1.8
Ash	3.5	0.8
Volatile matter (dry, CO_2 free)	34.0	34.6
Fixed carbon	60.0	62.8
(ii) Ultimate analysis		
Carbon (excluding CO_2)	74.00	76.60
Carbon (present as CO_3)	0.03	-
Hydrogen	5.10	5.20
Nitrogen	0.90	1.00
Sulphur (volatile)	0.95	0.80
Oxygen & errors (difference)	13.02	13.80
Calorific value B.Th.u./lb.	13270	13790
(iii) Evaluation of the mineral matter (K.M.C. formula)		
Total sulphur	1.01	0.80
Sulphate in coal (as SO_3)	0.06	-
Pyritic sulphur	0.13	0.02
Sulphur in ash (as % of ash)	1.71	-
Sulphur in ash (as % of coal)	0.06	-
SO_3 in ash (as % of coal)	0.15	-
Carbonate in coal (as CO_2)	0.11	-
Chlorine	0.01	0.01
Mineral matter	3.87	0.82

/(iv)...............

TABLE NO. 15
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	78.8	79.0	78.6	78.7
Hydrogen	5.4	5.3	5.3	5.3
Nitrogen	1.0	1.0	1.0	1.0
Sulphur	1.0	0.9	0.8	0.8
Oxygen & errors (difference)	13.8	13.8	14.3	14.2
Calorific Value B.Th.u./lb	14,140	14,180	14,160	14,160

TABLE NO. 16

DURAIN CONTAINING BRIGHT COAL (SAMPLE NO.4)

		Original sample (air dried) %	Acid treated sample (air dried) %
(i)	**Proximate analysis**		
	Moisture	2.0	3.8
	Ash	4.8	0.4
	Volatile matter (dry, CO_2 free)	38.6	39.5
	Fixed carbon	54.6	56.3
(ii)	**Ultimate analysis**		
	Carbon (excluding CO_2)	71.70	74.00
	Carbon (present as CO_3'')	0.05	-
	Hydrogen	4.50	4.60
	Nitrogen	1.20	1.20
	Sulphur (volatile)	1.13	0.59
	Oxygen & errors (difference)	14.62	15.41
	Calorific value B.Th.u./lb.	13340	13770
(iii)	**Evaluation of the mineral matter (K.M.C. formula)**		
	Total sulphur	1.23	0.59
	Sulphate in coal (as SO_3)	0.15	-
	Pyritic sulphur	0.51	0.045
	Sulphur in ash (as % of ash)	2.00	-
	Sulphur in ash (as % of coal)	0.10	-
	SO_3 in ash (as % of coal)	0.25	-
	Carbonate in coal (as CO_2)	0.20	-
	Chlorine	0.04	0.04
	Mineral matter	5.54	0.45

/(iv).............

TABLE NO. 16
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	77.1	77.5	77.2	77.3
Hydrogen	4.8	4.8	4.8	4.8
Nitrogen	1.3	1.3	1.3	1.3
Sulphur	1.2	0.7	0.6	0.6
Oxygen & errors (difference)	15.6	15.7	16.1	16.0
Calorific value B.Th.u./lb	14,340	14,430	14,370	14,380

TABLE NO. 17

A SAMPLE OF FUSAIN FROM DIAMOND SEAM, AYR COLLIERY (SAMPLE NO. 5)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	Proximate analysis		
	Moisture	8.2	2.8
	Ash	5.4	1.3
	Volatile Matter (dry CO_2 free)	19.6	14.2
	Fixed carbon	66.8	81.7
(ii)	Ultimate analysis		
	carbon (excluding CO_2)	78.00	87.60
	carbon (present as CO_3'')	0.33	-
	Hydrogen	2.60	2.80
	Nitrogen	0.90	1.10
	Sulphur (volatile)	1.21	0.90
	Oxygen & errors (difference)	3.37	3.50
	Calorific value B.Th.u./lb.	12,470	13,900
(iii)	Evaluation of mineral matter (K.M.C. formula)		
	Total sulphur	1.28	0.96
	Sulphate in coal (as SO_3)	0.06	-
	Pyritic sulphur	0.53	0.21
	Sulphur in ash (as % of ash)	1.32	-
	Sulphur in ash (as % of coal)	0.07	-
	SO_3 in ash (as % of coal)	0.18	-
	Carbonate in coal (as CO_2)	1.20	-
	Chlorine	0.16	0.12
	Mineral matter	7.05	1.49

/(iv) ....

TABLE NO. 17
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	91.6	92.0	91.4	91.5
Hydrogen	3.1	3.0	2.9	2.9
Nitrogen	1.1	1.1	1.1	1.1
Sulphur	1.4	0.9	0.9	0.7
Oxygen & errors (difference)	2.8	3.0	3.7	3.8
Calorific value B.Th.u./lb	14,630	14,680	14,500	14,520

TABLE NO. 18

FUSAIN SAMPLE FROM WARRIX COLLIERY (SAMPLE NO.6)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	**Proximate analysis**		
	Moisture	2.5	1.2
	Ash	23.4	3.0
	Volatile Matter (dry, CO_2 free)	21.5	23.1
	Fixed carbon	52.6	72.7
(ii)	**Ultimate analysis**		
	Carbon (excluding CO_2)	58.70	84.30
	Carbon (present as CO_3'')	1.95	-
	Hydrogen	2.40	3.00
	Nitrogen	0.80	1.10
	Sulphur (volatile)	2.45	1.92
	Oxygen & errors (difference)	7.80	5.48
	Calorific value B.Th.u./lb	9,550	13,440
(iii)	**Evaluation of mineral matter (K.M.C. formula)**		
	Total sulphur	2.65	1.92
	Sulphate in coal (as SO_3)	0.06	-
	Pyritic sulphur	1.03	0.33
	Sulphur in ash (as % of ash)	0.85	-
	Sulphur in ash (as % of coal)	0.20	-
	SO_3 in ash (as % of coal)	0.50	-
	Carbonate in coal (as CO)	7.18	-
	Chlorine	0.07	0.05
	Mineral matter	31.30	3.23

TABLE NO. 18
(Continued)

	ORIGINAL SAMPLE dry ash CO_2 free basis %	 dry mineral matter free basis %	ACID TREATED SAMPLE dry ash CO_2 free basis %	 dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	87.7	88.7	88.0	88.2
Hydrogen	3.6	3.4	3.1	3.1
Nitrogen	1.2	1.2	1.1	1.2
Sulphur	3.7	2.4	2.0	1.7
Oxygen & errors (difference)	3.8	4.3	5.8	5.8
Calorific value B.Th.u./lb	14,280	14,350	14,030	14,040

TABLE NO. 19

CANNEL FROM LOANBEAD COLLIERY (SAMPLE NO.7)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	**Proximate analysis**		
	Moisture	5.2	4.6
	Ash	2.9	0.7
	Volatile matter (dry CO_2 free)	50.0	50.2
	Fixed carbon	41.9	44.5
(ii)	**Ultimate analysis**		
	Carbon (excluding CO_2)	69.00	71.00
	Carbon (present as CO_3'')	0.03	-
	Hydrogen	6.40	6.60
	Nitrogen	1.30	1.40
	Sulphur (volatile)	0.97	0.79
	Oxygen & errors (difference)	14.20	14.91
	Calorific value B.Th.u./lb	14,040	14,460
(iii)	**Evaluation of mineral matter (K.M.C. formula)**		
	Total sulphur	0.98	0.79
	Sulphate in coal (as SO_3)	0.005	-
	Pyritic sulphur	0.33	0.17
	Sulphur in ash (as % of ash)	0.40	-
	Sulphur in ash (as % of coal)	0.01	-
	SO_3 in ash (as % of coal)	0.025	-
	Carbonate in coal (as CO_2)	0.12	-
	Chlorine	0.24	0.20
	Mineral matter	3.52	0.90

/(iv)...............

TABLE NO. 19
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	75.2	75.6	75.0	75.2
Hydrogen	7.0	7.0	7.0	7.0
Nitrogen	1.4	1.4	1.5	1.5
Sulphur	1.1	0.7	0.8	0.7
Oxygen & errors (difference)	15.3	15.3	15.7	15.6
Calorific Value B.Th.u./lb	15,300	15,360	15,270	15,300

TABLE NO. 20

CANNEL FROM COWDENBEATH COLLIERY (SAMPLE NO.8)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	Proximate analysis		
	Moisture	3.4	4.6
	Ash	3.9	0.5
	Volatile Matter (dry CO_2 free)	51.2	53.3
	Fixed carbon	41.5	41.6
(ii)	Ultimate analysis		
	Carbon (excluding CO_2)	75.60	77.80
	Carbon (present as CO_3'')	0.01	-
	Hydrogen	5.40	5.50
	Nitrogen	1.10	1.10
	Sulphur (volatile)	1.29	0.80
	Oxygen & errors (difference)	9.30	9.70
	Calorific value B.Th.u./lb	14,400	14,780
(iii)	Evaluation of the mineral matter (K.M.C. formula)		
	Total sulphur	1.37	0.80
	Sulphate in coal (as SO_3)	0.09	-
	Pyritic sulphur	0.47	0.06
	Sulphur in ash (as % of ash)	2.00	-
	Sulphur in ash (as % of coal)	0.08	-
	SO_3 in ash (as % of coal)	0.20	-
	Carbonate in coal (as CO_2)	0.03	-
	Chlorine	0.18	0.15
	Mineral matter	4.47	0.55

/(iv)...............

TABLE NO. 20
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	81.5	82.1	82.0	82.0
Hydrogen	5.8	5.8	5.8	5.8
Nitrogen	1.2	1.2	1.2	1.2
Sulphur	1.4	0.9	0.8	0.8
Oxygen & errors (difference)	10.1	10.0	10.2	10.2
Calorific value B.Th.u./lb	15530	15,600	15,570	15,590

TABLE NO. 21

CANNEL FROM RANDOLPH COLLIERY (SAMPLE NO.9)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	**Proximate analysis**		
	Moisture	4.4	5.6
	Ash	6.5	1.9
	Volatile matter (dry CO_2 free)	63.3	64.7
	Fixed carbon	25.8	28.8
(ii)	**Ultimate analysis**		
	carbon (excluding CO_2)	62.90	66.00
	carbon (present as CO_3'')	0.11	-
	Hydrogen	6.50	6.70
	Nitrogen	1.00	1.10
	Sulphur (volatile)	3.14	2.17
	Oxygen & errors (difference)	15.45	16.53
	Calorific value B.Th.u./lb	13,400	14,000
(iii)	**Evaluation of mineral matter (K.M.C. formula).**		
	Total sulphur	3.30	2.17
	Sulphate in coal (as SO_3)	0.30	-
	Pyritic sulphur	1.46	0.74
	Sulphur in ash (as % of ash)	2.50	-
	Sulphur in ash (as % of coal)	0.16	-
	SO_3 in ash (as % of coal)	0.40	-
	Carbonate in coal (as CO_2)	0.40	-
	Chlorine	0.06	0.04
	Mineral matter	8.03	2.36

/(iv)...............

TABLE NO. 21
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	70.9	71.9	71.4	71.7
Hydrogen	7.3	7.4	7.2	7.3
Nitrogen	1.1	1.1	1.2	1.2
Sulphur	3.5	2.0	2.3	1.6
Oxygen & errors (difference)	17.2	17 .6	17.9	18.2
Calorific value B.Th.u./lb	15,110	15,220	15,140	15,170

TABLE NO. 22

CANNEL FROM VIRTUEWELL SEAM, ROYAL GEORGE COLLIERY (SAMPLE NO.10)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	**Proximate analysis**		
	Moisture	3.9	5.2
	Ash	26.5	1.3
	Volatile matter (dry CO_2 free)	40.1	49.9
	Fixed carbon	29.5	43.6
(ii)	**Ultimate analysis**		
	Carbon (excluding CO_2)	53.00	74.40
	Carbon (present as CO_3'')	0.30	-
	Hydrogen	6.60	8.80
	Nitrogen	0.80	1.20
	Sulphur (volatile)	0.76	0.62
	Oxygen & errors (difference)	8.14	8.48
	Calorific value B.Th.u./lb	10,840	15,050
(iii)	**Evaluation of mineral matter (K.M.C. formula)**		
	Total sulphur	0.84	0.62
	Sulphate in coal (as SO_3)	0.08	-
	Pyritic sulphur	0.44	0.24
	Sulphur in ash (as % of ash)	0.30	-
	Sulphur in ash (as % of coal)	0.08	-
	SO_3 in ash (as % of coal)	0.20	-
	Carbonate in coal (as CO_2)	1.10	-
	Chlorine	0.06	0.08
	Mineral matter	29.88	1.48

/(iv)............

TABLE NO. 22
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	77.4	80.0	79.6	79.7
Hydrogen	9.6	9.6	9.4	9.4
Nitrogen	1.2	1.2	1.3	1.3
Sulphur	1.1	0.6	0.7	0.4
Oxygen & errors (difference)	10.7	8.6	9.0	9.2
Calorific value B.Th.u./lb	15,820	16,320	16,100	16,120

TABLE NO. 23.

CANNEL FROM KILTONGUE SEAM (SAMPLE NO.11)

		Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i)	Proximate analysis		
	Moisture	3.9	4.2
	Ash	33.8	1.2
	Volatile matter (dry CO_2 free)	48.8	54.6
	Fixed carbon	13.5	40.0
(ii)	Ultimate analysis		
	carbon (excluding CO_2)	46.60	74.60
	Carbon (present as CO_3'')	0.02	-
	Hydrogen	4.30	6.20
	Nitrogen	0.90	1.50
	Sulphur (volatile)	2.43	0.85
	Oxygen & errors (difference)	8.05	11.45
	Calorific value B.Th.u./lb	8750	13,720
(iii)	Evaluation of the mineral matter (K.M.C. formula)		
	Total sulphur	2.73	0.85
	Sulphate in coal (as SO_3)	0.24	-
	Pyritic sulphur	1.98	0.20
	Sulphur in ash (as % of ash)	0.90	-
	Sulphur in ash (as % of coal)	0.30	-
	SO_3 in ash (as % of coal)	0.75	-
	Carbonate in coal (as CO_2)	0.07	-
	Chlorine	0.04	0.04
	Mineral matter	37.32	1.34

TABLE NO. 23
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
carbon	74.9	79.3	78.8	79.0
hydrogen	6.9	6.8	6.6	6.6
Nitrogen	1.4	1.5	1.6	1.6
sulphur	3.9	1.1	0.9	0.7
oxygen & errors (difference)	12.9	11.3	12.1	12.1
calorific value B.Th.u./lb	14,060	14,700	14,500	14,510

TABLE NO. 24.

INFERIOR CANNEL - WHITEHILL COLLIERY
(SAMPLE NO.12)

	Original sample (air dried basis) %	Acid treated sample (air dried basis) %
(i) <u>Proximate analysis</u>		
Moisture	4.5	4.2
Ash	43.5	0.6
Volatile matter (dry CO_2 free)	40.8	62.4
Fixed carbon	11.2	32.8
(ii) <u>Ultimate analysis</u>		
Carbon (excluding CO_2)	38.20	76.00
Carbon (present as CO_3'')	0.41	-
Hydrogen	4.30	7.80
Nitrogen	0.70	1.40
Sulphur (volatile)	0.68	1.07
Oxygen & errors (difference)	7.71	8.93
Calorific value B.Th.u./lb	7,600	15,120
(iii) <u>Evaluation of mineral matter (K.M.C. formula)</u>		
Total sulphur	1.00	1.07
Sulphate in coal (as SO_3)	0.06	-
Pyritic sulphur	0.38	0.07
Sulphur in ash (as % of ash)	0.74	-
Sulphur in ash (as % of coal)	0.32	-
SO_3 in ash (as % of coal)	0.80	-
Carbonate in coal (as CO_2)	1.50	-
Chlorine	0.04	0.06
Mineral matter	48.00	0.67

/(iv)...............

TABLE NO. 24
(Continued)

	ORIGINAL SAMPLE		ACID TREATED SAMPLE	
	dry ash CO_2 free basis %	dry mineral matter free basis %	dry ash CO_2 free basis %	dry mineral matter free basis %
(iv) Ultimate analysis of "unit coal"				
Carbon	75.7	80.4	79.8	79.9
Hydrogen	8.5	8.2	8.2	8.2
Nitrogen	1.4	1.5	1.5	1.5
Sulphur	1.3	1.3	1.1	1.1
Oxygen & errors (difference)	13.1	8.6	9.4	9.3
Calorific value B.Th.u./lb	15,050	15,960	15,890	15,900

TABLE NO. 25

APPLICATION OF THE PARR FORMULA FOR THE DETERMINATION OF MINERAL MATTER IN COAL

Sample No.	Moisture %	Ash %	Mineral matter %	Mineral matter/ash ratio	Calorific value of dry mineral matter free coal B.Th.u./lb
(1)	3.0	1.3	2.00	1.54	14,870
(2)	3.9	2.5	3.28	1.31	15,980
(3)	2.5	3.5	4.34	1.24	14,190
(4)	2.0	4.8	5.86	1.22	14,410
(5)	8.2	5.4	7.83	1.45	14,770
(6)	2.5	23.4	34.49	1.47	14,950
(7)	5.2	2.9	3.67	1.27	15,360
(8)	3.4	3.9	4.96	1.27	15,630
(9)	4.4	6.5	8.84	1.36	15,260
(10)	3.9	26.5	30.26	1.14	16,400
(11)	3.9	33.8	38.00	1.12	14,830
(12)	4.5	43.5	49.15	1.13	16,290

NOTE: Because of the high CO_2 content of Samples (Nos. 5, 6, 10 and 12) the modified Parr formula ($1.08\ (A+CO_2)+0.55$ sulphur) was used in those cases.

TABLE NO. 26.

DETERMINATION OF THE MINERAL MATTER BY THE GRAPHICAL METHOD.

Cannel from Randolph colliery (Sample No. 9)
(Cf : graph No.1)

	Experiment No.	Ash (dry) %	Calorific value (dry) B.Th.u./lb
A:	I	17.3	12,000
	II	11.0	13,090
	III	6.8	14,020
	IV	2.0	14,830
B:	Ash equivalent of 100% mineral matter(from graph) %		77.0
	Mineral matter content of original sample from graph %		8.5
	Mineral matter/ash ratio		1.31
	Calorific value of the dry, mineral matter free coal by extrapolation B.Th.u./lb		15200

GRAPH No. 1.

(SAMPLE No. 9)

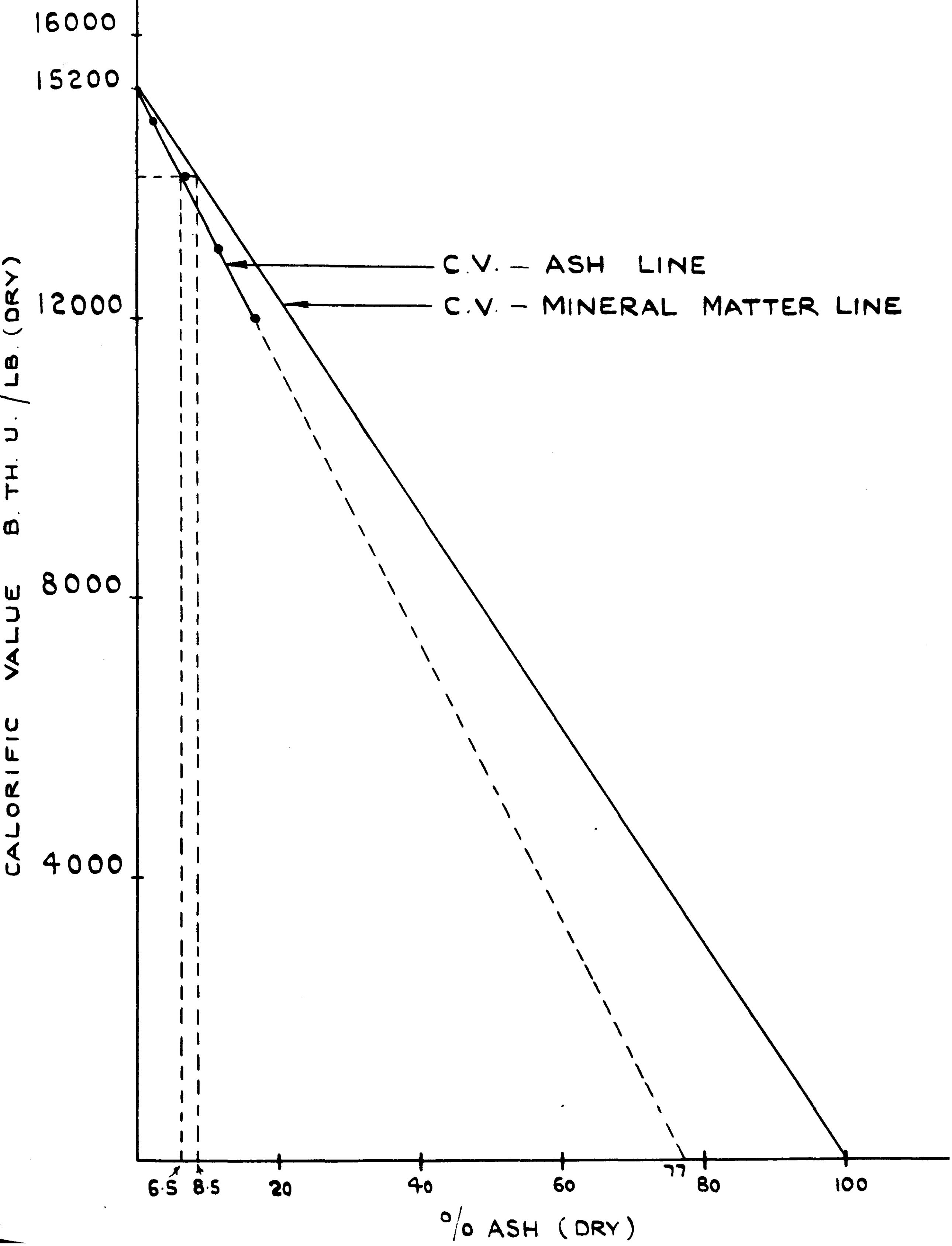


TABLE NO. 27

DETERMINATION OF THE MINERAL MATTER BY THE GRAPHICAL METHOD

Cannel, Virtuewell seam, Royal George Colliery
(Sample No. 10)
(Cf: graph No.2)

	Experiment No.	Ash (dry) %	Calorific value (dry) B.Th.u./lb
A.	I	27.6	11,280
	II	18.4	12,750
	III	10.2	14,320
	IV	6.8	14,900
	V	1.5	15,970
B.	Ash equivalent of 100 % mineral matter from graph } %		89.0
	Mineral matter content of the original sample from graph. } %		30.0
	Mineral matter/ash ratio		1.13
	Calorific value of the dry, mineral matter free coal by extrapolation B.Th.u./lb		16,250

GRAPH Nº 2.
(SAMPLE Nº 10.)

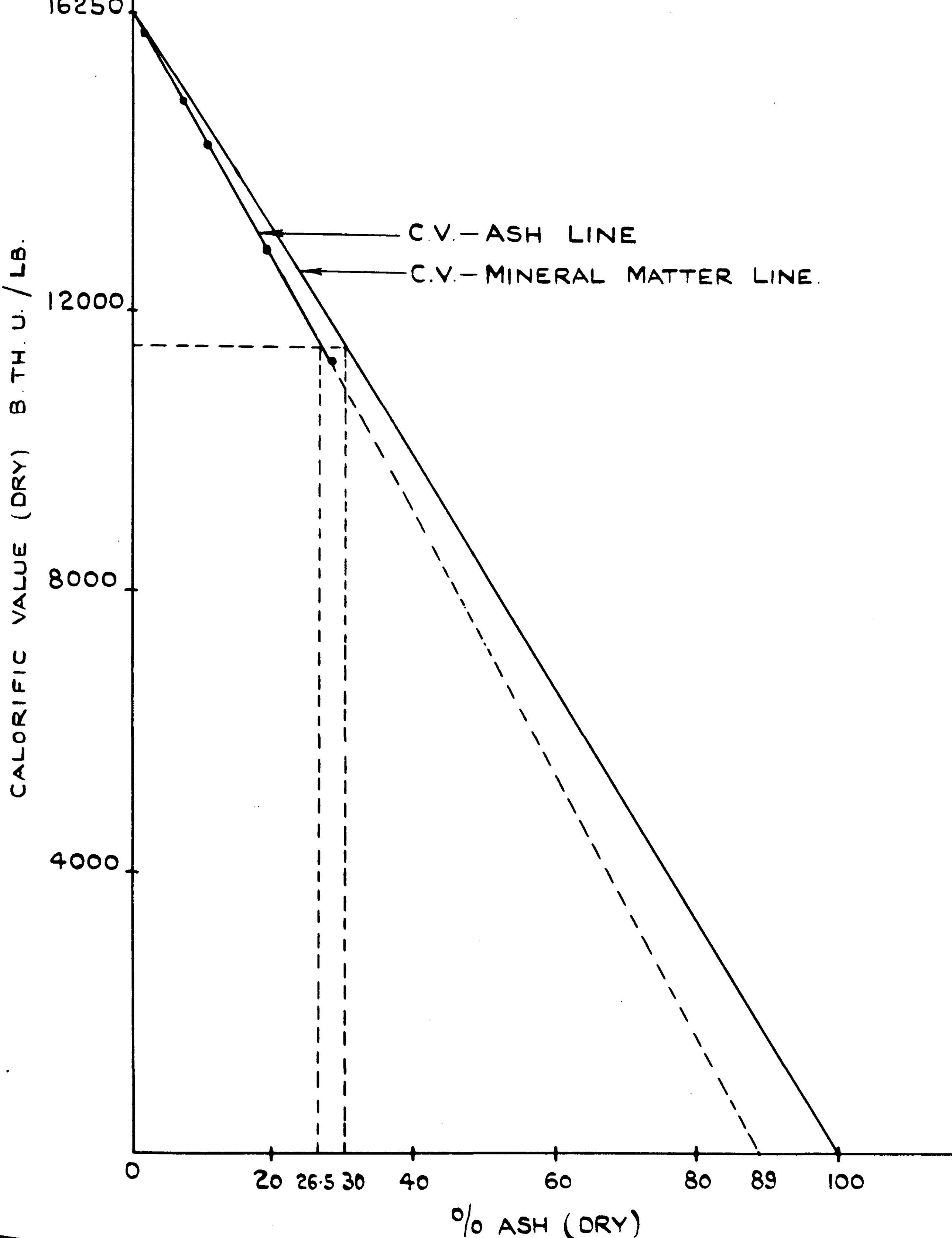
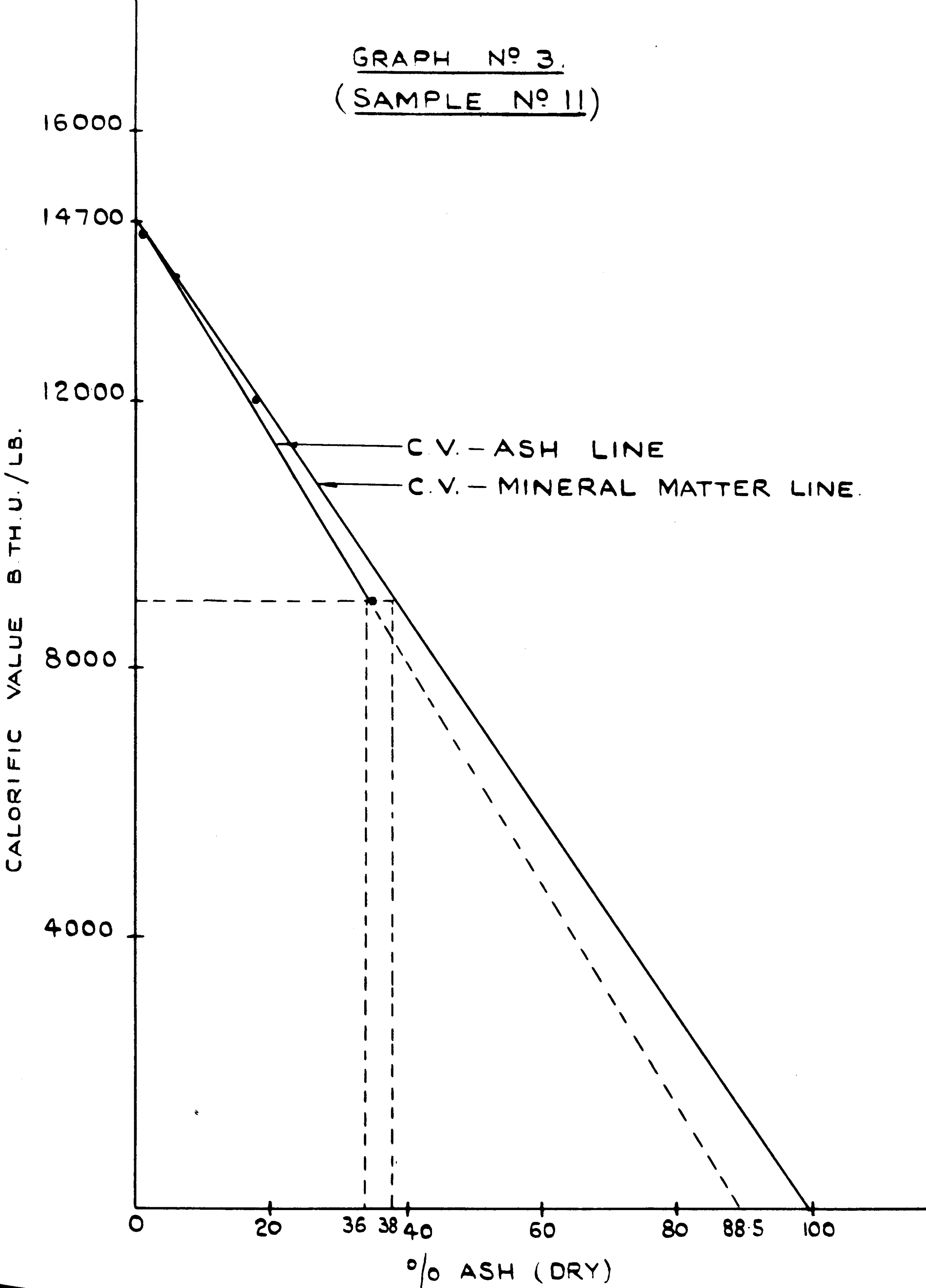


TABLE NO. 28

DETERMINATION OF THE MINERAL MATTER BY THE GRAPHICAL METHOD

Cannel, Kiltongue seam (Sample No.11)
(Cf: graph No.3)

	Experiment No.	Ash (dry) %	Calorific value (dry) B.Th.u./lb
A.	I	35.0	9,110
	II	18.0	11,980
	III	7.5	13,750
	IV	1.3	14,410
B.	Ash equivalent of 100 % mineral matter from graph	%	88.5
	Mineral matter content of the original sample from graph	%	38.0
	Mineral matter/ash ratio		1.12
	Calorific value of the dry, mineral matter free coal by extrapolation B.Th.u./lb		14,700



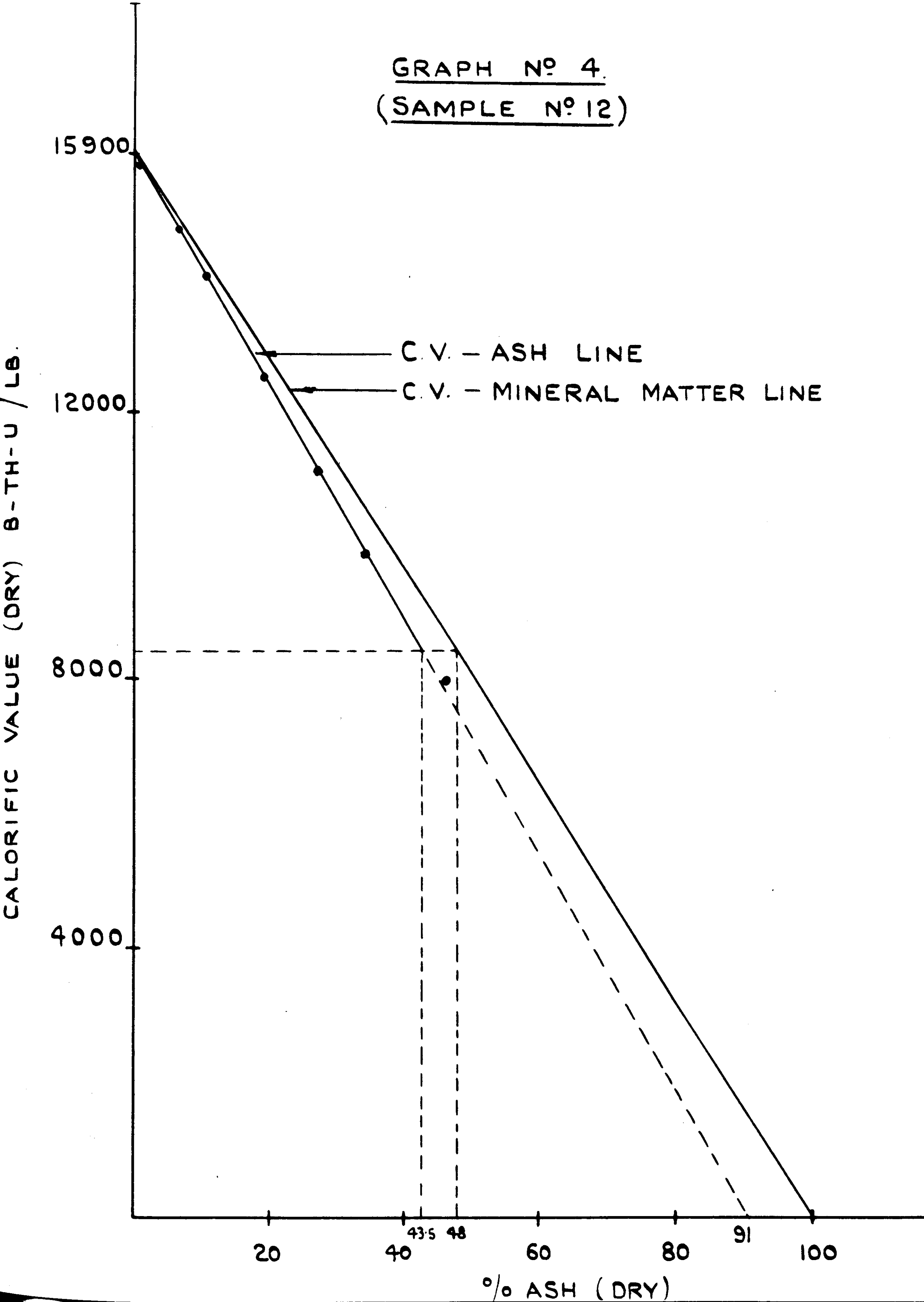
GRAPH No 3.
(SAMPLE No 11)

TABLE NO. 29

DETERMINATION OF THE MINERAL MATTER BY THE GRAPHICAL METHOD

Inferior cannel, Whitehill colliery (Sample No.12)
(Cf: graph No.4)

	Experiment No.	Ash (dry) %	Calorific value B.Th.u./lb
A.	I	45.5	7,960
	II	33.8	9,870
	III	26.4	11,090
	IV	18.8	12,500
	V	10.0	14,000
	VI	6.0	14,680
	VII	0.6	15,700
B.	Ash equivalent of 100 % mineral matter from graph	%	91.0
	Mineral matter content of the original sample from graph	%	48.0
	Mineral matter/ash ratio		1.10
	Calorific value of dry mineral matter free coal by extrapolation B.Th.u./lb		15,900



GRAPH No. 4.
(SAMPLE No. 12)

C. DISCUSSION OF RESULTS.

(1) General: In the Tables 13 to 24, the ultimate analyses of the original and acid treated samples are given, both on a dry, ash, CO_2 free basis and dry mineral matter free basis, the values for the mineral matter being calculated by the King, Maries and Crossley formula. The necessity for expressing the composition of a coal on a dry, mineral matter free basis rather than on a dry, ash, CO_2 free basis is clearly brought out by the markedly lower values for carbon obtained on a dry, ash, CO_2 free basis in the case of samples with over 5 percent ash (Nos. 6, 9, 10, 11 and 12).

In view of the theoretical considerations advanced earlier, it will be appreciated that, from the point of view of scientific justification, the most reliable means available at present for estimating the composition of the pure coal substance is the ultimate analyses of the coal on a dry, mineral matter free basis, the latter values being calculated by the K.M.C. formula. These values could, therefore, be taken as a standard for examining the accuracy of the values obtained by other methods.

/(2)...............

(2) The mineral matter content of acid treated coals.

An examination of the analyses of the original samples (Nos. 1, 2, 3, 4, 5, 7 and 8) revealed that the difference noted between the values on a dry, ash, CO_2 free basis and those from a dry, mineral matter free basis were of a low order for samples with ash content below 5 percent. So when the ash content of a sample of coal has been reduced to one percent and below by acid treatment, the error involved in expressing the composition on a dry, ash, CO_2 free basis should be negligible; but when the ultimate analyses of the acid treated samples on a dry,ash, CO_2 free basis were compared with the values of the original sample on a dry mineral matter free basis, the total difference between the two sets of values was between 0·1 and 1·5 percent. This discrepancy could partly be due to the ash content of acid treated coals not being strictly equal to the mineral matter content of the sample. Any difference between the two values could be easily ascertained by deriving a formula for the mineral matter content of the acid treated coal, on the same basis as the K.M.C. formula.

The King, Maries and Crossley (29) formula for the evaluation of mineral matter in coal involves corrections for (i) water of constitution of the shaly matter; (ii) decomposition of the pyrite and fixation of the SO_3 in the ash;

(iii) decomposition of the carbonates and (iv) the decomposition of the chlorides.

(i) Water of constitution of the shaly matter: In the case of the acid treated sample, no correction would be necessary for the water of constitution; for

(1) it has been noted earlier (Table No.8) that in eleven out of the twelve samples examined, more than eighty percent of the silicate minerals were removed by hydrofluoric acid;

(2) Karavaev and Rapoport (16) have pointed out that in coal analyses the errors due to the water of hydration of the clay minerals were avoided by a preliminary treatment of the coal with 1:10 cold hydrofluoric acid for 24 to 48 hours.

(ii) Decomposition of the pyrite and fixation of the SO_3 in the ash: It has been noted that pyritic iron was not completely extracted by treatment with hot, dilute hydrofluoric and hydrochloric acids (Table No.9). During incineration, the pyrite would be converted to the oxide as follows:-

$$\begin{array}{ccc} 2\,FeS_2 & \longrightarrow & Fe_2O_3 + 4SO_2 \\ \underline{112 \quad 128} & & 160 \\ 240 & & \end{array}$$

/The..............

The loss of weight due to the replacement of four atoms of sulphur by three of oxygen would be 80/128 or 5/8 times the percentage of pyritic sulphur. So for the acid treated coals, the correction for pyrites would be ash 0·6 pyritic sulphur.

No correction for the fixation of the SO_3 by the lime or the alkali oxides during 'ashing' would be necessary; for

(1) the results (Table No.8) showed that a high percentage of the mineral matter in coal corresponding to the water soluble portions of the ash (lime and alkali oxides) was extracted by acid treatment;

(2) the results detailed in Tables 13-24, showed that all the original sulphate present in coal was extracted by the acids and that the sulphur in the ash of the acid treated sample was negligible i.e. that the sulphur present in the acid treated coal sample could be regarded as completely volatile.

(iii) Decomposition of the carbonates: No correction would be necessary in this case also, for the coal sample did not contain any carbonates after treatment with hot acids. Thus, the conventional "dry, ash, CO_2 free" values would only be dry ash free values in the case of acid treated samples.

/(iv)............

(iv) Decomposition of the chlorides: To obtain a correction a factor for the conversion of the chlorides present in the acid treated coal samples, the chlorine content of these samples was determined. The difficulties of preparing a sample of acid treated coal completely free from the chloride reaction have been referred to earlier. So in the case of the samples used for chlorine determinations (Tables 13-24), besides repeatedly boiling with distilled water, as an additional precaution the samples were kept in distilled water for 24-48 hours. It was very unlikely that any free acid could still have been present.

Table 30 gives the relative chlorine contents of the original and acid treated samples (dry), along with the percentage of chlorine (per part of the dry, original sample) removed during acid treatment and subsequent extraction with water. It is noted that in four cases over 95 percent, in seven cases over 80 percent and in eleven cases over 60 percent of the chlorine present in the original sample was retained in the final sample. The two comparatively high values of 33 and 44 percent for the extraction of chlorine were obtained with the two fusain samples (Nos.5 and 6), which are known to contain high concentrations of water soluble chlorine (mainly sodium chloride).

TABLE NO. 30

EFFECT OF ACID TREATMENT ON THE CHLORINE CONTENT OF COALS

Sample No.	Ash content (dry)		Chlorine content of original sample % of dry coal	Chlorine content of acid treated sample % of dry coal	Chlorine extracted by acid treatment per part of dry original sample %	% of chlorine in the original sample retained in the acid treated sample %
	original sample %	Acid treated sample %				
(1)	1.34	0.53	0.17	0.11	35.3	64.7
(2)	2.60	0.52	0.01	0.01	2.1	97.9
(3)	3.59	0.82	0.01	0.01	2.8	97.2
(4)	4.90	0.42	0.04	0.04	5.0	95.0
(5)	5.88	1.34	0.17	0.12	32.9	67.1
(6)	24.00	3.03	0.07	0.05	44.3	55.7
(7)	3.06	0.73	0.25	0.21	18.0	82.0
(8)	4.04	0.52	0.19	0.16	18.9	81.1
(9)	6.80	2.01	0.06	0.04	36.7	63.3
(10)	27.57	1.37	0.06	0.08	1.7	98.3
(11)	35.18	1.25	0.04	0.04	35.0	65.0
(12)	45.55	0.63	0.04	0.06	17.5	82.5

King, Maries and Crossley (loc cit) stated that at least half the chlorine in coal is inorganic; they also mentioned that the remainder also could be inorganic but proof had not been obtained. According to the Fuel Research Survey Reports (quoted by Mott and Spooner (48)), in most English and North Welsh coal samples, between 8 and 60 percent (for most samples between 33 and 60 percent) of the chlorine is soluble. Chapman and Mott (63) mention that at least half the water soluble chlorine in coal is removed from small coals during wet washing. But in the present investigation, it will be appreciated, that after the use of hot dilute hydrochloric acid for over eight hours on finely divided coals, no definite conclusions either on the chemical nature or the percentage of soluble chlorine, could justifiably be drawn from the results in Table No.30.

King, Maries and Crossley (loc cit), after examining the oxides and chlorides of sodium, potassium, calcium and magnesium showed that the relationship between chlorine and the difference between the chloride and oxide is 1/0·78 irrespective of the base concerned. So for the original samples, since (chlorides - oxides)/chlorine = 0·78, (chlorides - 1·09 x oxides) would be 0·70. But in the case of acid treated coals, the factor 1·09 (for the water of constitution of the shaly matter) would not arise; so the conversion factor would be 0·78.

/If.............

If approximately half the chlorine in the original sample were inorganic, then according to the results in Table No.30, between 13 to 50 percent of the chlorine present in all the acid treated samples (excepting No.6) would be inorganic. Then the correction factor for the conversion of the chlorides would vary between 0·10 to 0·78; for seven of the samples, it would be between 0·62 and 0·78. In the absence of complete knowledge, the same factor as used in the original formula i.e. 0·5 chlorine was adopted.

So the final formula used for the evaluation of the mineral matter in acid treated coals was

$$\text{Mineral matter} = 1{\cdot}00 \text{ ash} + 0{\cdot}6 \text{ pyritic sulphur} + 0{\cdot}5 \text{ chlorine}$$

It should be stated that the correction factor for the chlorides in this case was not of much importance. The maximum and minimum values for the chlorine content of the acid treated samples were 0·20 and 0·01 percent (sample Nos. 7 and 2 respectively on an air dried basis); the increase in the carbon values due to the correction for the chlorides in the mineral matter in these two cases would be 0·09 and nil respectively.

Calorific value of acid treated coals: The same formula as in the case of the original sample, was applicable.

/(3)............

(3) The influence of acid treatment on the coal substance.

All the values given in this section are on a dry, mineral matter free basis unless otherwise stated; the values for the mineral matter content of the original samples were calculated by the King, Maries and Crossley formula and those for the acid treated samples by the formula given in the previous section. Table No.31 summarises the differences noted in the composition of the original and acid treated sample.

(i) carbon and hydrogen: Generally the carbon and hydrogen values for the acid-treated samples were lower than those of the original samples. The carbon content of only one acid-treated sample (No.2) was equal to that of the original one; for two samples (Nos. 1 and 8) the carbon contents were lower by 0·1 percent, for two others (Nos. 4 and 9) by 0·2 percent, for three others (Nos.3, 10 and 11) by 0·3 percent; only one (No.7) differed by 0·4 percent while three others were lower by 0·5 percent of dry mineral matter free coal (Nos. 5, 6 and 12).

In the case of hydrogen six of the acid treated samples (Nos.1, 3, 4, 7, 8 and 12) had the same values as the original ones, three samples (Nos. 2, 5 and 9) had values lower by 0·1 percent, two (Nos. 10 and 11) by 0·2 percent and only one by 0.3 percent of dry mineral matter free coal.

/Such.........

TABLE NO. 31

EFFECT OF ACID TREATMENT ON THE COAL SUBSTANCE ULTIMATE ANALYSES

Sample No.	DRY, MINERAL MATTER FREE BASIS				
	Decrease due to acid treatment in the values for:-				Increase in the value of oxygen and errors
	Carbon (1) %	Hydrogen (2) %	Organic sulphur (3) %	Calorific value (4) B.Th.u./lb	(5) %
(1)	0.1	nil	nil	40	0.1
(2)	nil	0.1	0.1	80	0.2
(3)	0.3	nil	0.1	20	0.4
(4)	0.2	nil	0.1	50	0.3
(5)	0.5	0.1	0.2	160	0.8
(6)	0.5	0.3	0.7	310	1.5
(7)	0.4	nil	nil	60	0.3
(8)	0.1	nil	0.1	10	0.2
(9)	0.2	0.1	0.4	50	0.6
(10)	0.3	0.2	0.2	200	0.6
(11)	0.3	0.2	0.4	190	0.8
(12)	0.5	nil	0.2	60	0.7

NOTE: For samples (Nos. 7, 9, 10 and 11), the values in Cols. 1, 2, and 3 do not add up to that in Col. (5) due to an increase of 0.1 percent of nitrogen noted in those cases. (experimental error).

Such differences as the above, between the composition of the original and acid treated samples might be due to (a)analytical errors; (b) the variations inherent in the assumption of average values in the K.M.C. formula for the water of constitution of shaly matter and/or (c) the effect of the two hot acids on the coal substance.

(a) Analytical errors: The maximum permissible difference between duplicate determinations of carbon and hydrogen by the British Standard method (B.S.I. No.1016 of 1942 page 71) on a dry, ash free basis would be 0·50 and 0·17 percent respectively for coals of moderate ash and moisture contents (of about 4 percent each). The results given in Tables 13-24 are the mean of values obtained for each sample, the differences in each case being within the permissible limits. If it could be assumed that such limits without much modification would be applicable for the processes involved in acid treatment, then it could be argued that in all cases the variations between the original and acid treated samples were within this limit (excepting for the value of hydrogen for sample No.6).

/(b).............

(b) Variations due to the factor for the water of constitution of shaly matter: It has been pointed out that the correction factor of 0·09 ash for the water of constitution of the shaly matter is based on the fact, that on an average, the clays associated with British coals contain 8 percent of water of constitution and yield 90 percent ash. The authors of the formula have shown that the proportion of the combined water in shales varies in different districts and suggested the acceptance of the combined water correction factors of 0·09, 0·13 and 0·07 for English (and British), Scottish and Welsh coals. It might be noted that the Parr formula adopted a factor 0·08.

Any variation in this factor is bound to affect the value for mineral matter and consequently the carbon, hydrogen values; also the magnitude of such variations would increase with increasing ash content. It will be noted that of the three cases where the maximum difference of 0·5 percent between the carbon contents of the original and acid treated samples was noted, two had high ash contents (Sample No.6 with 24·0 percent ash and No.12 with 45·6 percent ash (dry basis)). So the lower values in the case of the acid treated samples might partly be due to the

/correction.........

correction factor of 0·09 for the water of constitution of the shaly matter being slightly on the higher side. But no great stress could be laid on this argument; for the authors recommended a factor 0·13 as being more suitable for Scottish coals. If this factor had been adopted for the calculation of the mineral matter of the original samples, the differences between the values for the two would have been slightly higher than those given in Table No. 31. In the analyses of Scottish shales, there is nothing to suggest that the combined water content is much lower than the figures suggested by King and co-workers. So while the correction factor of 0·09 might have been slightly on the higher side in some cases, it would not be justifiable to assume, that it was so in all the cases.

Even granting the validity of these two arguments, it would still have to be explained as to why the acid treated samples had the lower values in all the cases. So the difference might probably be due to the effect of the hot acids on the coal substance.

(c) The effect of the two hot acids on the coal substance:

All the previous workers, who attempted the extraction of the mineral impurities in coal, with hydrofluoric and hydrochloric acids, reported a loss of organic carbon and hydrogen due to such treatment.

/Gallard............

Gallard (13) after reducing the ash content of a bituminous coal sample from 12·24 percent to 0·94 percent by treating with 2 parts of 40 percent hydrofluoric acid and one part of concentrated hydrochloric acid (both acids hot; conditions described in Part I) found that this procedure involved a loss of 0·80 percent carbon, 0·59 percent hydrogen, 0·13 of nitrogen and 0·10 of sulphur, all the results being expressed on a dry, ash free basis. The differences would have been higher, if expressed on a dry mineral matter free basis.

Fieldner and co-workers (14) also working with hot, concentrated acids on a bituminous coal found that acid treatment resulted in a loss of organic carbon of about 0·47 to 2·70 percent of coal and of hydrogen by about 0·2 percent of coal.

Turner and co-workers (15), after experiments under conditions similar to the above, reported that acid treatment resulted in a loss of carbon and hydrogen to the extent of 1·5 and 0·1 percent of coal respectively for anthracites and of 0·6 and 1·0 percent respectively for bituminous coal samples.

Himus and Basak (22), who followed the extraction of the bituminous coal with hydrofluoric acid by a treatment with dilute hydrochloric acid and zinc dust, found the loss of carbon to be between 1·4 and 2·7 percent and of hydrogen between 0·17 and 0·35 percent of coal on a dry ash free basis.

/Compared..............

Compared with the above methods, the conditions of acid treatment in the present investigation were very mild. The concentration of the hydrofluoric and hydrochloric acids used were only 5·0 percent; the extraction was carried out in a nitrogen atmosphere to prevent any oxidation. The results given in Table No. 31 are on a mineral matter free basis unlike those quoted above and are therefore more strictly comparable.

The results reveal a much closer agreement between the carbon and hydrogen values of the original and acid treated samples than that noticed in any one of the above cases. But for the fact that a decrease in carbon and hydrogen content is accompanied also by a loss in calorific value (this is discussed in a subsequent section) the differences noticed in all the samples, could be attributed mostly to analytical errors.

Subject to the limitations of drawing inferences about the coal substance solely from the ultimate analysis, it might be stated that acid treatment, under the conditions of the present investigation, reduced the loss of organic carbon in most cases to a negligible minimum. This procedure had almost no influence on the carbon content of the pure coal in the case of samples with an initial ash content below 30 percent; the use of hot acid did seem to affect the coal substance slightly in the case of readily oxidisable samples like fusain (Nos.5 and 6) and cannel samples with very high initial ash content (No.12;ash 45·6 percent (dry)).

/Similarly.................

Similarly the present procedure had no noticeable effect on the hydrogen content for samples of moderate ash content; the effect was slightly felt in fusain samples or in cannels, which, besides their generally high hydrogen content, were also high in ash. (In the case of sample No.12, a very high ash inferior cannel, the carbon content was noticeably affected but not hydrogen).

(ii) Nitrogen: The results in Tables 13-24 indicate that nitrogen has not been affected at all by acid treatment under the conditions of the present investigation. (In the case of sample Nos. 7, 9, 10 and 11, an increase of 0·1 percent in the nitrogen content of the acid treated sample was noted; this must have been due only to experimental errors and to the procedure of correcting the values in each case to the first decimal place).

Gallard (loc cit) indicated that there was a loss of nitrogen content of the coal due to treatment with concentrated hydrofluoric and hydrochloric acids. Apart from Gallard, the other workers on the acid treatment of coals have not referred to any effect of the acids on the nitrogen content of coals. Shacklock and Drakeley (64) showed that part of the nitrogen in coal could be extracted by dilute sulphuric acid. But generally it is known that the more mature the fuel, the lower the percentage of nitrogen extractable.

It is well known that nitrogen is the only element present in the coal that is exclusively inorganic combination. As a result of extensive chlorination studies, Heathcoat and Wheeler (65) concluded that nitrogen in coal is in a highly stable form and that it is an integral part of the ring structure of coals. Besides, the work of Bone, Horton and Ward (66) on the benzene Soxhlet pressure extraction of lignite indicated that the nitrogen compounds present in the humic acids are resistant to oxidation.

In the present investigation, the nitrogen in coal was completely unaffected by acid treatment. This must mainly be due to (1) the method of extraction being very mild compared to those of Gallard or Shacklock and Drakeley and (2) to the nitrogen in coal being present in a very stable form.

(iii) Sulphur

(a) distribution of the forms of sulphur in coal:

Table No.32 gives the percentage variations of the three different forms of sulphur present in coal. The sulphate sulphur content was generally below 5 percent but mostly below 2·6 percent of the total

/sulphur..........

sulphur; the pyritic sulphur content varied between 17 and 72 percent of the total sulphur, while the organic sulphur content was between 24 and 85 percent of the total sulphur.

In the introduction to Part II of this work, it has been mentioned that the Parr formula for the evaluation of the mineral matter in coal assumed that all the sulphur in coal was pyritic. With a view to modify the Parr formula, Tideswell and Wheeler proposed that total sulphur in excess of 1 percent could be taken as pyritic sulphur while Fieldner and Selvig (50) suggested that pyritic sulphur would approximately be equal to half the total sulphur.

The results in Table No. 32 indicated that none of the above assumptions was likely to be correct in all the cases; this confirmed the conclusion of King and co-workers that a separate determination of pyritic iron was necessary in each case.

The total sulphur of the acid treated sample consisted mostly of organic sulphur (between 60 and 94 percent of the total) with a little pyritic sulphur, (between 5 and 39 percent). The sulphate sulphur was completely extracted by acid treatment. The efficiency of extraction of pyritic sulphur by acid treatment would follow the same trend as that of pyritic iron

/(pyritic....................

TABLE NO. 32

DISTRIBUTION OF FORMS OF SULPHUR IN COAL.

Sample No.	ORIGINAL SAMPLE				ACID TREATED SAMPLE			
	Total sulphur	As % of total sulphur			Total sulphur	As percent of total sulphur		
	% of coal	Sulphate sulphur %	Pyritic sulphur %	organic sulphur %	% of coal	Sulphate sulphur %	pyritic sulphur %	organic sulphur %
(1)	1.08	1.1	17.6	81.3	0.90	Nil	5.6	94.4
(2)	1.06	2.3	20.8	76.9	0.85	"	10.6	89.4
(3)	1.01	2.4	12.9	84.7	0.80	"	25.0	75.0
(4)	1.23	4.9	41.5	53.6	0.59	"	7.6	92.4
(5)	1.28	1.9	41.4	56.7	0.90	"	23.3	76.7
(6)	2.65	0.9	38.9	60.2	1.92	"	17.2	82.8
(7)	0.98	0.2	33.7	66.1	0.79	"	21.5	78.5
(8)	1.37	2.6	34.3	63.1	0.80	"	7.5	92.5
(9)	3.30	3.6	44.3	52.1	2.17	"	34.1	65.9
(10)	0.84	3.8	52.4	43.8	0.62	"	38.7	61.3
(11)	2.73	3.5	72.5	24.0	0.85	"	23.5	76.5
(12)	1.00	2.4	38.0	59.6	1.07	"	6.5	93.5

(pyritic sulphur = 1·15 x pyritic iron), which has been discussed in Part I (Table No.9) of this work.

(b) Effect of acid treatmen t on organic sulphur.

The necessity for expressing the ultimate analysis of the acid treated sample also, on a dry, mineral matter free basis was clearly seen in the case of the organic sulphur values. It will be noted that it in the analyses of the acid treated samples on both dry, ash, CO_2 free basis and dry mineral matter free basis, apart from sulphur the differences in the case of the other values were of a minor nature. When the results are expressed on a dry, ash, CO_2 free basis, sulphur conventionally represents volatile sulphur, which in this case would include varying amounts of pyritic sulphur. If such values were used, the real difference between the values for organic sulphur content of the two samples could not be properly appreciated.

It is only organic sulphur that forms a part of the coal substance. The organic sulphur of the original and the acid treated samples is found to differ between nil to 0·7 percent of the coal; only two samples (Nos. 1 and 7) had the same organic sulphur contents for the original and acid treated sample; for four (Nos. 2,3,4 and 8) the difference was 0·1

/percent.............

percent of coal; for three others (Nos.5,10 and 12) it was 0·2 percent and for two more (Nos. 9 and 11) 0·4. Only in one case (No.6) the maximum difference of 0.7 percent of coal was noted.

Very little information is available on the nature of the sulphur compounds in coal. Stopes and Wheeler (67) suggested that a majority or all the complex molecules which form the coal conglomerate possess each a sulphur atom, in some grouping in their structure. Wheeler (68), in view of his finding that the pyridine and chloroform extracts and the extraction residue all had the same sulphur content as the original coal, concluded that organic sulphur compounds were part of the fundamental constitution of coal and were uniformly distributed.

Powell and Parr (69) distinguished between phenol soluble and phenol insoluble organic sulphur, but the significance of such a distinction is not clear. According to Powell, Fischer in 1899 concluded that by the use of bromine (or preferably sodium hypobromite) on coal besides the pyritic sulphur some organic sulphur also was dissolved. This observation has been confirmed by numerous workers; but relatively little is known about the sulphur compounds in coal affected by such a treatment.

/In................

In the present investigation, in view of the facts that

(1) the organic sulphur was determined by difference;

(2) the differences were small and within experimental limits in most cases (excepting Nos. 6, 9 and 11)

it would not be justifiable to draw any definite conclusions about the influence of the hot acids on the organic sulphur in coal. But in some cases (for e.g. Samples Nos. 6, 9, and 11) the present results indicated that a portion at least of the organic sulphur present in coal was relatively weakly attached to the coal molecule and that it was affected by the use hot dilute acids even in an inert atmosphere.

(iv) Oxygen: The oxygen content is usually obtained by deducting from 100, the percentages of carbon, hydrogen, nitrogen and organic sulphur of the pure coal. Since the oxygen values are obtained by difference, they include the possible analytical errors in the determination of carbon, hydrogen, nitrogen and sulphur.

It has been pointed out that the Parr formula is on a sulphur free basis. It is one of the chief merits of the King, Maries and Crossley formula that by allowing for the presence of organic sulphur in coal, it completely limits the probable error in oxygen values, obtained by

/difference............

difference, to analytical errors only.

It was one of the aims of the present investigation to avoid oxidation of the coal sample, during acid treatment; but the oxygen values of the acid treated sample were found to have increased by 0·1 to 1·5 percent (Col. 5, Table No.31) of the coal; for eleven out of the twelve samples, the increase was by less than 0·8 percent of the coal. Such variations were quite possible, due to experimental errors alone. But in the present investigation, the increase in oxygen content was in every case accounted for by a slight decrease of carbon, hydrogen and organic sulphur contents as also the calorific values. Of these the decrease in carbon, hydrogen and also sulphur in most cases have been shown to be not of a serious nature; but in some cases, like fusain samples or high ash cannels, the hot acids did seem to effect a very mild oxidation of the coal substance.

This would, perhaps, be the main criticism against the present procedure of acid treatment. But the chief merit of this procedure would be that its results on the extraction of the mineral impurities in coal were as good as those obtained by any other procedure employing more concentrated acids; but at the same time, it reduced the chances of oxidation of the coal substance to what might perhaps be, an irreducible

/minimum...............

minimum. In the results of the previous workers for bituminous coals, the minimum increase (of 1·6 percent) in oxygen content due to acid treatment was obtained by Turner and co-workers (loc cit) and the maximum (2·9 percent) by Himus and Basak (loc cit), the results being on a dry ash free basis. In the present investigation, with a much wider variation in the ash content of the samples examined (excepting in the case of a fusain, sample No.6), the maximum increase in oxygen content was less than half the minimum noted above.

(v) Calorific values: These are discussed along with the results obtained by the Parr formula and the graphical method.

(4) Comparative values for the mineral matter content of coals by the Parr and graphical methods.

(i) The Parr formula: This formula has received considerable attention from numerous investigators and it would not be strictly within the scope of the present investigation to deal at length with the implications of the formula. Table No. 25 gives the values for the mineral matter content and calorific values for the twelve samples on the Parr basis. The mineral matter values for samples (Nos. 5, 6, 10 and 12) were calculated by the modified Parr method (the samples had high CO_2 contents)

/and............

and others by the original Parr formula. Table No. 33 gives the comparative values for the mineral matter obtained by the Parr, K.M.C. and graphical methods. The results are also expressed as mineral matter/ash ratios, since these offer a better means of comparison.

It is noted that for all the twelve samples under consideration, the mineral matter values obtained on the Parr basis were always higher than those obtained by the K.M.C. formula.

The mineral matter/ash ratio, as determined by the Parr formula may be expressed as follows:-

$$\text{Mineral matter/ash} = 1{\cdot}08 + 0{\cdot}55 \times \left(\frac{\text{Sulphur}}{\text{ash}}\right)$$

It is clear from this manner of expression, that the ratio could never be below 1·08 and the amount by which it exceeded 1·08 would be determined entirely by the sulphur to ash ratio. But the sulphur to ash ratio does not represent any fundamental relation between the components of the mineral matter and so any value obtained from it could only be arbitrary. Himus and Basak (loc cit), whose work is perhaps the most recent attempt to examine the validity of the Parr formula (March 1949) concluded, that while it would be justifiable to apply the formula for coals with ash contents below 15 percent, its application to

/Kerogen.............

TABLE NO.33

COMPARATIVE VALUES FOR THE MINERAL MATTER CONTENT OF COALS.

Sample No.	Ash content (air dried)	MINERAL MATTER (AIR DRIED SAMPLE)			MINERAL MATTER/ASH RATIO		
		Parr basis	K.M.C. basis	The graphical method	Parr basis	K.M.C. basis	graphical method
	%	%	%	%			
(1)	1.3	2.00	1.68	-	1.54	1.29	-
(2)	2.5	3.28	2.82	-	1.31	1.13	-
(3)	3.5	4.34	3.87	-	1.24	1.11	-
(4)	4.8	5.86	5.54	-	1.22	1.15	-
(5)	5.4	7.83	7.05	-	1.45	1.31	-
(6)	23.4	34.49	31.30	-	1.47	1.34	-
(7)	2.9	3.67	3.52	-	1.27	1.21	-
(8)	3.9	4.96	4.47	-	1.27	1.15	-
(9)	6.5	8.84	8.03	8.5	1.36	1.24	1.31
(10)	26.5	30.26	29.88	30.0	1.14	1.13	1.13
(11)	33.8	38.00	37.32	38.0	1.12	1.10	1.12
(12)	43.5	49.15	48.00	48.0	1.13	1.10	1.10

Kerogen rocks, high in ash and possibly in carbon dioxide and sulphur, might give 'misleading and even absurd' results. In the present instance also, the maximum difference in the values for mineral matter obtained by the Parr and K.M.C. formulae was noted with the fusain sample No.6 (ash 23·4 percent and CO_2 7·2 percent) in spite of the application of the recommended CO_2 correction.

It is also noted that in some cases (Samples 4, 7, 10, 11 and 12) the Parr method gave a reasonably close approximation to the K.M.C. values. This, according to Cady (70) could be ascribed to "the probable compensation of opposing errors involved in the calculation".

(ii) The improved graphical method (Cf Tables 26-29 and graphs 1-4): It was stated in the introduction to Part II of this work, that one of the sources of error in the application of the graphical method to the acid treated coals would be the absence of correction for the heat of formation of the ferric oxide from pyrite. For the four samples (Nos. 9, 10, 11 and 12) used in this investigation the pyritic sulphur contents were 1·46, 0·44, 1·98 and 0·38 percent respectively. Since the accepted figure for the heat of formation of ferric oxide from pyrite is 3032 gm. cal. per gm. pyrite for these samples, the correction necessary for the calorific value of the original sample would be between 20 and 110 B.Th.us /lb. In the graph, the calorific values are plotted only to the nearest hundred B.Th.us; so the correction necessary for samples (Nos. 10 and 12) would not make any appreciable difference. But in the other two cases (Nos.9 and 11) the calorific value of the initial sample would be in error by 100 B.Th.us; in the subsequent samples from each of these cannels, the error would be much less, since pyrite has been shown to be extracted by acid treatment.

For the four samples examined, the linear relation between calorific value and ash held good even up to an ash content of 45 percent; the very mild oxidation of the sample due to the solution of a portion of the organic sulphur did not depress the calorific value to any noticeable extent.

By the very nature of the graphical methods, the mineral matter values could be determined correct only to the nearest half of the whole number. With this limitation, the mineral matter values showed close agreement (Table No.33) with the K.M.C. values; they were a definite improvement over the Parr values, though not as exact as the K.M.C. values. In spite of this agreement, the mineral matter values obtained from the graphical method could only be studied with reserve, since the

/extrapolation..............

extrapolation of the graph both ways could not be easily justified.

(5) A comparison of the calorific values by the different methods.

The values obtained by the different methods are summarised in Table No. 34.

(i) Calorific value of the pure coal - K.M.C. basis and dry ash CO_2 free basis (Col. 1 and 5 of Table No. 34):

The results show that the expression of the calorific value on a dry, ash, CO_2 free basis, while justifiable in the case of samples with very low ash contents, introduced increasing errors with increase in ash content.

(ii) Calorific value of pure coal (calculated from the acid treated sample on a dry, mineral-matter free and dry ash, CO_2 free basis - Cols. 4 and 6 of Table 34).

The difference between the two values seldom exceeded 30 B.Th.us and was mostly below 20 B.Th.us. In the case of the dry, mineral matter free basis, the slightly higher values were due to; (1) the use of the special formula for the derivation of the mineral matter content of the acid treated samples and (2) correction for the heat of formation of ferric oxide from pyrite; this was necessary, since the previous results

/(Table.................

TABLE NO. 34

VARIATIONS IN THE CALORIFIC VALUE OF PURE COAL SUBSTANCE.

Sample No.	Calorific Value dry mineral matter (K.M.C.) free basis B.Th.u./lb (1)	VARIATIONS IN CALORIFIC VALUE FROM K.M.C VALUES (1); B.Th.u./lb				
		Dry mineral matter free basis			Dry ash CO_2 free basis	
		Parr (2)	Graphical method (3)	Acid treated coal (4)	Original sample (5)	Acid treated sample (6)
(1)	14880	-10	..	-40	-40	-40
(2)	15950	+30	..	-80	-30	-90
(3)	14180	+10	..	-20	-40	-20
(4)	14430	+80	..	-50	-90	-60
(5)	14680	+90	..	-160	-50	-180
(6)	14350	+600	..	-310	-70	-320
(7)	15360	Nil	..	-60	-60	-90
(8)	15600	+30	..	-10	-70	-30
(9)	15220	+40	-20	-50	-110	-80
(10)	16320	+80	-70	-200	-500	-220
(11)	14700	+130	Nil	-190	-640	-200
(12)	15960	+330	-60	-60	-910	-70

(Table No.9, Part I) showed that the pyrite in the mineral matter of coal was not completely extracted by acid treatment. Thus of the two sets of values, there would be greater justification for comparing the values on a dry mineral matter free basis with those from the K.M.C. formula.

(iii) Calorific value of the pure coal (values from the K.M.C. formula applied to the original sample and the special formula for the acid treated sample. Cols. 1 and 4 of Table No.34).

The difference between the two values was between 10 and 310 B.Th.us/lb; the variations noted in the case of eight samples (Nos.1, 2, 3, 4, 7, 8, 9 and 12) were below 80 B.Th.u./lb and could normally be attributed to experimental variations; but that could not account for the acid treated samples always having the lower values. So apart from experimental errors, the decrease in calorific value must have been due to the slight decrease noted in the carbon, hydrogen and sulphur values noted earlier.

The Dulong's formula for the calculation of calorific values from ultimate analysis ascribes a value of 4050 B.Th.us/lb. of sulphur in coal. Thus a loss of 0·1 percent sulphur would involve a decrease of 4 B.Th.us./lb.

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But for hydrogen the value is about 62000 B.Th.u./lb. Each 0·1 percent of hydrogen would account for 62 B.Th.us and similarly each 0·1 percent of carbon for 14·5 B.Th.us. So assuming the general validity of these figures, the decrease in calorific value due to the loss of sulphur would be negligible; it is the decrease in hydrogen content and to a much smaller extent the decrease in carbon content that could produce any significant lowering of the calorific value. Thus in the above eight samples, the decrease in carbon and hydrogen values were of the order of nil to 0·4 and nil to 0·1 percent respectively and so the difference in calorific value never exceeded 80 B.Th.us./lb. But in the case of the two fusain samples (Nos. 5 and 6) and the two cannels (Nos. 10 and 11) where the decrease in hydrogen content was between 0·1 to 0·3 percent of the coal, the calorific value also registered a definite decrease (between 160 and 310 B.Th.us./lb).

This suggested that, even under the controlled conditions of acid treatment as in the present investigation, the use of hot dilute hydrofluoric and hudrochloric acids, did mildly oxidise the coal substance in the case of fusain samples (Nos. 5 and 6) and high ash cannels (Nos. 10 and 11; No.12 seems to be an exception).

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(iv) Calorific value of pure coal from the K.M.C. and the Parr formulae. (Cols. 1 and 2 of Table No.34):

The results again bore out the earlier conclusions regarding the mineral matter values by the Parr method; in 10 out of the 12 cases, the calorific value obtained by the Parr method was higher than the K.M.C. values; with samples of low ash content, the difference was within the permissible limits, while for samples high in ash and CO_2, the error introduced by the Parr method was considerable.

(v) Calorific value of pure coal - K.M.C. values and the graphical method (Cols. 1 and 3 of Table No.34):

The values from the graphical method were higher than those obtained from acid treated samples on a dry, mineral matter basis and were reasonably close to the values for the original sample on a dry, mineral matter free basis (K.M.C.). In three (Nos. 9, 11 and 12) out of the four cases, the values from the graphical method were closer to the K.M.C. values than those by any other method.

Thus the two main conclusions are (1) the linear relation between ash and calorific value held good for samples obtained by acid treatment and (2) the pure coal calorific value obtained by extrapolation agreed within reasonable limits with the K.M.C. value. These facts might indicate that coal substance had not been affected

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by the acid treatment. This would be particularly true of the samples, Nos. 10 and 12, for in the case of the other two samples, which contained nearly two percent pyritic sulphur, the absence of a correction to the calorific value for the heat of formation of ferric oxide might have resulted in a slightly higher value.

(vi) The limitations of the improved graphical method:

(1) This method is obviously limited to samples high in ash, at least over 20 percent; with samples of lower ash content, it would not be possible to plot correctly the slope of the ash calorific value line.

(2) Better results would be obtained with samples low in pyritic iron.

(3) Being a graphical method, the calorific values obtained by extrapolation would be correct only to the nearest 50 B.Th.us and the mineral matter values to the nearest half of a whole number.

(4) The improved graphical method has one specific advantage over the earlier Stansfield and Sutherland method. Thiessen and Reed (55) concluded that the latter graphs did not give values, more accurate than the Parr formula. It is also known that for very high ash coals, the Parr formula is not

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applicable. The present experiments showed that the for high ash coals, the calorific value of pure coal as determined by the improved graphical method was definitely more accurate than the value obtained by the Parr formula.

(5) The most serious objection against both the original and improved graphical method would be the procedure of extrapolating the ash-calorific value line both to zero ash and zero calorific value. Extrapolation of the line to zero ash, which gave the pure coal calorific value could easily be justified; for in each case, the calorific values of samples of gradually decreasing ash content ~~up~~ down to 2 percent and below had been obtained and the extrapolation to zero ash could not have introduced any error. But the same could not be said of extrapolating the ash-calorific value line to zero calorific value, for besides the theoretical objections already mentioned (see introduction to Part II), such a procedure meant that in all cases more than half the total length of the graph was obtained by extrapolation. It could therefore be stated that the graphical method could best be used as a means of determination of pure coal calorific value; the mineral matter values obtained by this method, in spite of the relatively accurate values noted in the course of the present investigation, were likely to be erroneous.

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This improved method, like its predecessor, is unlikely to gain wide acceptance; for, inspite of the labour involved, the values are less accurate than those obtained by the K.M.C. formula.

(6) <u>The K.M.C. formula and the acid treatment of coals</u>:

It was one of the main aims of the present investigation to compare the values of the composition of the coal, freed as much as possible of the mineral matter associated with it by acid treatment, with the composition of the mineral matter free coal derived from the K.M.C. formula.

The results (Table No.31) indicated:

(1) in the case of six at least of the twelve samples, the acid treatment left the coal substance virtually unaffected;

(2) the results of the analyses of the acid treated samples in these cases showed close agreement with the values derived from the K.M.C. formula and

(3) in the other six samples (Nos. 5, 6, 9, 10, 11 and 12), where there were reasons to suspect a mild oxidation of the coal substance, the results did not show any unaccountable variations from the K.M.C. values.

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It might therefore be concluded:

(1) that for coal and cannel samples verying in ash contents from 1 to 46 percent, the K.M.C. formula for the evaluation of the mineral matter associated with them, held good and

(2) by the use in an inert atmosphere of hot dilute hydrofluoric and hydrochloric acids, it was possible in most cases to extract between 65 and 99 percent of the mineral matter associated with coals (Table No.12, Part I) without noticeably affecting the composition of the coal substance by such a treatment.

D. SOME PROPERTIES OF ACID TREATED COALS

(1) Volatile matter.

Among the previous workers, Gallard (13) was the first to mention that a small amount of volatile components had been eliminated by acid treatment. Nicolls and Swartzman (17) and later Sustmann and Lehnert (25) confirmed the same.

The proper basis for expressing the volatile matter is still controversial. Parr recommended a mineral matter free basis. King, Maries and Crossley (loc cit) pointed out that during the coking of coal in the determination of

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volatile matter, so many changes of an indeterminate nature occurred in the mineral matter, that it was impracticable to calculate an exact figure on the basis of pure coal. Some changes like the loss of water of constitution of shaly matter and the loss of carbon dioxide are complete and properly understood. The behaviour of pyrite is more complex; Powell (according to King and co-workers (loc cit)) stated that the decomposition of pyrite, which began at 400°C and was complete at 500°C, brought about the formation of ferrons sulphide containing dissolved free sulphur. In addition to this change, reactions between organic compounds and inorganic sulphur compounds resulted in an increased amount of organic sulphur.

In the case of chlorine, experiments at the Fuel Research Station (King and co-workers, loc cit) have shown that up to two thirds of the chlorine in coal might be volatilised during coking at 925°C. The manner of combination of the residual chlorine is not known.

Hence in the absence of exact information, King and co-workers concluded that it would be best to continue to represent volatile matter values on a dry ash CO_2 free basis only. This conclusion has been criticised by Mott and Spooner (48), who suggested the adoption of a dry, mineral matter free basis, with a formula similar to that of Parr. In the present

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investigation, the results are represented only on a dry, ash CO_2 free basis (Table No.35).

The results indicated that there was a noticeable decrease in the volatile matter content due to acid treatment; in nine out of the twelve samples. The decrease was least noticeable in the low ash samples (No.3, 4 and 7) but the fusain sample No.5, though low in ash showed a decrease of over 6 percent; in most of the high ash samples also the decrease did not exceed 4 percent excepting samples Nos. 11 and 12, which showed a difference of over 18 and 9 percent respectively.

The results in Table No.36 (Cf graph No.5) showed that with the gradual extraction of mineral matter by acids, the volatile matter content also decreased gradually.

Gallard (loc cit) and others attributed the loss of volatile matter to an attack by the acids on the coal substance.

The volatile matter content of coals has been shown to be influenced by the addition of inert matter to coal by Sinnatt and Grounds (71). They used three distinct types of inert matter pure sand, coal ash from the same coal as used, and electrode carbon. With the weight of electrode carbon/unit weight of coal varying between nil and twenty, they noticed an increase of 0·2 to 4·4 percent of volatile matter for the eight coals

TABLE NO. 35

EFFECT OF ACID TREATMENT ON THE VOLATILE MATTER CONTENT OF COALS.

Sample No.	ASH (DRY) Original sample %	Acid treated sample %	Volatile matter; dry ash CO_2 free basis Original sample	Acid treated sample
(1)	1.34	0.53	51.3	51.7
(2)	2.60	0.52	46.2	46.2
(3)	3.59	0.82	35.2	34.9
(4)	4.90	0.42	40.6	39.7
(5)	5.88	1.34	20.7	14.4
(6)	24.00	3.03	27.4	23.8
(7)	3.06	0.73	51.5	50.6
(8)	4.04	0.52	53.3	53.6
(9)	6.80	2.01	67.7	66.0
(10)	27.57	1.37	54.6	50.6
(11)	35.18	1.25	73.7	55.3
(12)	45.55	0.63	72.2	62.8

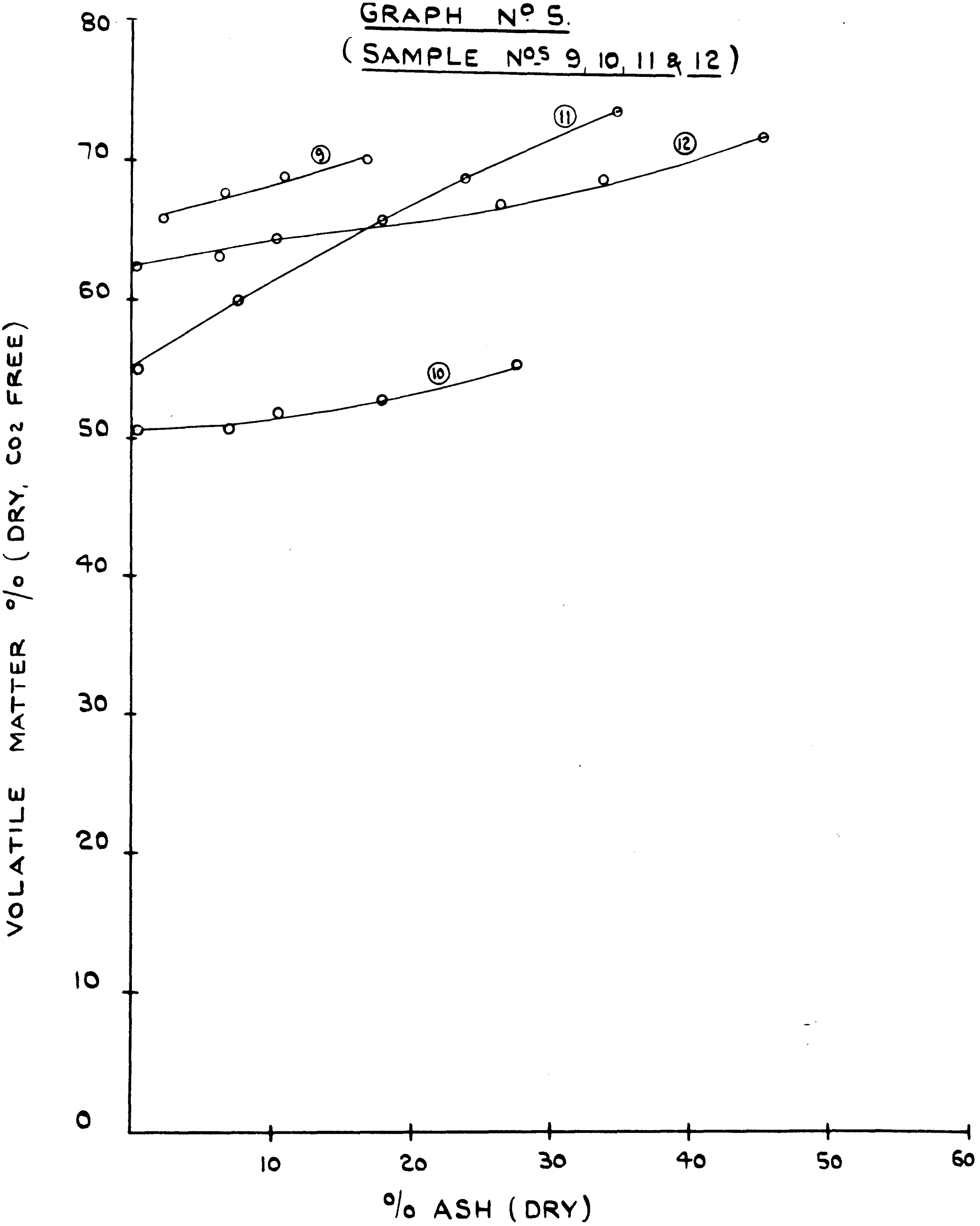
TABLE NO. 36

VARIATION OF VOLATILE MATTER WITH REDUCTION IN ASH CONTENT
(Cf: graph No.5)

Sample No.	Ash (dry) %	Volatile matter (dry, CO_2 free) %
(9)	17.3	70.6
	11.0	68.8
	6.5	67.7
	2.0	66.0
(10)	27.6	54.6
	18.4	53.1
	10.2	52.8
	6.8	51.4
	1.5	50.6
(11)	35.0	73.7
	24.0	70.0
	18.0	65.5
	7.5	60.0
	1.3	55.3
(12)	45.5	72.2
	33.8	69.0
	26.4	67.2
	18.8	66.5
	10.0	64.6
	6.0	63.5
	0.6	62.8

GRAPH No. 5.

(SAMPLE Nos. 9, 10, 11 & 12)



examined by them; the maximum increase was obtained with inert matter to coal ratios of 4 and 8.

The results in the present investigation could be explained in the light of the above findings. Since the addition of inert matter to coal is known to increase the volatile matter content of coals the gradual removal of the mineral matter might likewise be expected to cause a decrease in volatile matter; but it is not clear, why this should be so.

Since the quantity of the inorganic matter associated with coal is likely to influence the volatile matter content, it would not be justifiable to infer a loss of the coal substance due to acid treatment, by the decrease in volatile matter alone.

(2) Solvent extraction of the original and acid treated coals.

The solvent extraction of coal has for a long time been an important method of examination of the constitution of coal and a vast amount of literature is available on this topic. Of the various solvents in use, one of the most important is pyridine.

Wheeler and his coworkers (72) have developed the use of this solvent and divided the extract into fractions according to its solubility in chloroform. Wheeler stated that the extraction of coal by pyridine followed by the extraction of the pyridine extract with chloroform made a complete or near complete separation between the resinous constituents and the degradation products of cellulose of which coal is conglomerated. The nature of the fractions were described as follows:-

α fraction, insoluble in pyridine consisting of undispersed ulmins plus resistant plant remains.

β fraction soluble in pyridine but insoluble in chloroform consisting of dispersed ulmins and;

γ fraction, soluble in both pyridine and chloroform consisting mainly of resins and hydrocarbons.

Thus one of the methods of examining the effect of the acids on the coal substance would be to study the pyridine extraction of the original and acid treated sample.

Table No. 37 gives the results of pyridine extraction for four original and acid treated samples (Nos. 1, 2, 3 and 7). Both the pyridine and the subsequent chloroform Soxhlet extractions were carried out at atmospheric pressure under a nitrogen atmosphere, the former for 240 hours and the latter for 48-60 hours. The experimental procedure recommended by Illingworth (Analysis of coal and bye-products - Page 334-38) was closely followed.

TABLE NO. 37

PYRIDINE EXTRACTION OF COAL SAMPLES

PARTICULARS	DRY, ASH FREE COAL BASIS			
	Total Pyridine Extract % of coal	Fractions % of total		
		α %	β %	γ %
Sample No. 1				
(a) Original sample	30.6	69.4	19.5	11.1
(b) Acid treated sample (per part of the original sample).	20.9	79.1	15.5	5.4
Sample No. 2				
(a) Original sample	28.2	70.8	20.9	8.3
(b) Acid treated sample (per part of the original sample).	19.1	77.9	17.1	5.0
Sample No. 3				
(a) Original sample	20.6	78.2	13.0	8.8
(b) Acid treated sample (per part of the original sample).	14.6	84.2	10.5	5.3
Sample No. 7				
(a) Original sample	14.1	85.9	10.0	4.1
(b) Acid treated sample (per part of the original sample).	10.0	87.9	8.1	4.0

According to the results in Table No.37, the main effect of the acid treatment on the coal substance was to render it less dispersible in pyridine.

A similar feature has been noted in the case of a Don basin coal (78); after extraction with solvents under pressure at 350-390°C, in no case was all the organic matter dissolved. So when the residue was treated with hydrofluoric and hydrochloric acids to remove the ash, a second extraction removed no more organic matter.

The results in the present case could be explained from our present-day knowledge of the structure of coals.

Coal has long been assumed to be a colloid; the first proof of its colloidal nature was obtained through microscopic observations by Thiel. Thiessen (73) using very thin, transparent sections of the coal photographed the coal micelle. The available literature on the colloidal structure of coals is summarised by Hirst (74). Coals are likened to isogels, gels whose micelle is composed of molecules of similar composition but of varying degree of polymerisation. The variation of coal properties with rank is attributed to a variation of the shape of the micelle.

Tideswell (75) suggested that the extraction of coal by solvents could be considered as a colloidal dispersion process. Pertierra (76) confirmed the same by observing Brownian movement in an aniline extract of coal. Available literature tends to support the view that the pyridine extraction of coal is mainly a colloidal dispersion of the coal substance in the solvent. The arguments for and against such a view have been summarised by Kiebler (77).

In view of the above, it might be inferred that the action of the acids on the coal substance was mainly a case of partial coagulation of the coal colloid by the electrolyte; due to this partial coagulation the coal substance became much less dispersible in pyridine than before.

Nature of the three fractions: Of the three, the α and β fractions have been shown to be chemically similar by their analyses and Xray diffraction studies. It is also established that the gamma fraction contains resinous materials, since both this material and true resins affect a photographic plate.

The γ fraction has been divided into sub-fractions by the use of suitable solvents; according to Wheeler and coworkers, the nature of the various fractions is as follows:-

/γ_1 ....

γ 1: hydrocarbons, saturated and unsaturated, normal and aromatic;

γ 2: resinols, resines and resenes;

γ 3 & 4: resin-like substances.

Cockram and Wheeler (quoted by Kiebler, loc cit) stated that the active coking principle necessary for the production of good coke was provided by resins and hydrocarbons of the coal, since a mixture of α , β and γ_1 fractions gave the best coke. But it is still a matter of controversy, as to which of the gamma fractions constituted the active coking principle.

In the present investigation, though no separate determination of the caking index was carried out, the coke "button" left behind after the volatile matter determinations for acid treated samples was always powdery; so acid treatment had completely destroyed the coking property. Previous workers also have confirmed the loss of coking property due to the use of hot acids on coal.

It is interesting to note that this loss corresponded to the definite decrease noted in the values for the gamma fractions of the acid treated sample in three cases (Nos.1,2 and 3); the fourth, Sample No.7, in which case there was almost no decrease, was a cannel and hence non-coking.

This might suggest a preferential coagulation by the two acids of the resinous components (γ fractions) of the original coal samples.

SUMMARY

PART II

A: INFLUENCE OF ACID TREATMENT ON THE COAL SUBSTANCE.

(i) Ultimate analysis: The use of hot dilute hydrofluoric and hydrochloric acids, in an inert atmosphere, did not affect the carbon and hydrogen contents of bituminous coal samples and cannels of moderate ash content. In fusain samples and high ash cannels a very slight decrease in carbon and hydrogen contents might be attributed to the use of hot acids.

The treatment did not affect the nitrogen content of any sample.

A small part of the organic sulphur of the coal was found to have been extracted by the two acids in some cases.

The calorific values also were not noticeably affected except in the case of fusain and high ash cannels.

So the acid treatment of coals by the suggested procedure did not involve an oxidation of the coal substance, detectable by ultimate analysis in most cases; but in the case of fusain and high ash cannels, there were reasons to suspect mild oxidation.

/(ii)..........

(ii) Volatile Matter: The removal by acid treatment of the inorganic matter associated with coal was followed by a slight decrease in the volatile matter contents of the samples, even when the latter were expressed on a dry, ash CO_2 free basis.

(iii) Solvent extraction: The main effect of the hot dilute acids on the coal substance was to coagulate the coal colloid partially and thereby render it less dispersible in pyridine.

The complete loss of the coking property due to acid treatment corresponded with a reduction in the γ fraction of the acid treated sample.

B:. THE APPLICABILITY OF THE DIFFERENT FORMULAE FOR THE EVALUATION OF THE MINERAL MATTER IN COAL.

There was close agreement between the values for the composition of dry, mineral matter free coal obtained by the King, Maries and Crossley formula and those from the analysis of the acid treated samples. In the case of the latter, since acid treatment did not completely extract the pyrite and chlorides in the mineral matter of coal, it was necessary to use a special formula (Mineral matter of acid treated sample = 1·00 ash + 0·6 pyritic sulphur + 0·5 chlorine).

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In spite of the theoretical errors involved, the Parr formula gave reasonably accurate values in the case of low ash coals, but for samples high in ash, carbon dioxide or sulphur, it introduced considerable errors.

The improved graphical method gave values more accurate than the Parr formula but not as exact as the King, Maries and Crossley formula.

THE STUDY OF ULTRA-CLEAN COAL

GENERAL DISCUSSION

THE STUDY OF ULTRA-CLEAN COAL

GENERAL DISCUSSION

(a) The possibilities of industrial development of acid treatment as a coal cleaning process.

In Part I of this investigation, a study has been made of the optimum conditions under which the acid extraction of the mineral impurities in coal could be carried out. Part II of this work is concerned mainly with the effect of hot dilute acids on the coal substance. On the basis of the available data, it would be reasonable to examine whether, in the near future, the preparation of ultra-clean coals would find wider industrial application than at present.

(i) The influence of the rank of the coal: The present investigation was concerned only with the different types of coals, all of which were of the same rank. The samples examined were limited mainly to the different banded constituents of bituminous coals and to bituminous or sub-bituminous cannels. It could be stated with regard to these samples, that the efficiency of extraction of the mineral matter was influenced largely by the chemical nature and physical distribution of the impurities.

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According to Fischer (as quoted by Sustmann and Lehnert (25)) the acid treatment was more effective with brown coals than with bituminous coals. But Turner and coworkers (15) were able to reduce the ash of samples of anthracite, graphite and bituminous coals to well below 1 percent by treatment with concentrated hydrochloric and hydrofluoric acids. Available literature does not indicate that the rank of a coal has any definite bearing on the effectiveness of the extraction of the mineral impurities by acid treatment. Thus it would be possible to treat by this process a much wider range of coals than by any of the physical processes.

(ii) The production of ultra-clean coals suitable for electrode manufacture: It has been mentioned that one of the important uses of ultra-clean coals produced by acid treatment would in the field of the electrometallurgy of aluminium and other light metals. Table 12(A) (Part I) indicated that five out of the twelve samples examined would comply with the normal specifications for the manufacture of electrode coke and three out of the twelve samples would be suitable for the manufacture of very special electrodes.

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The significance of these values will be better appreciated, when it is realised that the original samples were chosen at random without reference to the needs of any particular industry. This makes it clear, that by a careful selection of the original sample, acid treatment of coals would make it possible to comply with any particular specification, regarding the presence of inorganic impurities in coal.

In the last decade the electrodes for the aluminium industry were manufactured almost exclusively from oil coke, which is the residue from crude oil distillation in petroleum industry. Due to improved methods of distillation and cracking, the supply of oil coke has gone down considerably.

Among the prevalent methods for the manufacture of electrode coke, the most important are (1) froth floatation and (2) the carbonisation of pitch.

The first process suffers from the defect that the pyrite in coal, being a sulphide, is more difficult to remove by froth floatation than are other impurities like fine clay or shale particles. According to Proctor and Carlson (81) a better reduction of free pyrite is possible when the floatation units are operated on a low over-all efficiency.

In in this respect acid treatment of coals has distinct advantages over froth floatation. It has been shown (Table No.9 Part I) that, in most cases, between 65 and 99 percent of the iron present in coal could be successfully removed by acid treatment. As regards the yield, it is one of the chief merits of this process, that its effective yield would almost be equal to the pure coal content of the original sample. Acid treatment could be worked with slightly "coarser" sizes than that required by froth floatation. The absence of any product of intermediate ash content is likely to be another advantage.

The carbonisation of pitch was practised widely in pre-war Germany; this process required nearly two tons of pitch for every ton of coke and was uneconomical.

The only known instance of the production of ultra-clean coals for electrode manufacture by acid treatment is the Carl Alexander Mine Process (26). Any future process employing the same principle is likely to use a carbon pot as the reaction vessel. The different operational results of the German process have been referred to in Part I of this work.

The following are some of the main considerations which weigh against the widespread adoption of this process:-

(1) The acid treated samples are likely to contain free acid, since it would be very difficult to wash fine coal particles completely free of acid on an industrial scale. It is well known that appreciable quantities of chlorides in coals to be carbonised is very detrimental to the brick work of the coke ovens.

The difficulties due to this could be minimised by using as low a concentration of acids as is consistent with efficiency Thus in the Carl Alexander Mine process (loc cit),which used only 1·4 percent hydrochloric acid, it is reported that no deleterious effect on the oven walls, due to the presence of halogen acids, was noticed. But the use of hydrofluoric acid in large scale industry might create some new problems. The development of acid resistant filters, and the disposal of large quantities of water containing traces of hydrofluoric acid are likely to constitute a problem of some magnitude.

(2) The acid treated sample would be completely non-coking. Carbonisation would be possible only by blending the acid treated sample with pitch or with ultra-clean coal samples produced by any of the physical methods. Such a procedure is likely to increase the cost of this process.

The German war time practice (26) was to blend pitch and Pott-Broche extract with the acid treated product. Even then the final product left much to be desired. This is an aspect of the problem, which could be satisfactorily solved by further research.

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(3) Period of Treatment: Available evidence shows (see Table No.7) that the acid extraction of the mineral impurities in coal to be a slow process. The comparatively longer period of treatment is likely to prevent the development of any single stage process for the preparation of ultra-clean coals from coals of moderate ash content by acid treatment alone; but this difficulty should be viewed against the advantage that this is the only process likely to give the maximum yield of ultra-clean coal of uniform ash content.

(4) Cost: The data available on cost is very meagre; the cost of the coke obtained by both the war time German processes - one employing acids and the other alkali - was high even according to war time standards. The general tendency seems to be to try acid treatment on coals already cleaned by any of the physical methods. The German process attempted acid treatment on samples from a froth floatation unit. But among the different methods of coal cleaning, froth floatation is one of the costliest; in any process employing acid treatment, if there were to be an initial froth floatation unit, the over-all cost is bound to be excessive.

The future of acid treatment of coals as an industrial process will depend largely on a solution of these problems or on the development of some unforeseen demand for ultra-clean coals; till then the use of this method is likely to be limited to the preparation of small quantities of ultra-clean coals for special purposes.

(b) The possibilities of oxidation of the coal sample during acid treatment.

It has been pointed out that acid treatment even in an inert atmosphere might involve mild oxidation of the coal in the case of fusain samples and high ash cannels.

It is known that the absorption of relatively small quantities of oxygen can change profoundly the coking properties of a coal. Wheeler and Woolhouse (79) have shown that a degree of oxidation insufficient to affect the ultimate analysis, can reduce the caking power of a coal almost to zero. Schmidt, Elder and Davis (80) report that most of the coals they studied, showed serious impairment of coking power before they were oxidised sufficiently to decrease the calorific value by 1 percent or before their proximate and ultimate analyses showed any discernible changes.

But in the present instance, one cannot suggest that all the samples were oxidised merely because of the loss of coking property. For Nesterenko's (78) Xray studies on coal has related the loss of coking property to the loss of the

/colloidal.........

colloidal micellar structure. In the course of the present work also, the experiments on the pyridine extraction of coal indicated that the colloidal structure of coals was affected by acid-treatment. Besides, since the acid treatment was carried out in an inert atmosphere, it will be more justifiable to attribute the loss of coking property to the loss of the colloidal micellar structure than to oxidation.

It could therefore be claimed as one of the chief merits of the suggested procedure of acid-treatment, that it limited the chances of oxidation even of fusain samples and high ash cannels to what might perhaps be an irreducible minimum.

(c) Acid treatment and coal classification.

It has been shown that the ultimate analysis of acid treated coals agreed closely with those obtained from the K.M.C. formula.

The correction of the results of the acid treated coals to a mineral matter free basis did not show any marked variation from the dry, ash free values except for organic sulphur. On the basis of these results, one might find an important use for the suggested procedure of acid treatment of coals in routine coal analyses.

Karavaev (16), Nicolls and Swartzman (17) have used cold hydrofluoric acid and hot hydrochloric acid for the preparation of coal samples free from inorganic matter for purposes of classification. The present procedure laid down the conditions for the use of hot hydrofluoric acid by which the ash content of the sample could be much further reduced without noticeably affecting the ultimate composition of the pure coal.

It is therefore suggested that wherever it is not possible to carry out the necessary determinations for the use of the K.M.C. formula, the samples, if amenable to acid-treatment, could be treated by the recommended procedure and the results examined on a dry ash-free basis. Such results would vary very little from the K.M.C. values; in the case of samples with high ash and carbondioxide, such values would definitely be more accurate than the corresponding values by the Parr formula.

BIBLIOGRAPHY

ABBREVIATIONS USED

Br. Abs.	The British Abstracts.
Am. Chem. Abs.	American Chemical Abstracts.
J.S.C.I.	Journal of the Society of Chemical Industry.
J.Inst.F. or Bull Inst. F.	Journal or Bulletin of the Institute of Fuel.
J.C.S.	Journal of the Chemical Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
B.C.U.R.A.Bull	British Coal Utilisation Research Association Bulletin.
Ind. Eng. Chem.	Industrial and Engineering Chemistry (Journal).
Trans.Ins.Min.Eng.	Transactions of the Institute of Mining Engineers.
U.S.Bu. of Mines R.I.	United States Bureau of Mines: Report on Investigations.
Trans.Am.I.M & M Eng. Coal Div.	Transactions of the American Institute of Mining and Metallurgical Engineers Coal Division.
J.Inst.Pet.	Journal of the Institute of Petroleum.
Bren. Chemie	Brennstoffe Chemie
Univ. Illinois Bull.	University of Illinois Engineering Experiment Station Bulletin.

Illinois Geo. Survey	Illinois State Geological Survey.
Eco. Geo.	Economic Geology.
Gas. Jour.	Gas Journal.
Lanc. and Ches. coal Res. Assn.	Lancashire and Cheshire Coal Research Association.
B.I.O.S.	British Intelligence objectives Sub-committee.
C.I.O.S.	Combined Intelligence objectives Sub-committee.

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