

STUDIES IN THE QUARTZ SERIES:  
THE SOLUBILITY OF SILICEOUS DUSTS

by

D.W. CLELLAND, B.Sc., A.R.T.C., A.R.I.C.

A thesis submitted to the University of  
Glasgow in fulfilment of requirements  
for the Ph.D. degree in Science.

April, 1951.

ProQuest Number: 13838376

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 13838376

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by the Author.

All rights reserved.

This work is protected against unauthorized copying under Title 17, United States Code  
Microform Edition © ProQuest LLC.

ProQuest LLC.  
789 East Eisenhower Parkway  
P.O. Box 1346  
Ann Arbor, MI 48106 – 1346

### ACKNOWLEDGMENTS

The author gratefully records his thanks to Professors P.D. Ritchie and W.M. Cumming for providing the necessary laboratory facilities and for their generous interest, help, and encouragement.

Thanks are also due to Professor G. Hibberd and Dr. E.A.C. Chamberlain (N.C.B.) for advice and stimulating discussions during the course of the work and to the late Dr. J.R. Campbell who supervised its early stages.

The work was part of a pneumokoniosis research programme supported financially by the National Coal Board (Scottish Division).

The author is also indebted to Mr. A. Clunie and staff (Tech. Chem. Dept. (Workshops) ), and to Mr. Barbour (Glass-blower) for their help in preparing various pieces of apparatus.

## CONTENTS

	<u>Page</u>
<u>INTRODUCTION</u>	4
<u>PART 1</u> <u>A High-Solubility Layer on Siliceous Dust Surfaces</u>	17
<u>PART 2</u> <u>Nature and Initial Production of the High-Solubility</u> <u>Layer</u>	52
<u>PART 3</u> <u>Removal and Regeneration of the High-Solubility Layer</u>	68
<u>PART 4</u> <u>Effect of the High-Solubility Layer on adsorption at</u> <u>Siliceous Dust Surfaces</u>	75
<u>PART 5</u> <u>The effect of X-ray Irradiation on the Solubility of</u> <u>Siliceous Dusts</u>	91
<u>PART 6</u> <u>Discussion of Results and Suggestions for Future Work</u>	102
<u>APPENDIX</u> <u>Introduction</u>	108
<u>Section 1</u> <u>An Investigation of the Molybdenum Blue</u> <u>Method of Silica Estimation</u>	109
<u>Section 2</u> <u>The Temperatures reached by Drilling Bits</u> <u>in Mining Operations</u>	122
<u>REFERENCES</u>	127

SUMMARY

1. Chemical aspects of pneumokoniosis are reviewed and the development of the 'solubility theory' of silicosis is traced. The general validity of, and some important exceptions to, this theory are discussed.

2. The effect of pre-treatment with various salt solutions, acids and buffers (pH 2-11) upon the solubilities of siliceous dusts has been investigated; and the existence of a high-solubility layer on the surface of such dust particles has been demonstrated by extractive solubility methods. Comparative solubility data have been obtained for five siliceous dusts - rock crystal, silica sand from Loch Aline, fused amorphous silica, olivine, and orthoclase feldspar. Analytical methods are described for estimating 'colloidal' and 'dissolved' silica in silicic acid dispersions.

The dispersion in a solvent of appreciable amounts of 'colloidal' silica from siliceous dust surfaces is shown to be connected with the dissolution of the high-solubility layer.

The known effect of the addition of metallic aluminium to liquid/siliceous dust systems has been further investigated, and also the effect of aluminium upon the composition of the resulting silicic acid dispersions.

3. The nature of the high-solubility layer is discussed, and the effect of grinding upon the density of quartz has been investigated. It is concluded that prolonged grinding of quartz converts a portion

of it to the vitreous state. It is suggested that this conversion is a similar process to the formation of a Beilby layer produced by polishing, that the high-solubility layer is similar in nature to the Beilby layer, and that it is produced on the dust particle surfaces by the grinding process in the formation of the dust.

4. By employing a polishing treatment it was found possible to regenerate a new high-solubility layer on dust particle surfaces from which the original layer had previously been removed.

Such a regeneration by purely mechanical means is considered to emphasise the similarity in nature of the high-solubility and Beilby layers.

5. The adsorption of a number of dyestuffs on silica dust surfaces has been investigated and it has been found that from a wide range of dyes only those of the basic class are adsorbed. The colour ions of these dyes in solution are positively charged, and it has been shown that the siliceous dust particles employed are negatively charged in water suspension. It is suggested, therefore, that the adsorption mechanism is ionic in character.

The presence of a high-solubility layer on the surfaces of quartz dusts has been found to have a major effect upon their adsorptive properties.

6. Pre-treatment by X-ray irradiation is shown to increase the

solubilities of five siliceous dusts (rock crystal, Loch Aline sand, fused amorphous silica, olivine, and orthoclase feldspar) from which the high-solubility layers had been previously removed; the three almost pure silica dusts (rock crystal, Loch Aline sand, and fused amorphous silica) exhibiting the greatest changes after such treatment. The additional silica yielded into solution, due to the irradiation treatment, is shown to be mainly in the colloidal form.

Similar treatment has been found to cause a slight increase in the solubility of a Loch Aline sand dust with its high-solubility layer intact; while no measurable change in solubility was effected by similar irradiation of a rock crystal dust with its high-solubility layer.

It has been reported by the Bureau of Pathology and Bacteriology that the solubility of various kinds of dusts, especially those containing silicates, is affected by the degree of their crystallinity. The more crystalline the dusts are, the less soluble they are. It is generally believed that the exposure of the victim to dust for at least 5-10 years, and the condition is generally associated with tuberculosis, most of the advanced cases showing the latter infection.

The presence of this disease among miners and workers in general has been recognized for centuries and as early as 1830 was described by Hirschmann (2) who made the symptoms (shortness of breath and rigidity of chest) of the disease exhibited by gold miners in the

### INTRODUCTION

The present work was begun with the object of providing basic data on the mechanism of solution and sorption phenomena of siliceous dusts. This subject was related to the problem of pneumokoniosis and silicosis in particular since the causative agent of the latter disease is known to be finely divided silica.

Pneumokoniosis, the most serious industrial disease in this country, claims many victims from the coalmining industry each year. In 1947, for example the certified number of sufferers from the disease was 3,779 (1). The disease is caused by the inhalation of airborne dust particles, which, becoming lodged in the lung tissues, cause pathological changes which incapacitate the lung. Silicosis is the term applied to the type of pneumokoniosis caused by the inhalation of siliceous dusts which, produce at first irritation and fibrosis, and in the later stages nodular fibrosis, which completely disables the lung. Slow in establishing itself, it normally requires exposure of the victim to dust for at least 5-10 years; and the condition is generally associated with tuberculosis, most of the advanced cases showing the latter infection.

The presence of this disease among mineworkers and stone masons has been recognised for centuries and as early as 1649 a reference by Dimerbrock (2) was made to the symptoms (shortness of breath and rigidity of chest) of the disease exhibited by granite workers in the Carpathians.

Peacock (3) in 1861 and Greenhow (4) in 1865 were the first to

record an understanding of the true nature of the disease; on the examination of lung tissue from sufferers they isolated what they termed "sand" and concluded that the condition was due to the inhalation of abnormally large quantities of dust. The mechanism of the disease was, however, still obscure. First thoughts were centered upon the possibility of the abrasive qualities of the dust particles being responsible for the destruction of the lung tissue since the mineral particles, when viewed under the microscope, were observed to have extremely sharp edges. This mechanical theory of silicosis was reflected in the conclusions of Haldane (5) after a study of the pathogenic effects of dusts used for stone dusting in mines. The practice of stone dusting for preventing coal explosions raised the question of the physiological effects of such dusts when inhaled. Haldane concluded that powdered clay, shale, chalk or other soft inert materials are harmless, whereas flue dust, crushed granite, flint, gannister and other similar gritty media are dangerous giving rise to chronic inflammation of the lung tissues. Doubts were early expressed as to whether such small particles, however sharp, could lacerate the lung tissue, and in 1918, Lanza (6) suggested that the pathogenicity of a dust was connected with its chemical composition in that the most dangerous dusts contained the greatest amounts of silica. He considered that the use of respirators to prevent the disease was futile since the particle size of the dust in the lung was so small (2-5  $\mu$  or less); and he also suggested that the use of

pneumatic drilling machines had increased the number of cases of the disease.

In 1922, Gye and Kettle (7) provided further evidence that the chemical nature of the dust was important in the causation of the disease by showing that silica when injected into animals subcutaneously produced characteristic lesions in the body tissue. These consisted of a central area of necrosis (dead tissue) surrounded by a zone of leucocytes (white blood-corpuscles); round this again was a second zone of necrosis limited by granulation tissue (scar tissue produced when wounds heal where the edges are not in apposition). These workers also found that tubercle bacilli proliferated rapidly in the necrotic areas and concluded that the action of silica aids in the establishment of this infection.

The classic experiments of Gardner (8) in 1923 provided convincing evidence against the mechanical theory of silicosis. He showed that silicon carbide dust, the particles of which are very hard and have as sharp edges as those of mineral dusts, did not produce the typical fibrous reaction of the tissue brought about by quartz dusts when introduced into the lungs of animals. These results quite finally rejected the mechanical explanation of the action of dust particles upon lung tissue and supported the suggestion that the physiological reaction was closely connected with the chemical properties of the dust. This chemical theory of silicosis was reflected in the work of Sayers (9) in 1925, who suggested that those

rock dusts which were high in free silica were most injurious, and that the solubility of silica in body fluids might cause injury to the lung tissue by a poisonous action.

An apparent contradiction of the work up to this point came in the report by Heffernan (10) in 1926 on dusty conditions arising in the manufacture of Derbyshire gannister bricks. The dust contained ca. 84% silica and ca. 16% clay and earth, with some organic matter; nevertheless, the workers exposed to it did not develop silicosis. He concluded that the non-siliceous constituents of the dust were exerting some influence on its usual toxic properties. These findings were a reminder that although in animal experiments the chemical composition of the dusts used may be closely controlled, the dust to which workers are exposed in industry will in the majority of cases be a complex mixture of a number of different mineral dusts, and that even when silica is present to a large extent the minor impurities in the dust may play a major role in determining its pathogenic qualities.

In further advancing the chemical theory, Kettle (11) in 1926 offered an explanation of the mechanism of the disease. He suggested that the silica dissolved in the lung fluid forming colloidal silicic acid, and that this acted as a cell poison producing necrosis and inflammation, and finally the invasion of fibrous tissue. He concluded that silica itself promoted the growth of the tubercle bacillus rather than the fibrous condition of the tissue or lack of

lymphatic drainage caused by blockage by the dust particles.

The chemical theory was supported in 1929 by Heffernan (12) who outlined a further possible mechanism of the disease. He suggested that the silica dust particles (crystalline, cryptocrystalline, or amorphous) are engulfed by phagocytes in the walls of the air sacs of the lungs and carried into the pulmonary lymphatic channels where they come to an arrest. The silica particle within the phagocyte causes the death of this cell, leaving a "ghost" of cell wall and stroma. After the death of the phagocyte the action spreads to the surrounding tissue cells, which are similarly influenced. A number of possible reactions which might cause the death of the cells are suggested, such as hydration of the silica particles at the expense of the cells with the formation of colloidal silicic acid, selective adsorption by the dust particles of constituents of the cell protoplasm, coagulation of cell colloids, or the formation of silico-organic compounds. It is also suggested that these processes are retarded if the silica particles have a protective coating, e.g. of clay, and are accelerated by the presence of alkali, e.g. with a coating of alkaline soap. It is postulated that an equilibrium condition may be brought about by the formation of relatively stable silico-organic substances or adsorption compounds, the coagulation of the silicic acid into an irreversible gel, or by the elimination of the silica in its soluble form in the urine.

In 1932, Kettle (13) carried out a series of experiments on mice

and rabbits and by injecting them subcutaneously with saline suspensions of a number of different dusts assessed the harmful properties of these by subsequent examination of the tissue reactions produced. All the siliceous dusts tested (quartz; a mine dust of high silica content; a shale dust, 35% silica; kaolin; and asbestos) were found to be active, producing necrosis and exciting a pronounced cellular reaction, whereas the non-siliceous dusts (aluminium oxide; iron oxide; carbon; coal; and marble) were inert and remained quiescent at the sites of their introduction. By injecting an emulsion of living tubercle bacilli in normal saline into the general circulation the effect of the dust reaction upon a tuberculous infection was found. The active dusts (siliceous) assisted the growth of the bacilli while the inert dusts (non-siliceous) in no way aided the establishment of the infection. Probably the most valuable part of Kettle's work was the discovery that a quartz dust which had been shown to be highly toxic was rendered completely innocuous by coating the dust with a thick layer of ferric oxide (the composition of the coated dust was - silica 59.9%, ferric oxide 40.1%). He suggested that the harmless quality of this treated dust arose from the inability of the silica to dissolve in the body fluids because of the surface coating. This finding further supported the postulate that the pathological changes resulting in a silicotic condition of lung tissue are initiated and controlled by the particular chemical properties of silica.

In 1933 Policard (14) observed that body cells are poisoned by dissolved silica, and that cells so treated do not disintegrate and disappear in the normal way, but preserve their structure in a manner which suggests mummification.

The pathogenic properties of silica were further investigated by Seigmund (15) in 1935, who showed that quartz particles when injected into the blood stream of rabbits are removed by the reticulo-endothelial cells, and are deposited according to their size in different tissues where they initiate characteristic tissue reactions, while colloidal silicic acid similarly administered produces fibrosis in the liver. In the same year Geise (16) observed that the intravenous injection of pure silica dust, having a particle size range 1-10  $\mu$  in diameter, caused nodular growths which resembled those found in silicosis in man; while calcite, clay or asbestos dusts introduced in a similar way did not produce changes characteristic of silicosis.

These results confirmed the findings of Kettle (13), that only siliceous dusts produced the nodular fibrotic conditions characteristic of silicosis, and left no doubt that some aspect of the individual chemical properties of silica controls the initiation and development of the pathological changes associated with the disease. Since dissolved silica had been shown (14) to be a tissue poison, it was suggested that the toxic properties of a siliceous dust were dependent upon the quantities of silica which the dust would yield

into solution in body fluids. Thus from the broad chemical conception developed the solubility theory of silicosis.

The modern solubility theory was the subject of extensive work by King (17). In general, his results supported this theory, the dusts producing dissolved silica at the greatest rates (quartz and flint) being the most pathogenic, whereas those mineral dusts yielding the least dissolved silica (shales and mica) are least harmful.

The solubility theory is further supported by the fact that the admixture of shale with a quartz dust lowers the solubility of the quartz, while, at the same time, such a mixture has been found to be markedly less pathogenic than the quartz dust alone. The treatment of shale dust with strong mineral acid has the effect of greatly increasing its silica solubility while such treatment has also been found to markedly increase its pathogenicity.

Further evidence in support of the solubility theory was provided by the work of Denny, Robson, and Irwin (18), who found that the development of silicosis, in animals exposed for long periods to a quartz laden atmosphere, could be prevented by the addition of small amounts of finely divided aluminium metal powder to the quartz dust. This finding was not substantiated by Belt and King (19) using an intratracheal injection technique by which a single dose of the dust is injected into the animals' lungs. King has suggested that the failure of the aluminium in the single dose tests was probably due to this metal being eliminated by the body, leaving the quartz dust in

the lung to continue its normal action.

This suggestion, that the failure of aluminium to affect the silicotic reaction was due to the method used in administering the dust, was borne out by the further work of King, Wright, Ray and Harrison (20) which supported the results of Denny *et al.* (18), and showed that in the lungs of rats, exposed to an atmosphere heavily laden with quartz dust, a retardation and possibly a prevention of the development of silicotic lesions could be achieved by the addition of 2% aluminium powder to the dust.

These results support the solubility theory of silicosis, since it was also shown by Denny, Robson and Irwin (18) that the presence of a small percentage of metallic aluminium in a quartz dust almost completely inhibited the solubility of the quartz. This was shown to be due to the adsorption of aluminium hydroxide on the quartz surfaces causing a depression of the solubility by preventing contact of the quartz and solvent. The aluminium adsorption was demonstrated by exposing quartz pebbles in distilled water to the action of metallic aluminium powder; after such contact, the pebbles could be stained pink with aurine tri-carboxylic acid, which is specifically adsorbed by aluminium hydroxide. These workers also demonstrated by X-ray diffraction that the adsorbed layer was composed of alumina.

The 'solubility' theory, however, does not always hold good, and King (17) quotes a number of contradictory cases; in one of these a finely divided silica, produced as a condensate in furnaces in which

silica sand is melted and designated 20 Angstrom<sup>"</sup> silica, was found to cause no fibrosis in the lungs of animals although it is highly soluble. Similarly, certain sandstone dusts having very low solubilities were found to be almost as pathogenic as quartz. King suggested that the innocuous nature of the 20 Angstrom<sup>"</sup> silica is due to its being quickly dissolved and eliminated from the body too rapidly for a fibrotic condition to become established.

The solubility theory, therefore, while it may be considered as a good general hypothesis, is not complete as it stands and King has suggested that this may be due to the difficulty of simulating body processes in vitro, and that although one siliceous dust dissolves less rapidly than another in solubility tests, this does not prove that it will behave similarly in the lung. It has been further suggested by King that the dissolved silica yielded by siliceous dusts, and determined in vitro, may not be identical with the poisonous material leached from similar dust particles in the lung. He has also suggested that there may be some particular form of dissolved silica, a "nascent" silica, which has the property of evoking in body tissue the characteristic fibrotic reaction of silicosis, and that the precise nature of the "nascent" silica has so far escaped detection by the chemical methods employed in solubility measurements.

The solubility theory of silicosis stimulated the study of the solubility of siliceous dusts and a number of workers (Briscoe and

Holt (21); Denny, Robson, and Irwin (18); King and McGeorge (22); Whitehouse (23) ) have carried out solubility tests on a large variety of siliceous dusts.

Earlier work was carried out by Lenher and Merrill (24) in 1917, with the object of estimating the losses incurred in the gravimetric estimation of silica. The values obtained by these workers for the solubility of finely divided silica were inaccurate since they had not the means at their disposal to effect an efficient separation of the suspended silica particles and the truly dissolved silica. Their results were high, being obtained by gravimetric estimation of the silica after passing the solution through a filter paper - a method which estimates suspended particulate matter in addition to the truly dissolved silica. These workers were aware of this difficulty and observed that:- "By this procedure what was measured was the amount of silica which had changed from an unfilterable to a filterable state of division, without regard as to whether the amount thus dissolved went into true solution or became the colloidal hydrogel of silicic acid".

In more recent work the ultracentrifuge and ultrafilter have been employed to obtain separation of the suspended particles from the dissolved silica. In addition, the Molybdenum Blue colorimetric method of silica analysis of Isaacs (25) and King (26) has now largely replaced gravimetric methods for the determination of small amounts of silica in solution. The basis of this method is the formation of

yellow silicomolybdic acid on the addition of ammonium molybdate to a silica solution under suitable pH conditions, and the reduction of this product to a blue complex by the addition of sodium sulphite and quinol solutions. The intensity of the blue colour produced under standard conditions is calibrated with the silica concentration.

King and McGeorge (22) have observed that the truly dissolved silica and some of the smaller colloidal particles react with the molybdate reagent of this colorimetric method and have accordingly named the material estimated "molybdic acid-reactible" silica, as distinct from the truly dissolved form.

In measuring the solubilities of a large variety of industrial siliceous dusts, King (27) used the Molybdenum Blue method and estimated the amounts of "molybdic acid-reactible" silica released; he suggested that since this type of silica acted as dissolved silica with the molybdate reagent, this was probably a fair estimation of the silica which was "biologically available" and so physiologically active.

When a pure silica dust is agitated with water an equilibrium condition is not reached in a reasonably short period of time and silica dust in dissolving does not form a simple monomolecular disperse system; the liquid phase contains particles ranging in size from large colloidal particles to simple ions. The comparison of the solubilities of two siliceous dusts is therefore made by measuring the dissolved silica liberated from these dusts after similar time periods.

Briscoe and Holt (21) have shown that the ratio of the mass of dust to the volume of solvent has an influence upon the solubility value obtained, and when comparative solubilities are required this ratio must therefore be kept constant.

The solubilities of siliceous mineral dusts in aqueous solvents are greatly affected by the impurity constituents. The effect of small amounts of aluminium has already been mentioned; and Denny, Robson, and Irwin (18) have shown that the presence of calcium hydroxide also decreases the solubility of quartz dusts, while small amounts of the carbonates or hydroxides of magnesium, sodium and potassium were found to enhance the solubility.

Because of the complex chemical nature of the siliceous mineral dusts inhaled by industrial workers, and the involved nature of the chemical composition of the body fluids bathing these dust particles in the lung, it would appear that a full understanding of the chemical processes involved in the development of silicosis must necessarily be preceded by the securing of fundamental physicochemical data on the solution and sorption phenomena of the dusts involved.

The present work was, therefore, initiated with the object of providing such basic data on the solubility mechanisms of simple siliceous dusts in aqueous solvents.

PART 1A High-Solubility Layer on Siliceous Dust Surfaces(a) Introduction

The first tests were designed to investigate the effect of pretreatment with various salt solutions, buffers, and acids, upon the solubilities of siliceous dusts. Evidence is adduced for the existence on siliceous dust surfaces of a high-solubility layer which has not hitherto been investigated, and the bearing of this layer upon dust solubility is discussed.

(b) Experimental1. Materials: source and preparation of dusts.

The dusts examined were prepared from the following five siliceous materials, identified in subsequent sections of this work by the letters quoted in parentheses (e.g. RC = rock crystal), followed in some cases by a number referring to a particular experimental batch.

(i) Rock Crystal. - Well-formed quartz crystals (length 1-5 cms.), specially selected for transparency and freedom from included foreign matter, were reduced to dust in a steel roller mill, a steel mortar, or an agate mortar. The particular tests to be performed dictated the method of grinding, since iron contamination introduced by the first two methods necessitated a subsequent purification by extraction with hydrochloric acid, and for certain experiments such treatment was undesirable. The products were separated, by sieving and sedimentation from water, into rock crystal dusts (RC), silica content 99.92 ( $\pm$  0.02)%

(ii) Silica sand. - A high-grade silica sand was used, as mined

from the 40-foot Upper Greensand bed at Loch Aline, Argyllshire, for the manufacture of optical glass. A typical sample as received contained ca. 99.6-99.7% silica and ca. 0.2% alumina, with traces of iron oxide, magnesia, titania and vanadia. Fractions of the desired particle size were prepared without grinding, by sieving and separation of "fines" by sedimentation from water, yielding Loch Aline sand dusts (LAS), silica content 99.85 ( $\pm$  0.03)%.

(iii) Fused amorphous silica. - The translucent grade of the commercial product Vitreosil (28) was ground in an agate mortar, and the powdered material sized by sedimentation from water, yielding Vitreosil dusts (VTL), silica content 99.8%.

(iv) Olivine (OL) and (v) orthoclase feldspar (OC), from Arendal, Norway (29) were ground in an agate mortar, and sized by sieving and sedimentation from water.

For all the above dusts, particle-size and distribution was estimated microscopically with the help of a calibrated graticule.

## 2. Conditions of Solution.

The amount of silica extracted from a siliceous dust by a solvent depends upon such factors as period of contact of solid and liquid phases, temperature, pH of solvent, specific surface area of dust, and the ratio of mass of dust to volume of solvent (21). To maintain analogy with conditions in vivo, all experiments were carried out at 37°C. (approximately normal body temperature), while the pH of body

fluids (30) was simulated by using as a solvent a borate buffer of pH 7.5, containing 11.16 g. of boric acid (Analar) and 1.81 g. of sodium borate decahydrate (Analar) dissolved in 1 litre of water.

The specific surface area of the dust and the mass/liquid ratio were kept constant in experiments where comparison of solubility values was desired. This ratio was generally 1:10, the usual amounts being 4 g. of dust in 40 ml. of solvent, though a few departures were made from this standard ratio, generally owing to shortage of dust of the desired type.

Solubility/time curves were obtained by maintaining all the above-mentioned factors constant, with the exception of the period of contact of dust and liquid. The dusts were agitated with the solvent in cellulose acetate tubes (capacity 50 ml.), thus eliminating errors attributable to the dissolution of silica from glassware. The tubes (Lusteroid brand) (31), closed with rubber stoppers, were continuously agitated by clipping to a shaft revolving (30 r.p.m.) inside an air-thermostat cabinet.

### 3. Separation of solid and liquid phases.

After the dust had been agitated with solvent for a measured time the tube was removed from the thermostat and the dust allowed to settle. All dusts used settled completely in less than one minute, and had average particle sizes between 100 and 400  $\mu$ ; the smaller particles (less than 50  $\mu$ ) had been completely removed by repeated sedimentation

during the preparation of the dusts. 25 ml. of the supernatant liquid was pipetted to another Lusteroid tube for the silica determination; if cloudy, it was first filtered through a Ford Sterimat filter pad (Grade SB) (32). This procedure was found to have no effect upon the amount of silica which in any given solution would react with ammonium molybdate in the method of analysis described below.

#### 4. Estimation of silica in solution.

(i) General. The method employed for estimating the amount of silica in solution was a modification of the Molybdenum Blue colorimetric method of Isaacs (25), King (26), and Harrison and Storr (33). An investigation of this method and its subsequent modification for use in the present work is described in the Appendix p.109.

The method is based upon the reaction of silica with ammonium molybdate at suitable pH values to form the yellow silicomolybdic acid. Reduction of this yellow acid produces a blue colour, the intensity of which, when produced under standard conditions, may be calibrated against silica concentration.

(ii) Preparation of reagents. The following standard reagents were employed.

A. 5% Ammonium molybdate solution. 20 ml. of 6N  $H_2SO_4$  is added with stirring to a filtered solution of 6 g. of ammonium molybdate ( $(NH_4)_6 Mo_7 O_{24} \cdot 4H_2O$ ) (Analar) in 100 ml. of distilled water.

B. Reducing solution. 6 g. of sodium sulphite ( $Na_2SO_3 \cdot 7H_2O$ )

(Analar) and 1 g. of hydroquinone are dissolved in 50 ml. of distilled water.

(iii) Method. 25 ml. of the silica solution to be estimated is pipetted into a Lusteroid tube, and to this is added 18 ml. of distilled water (total volume 43 ml.). 2 ml. of solution A is added. The solution is stirred with a cellulose acetate spatula for 30 seconds and the yellow colour of silicomolybdic acid is then allowed to develop for a further 4.5 minutes. When this development is complete 5 ml. of solution B is added, the mixture is again stirred for 30 seconds, and the resulting blue colour allowed to develop for 30 minutes. The intensity of the fully developed colour is finally measured by an EEL Colorimeter (34) using a red filter (Ilford No. 608).

(iv) Accuracy. For maximum accuracy, it is essential to adhere strictly to standard development times; and this becomes difficult when a series of estimations, each involving addition of reagent followed by mixing, must be made almost simultaneously. It was found satisfactory to measure out all reagents into a series of tubes equally spaced in a rack, so that they could be added simultaneously to a number of solutions to be estimated. The solutions were stirred by a series of correspondingly-spaced spatulas fixed comb-wise to a holder. This technique much increased the accuracy of the method for rapid estimation of silica in solution.

Preliminary light absorption measurements with Spekker and EEL

absorptiometers showed that readings were made more rapidly with the latter; hence, for the reason outlined above, the latter instrument was used throughout. Since the EEL colorimeter has a logarithmic scale, the overall accuracy of the method depends upon the part of the scale on which a reading falls. Maximum accuracy ( $\pm 2.0\%$ ) was obtained at scale readings between 30 and 60.

(v) Calibration curves. These were obtained by adding measured volumes of a silica solution of known concentration to 25 ml. of borate buffer solution, diluting to 43 ml. with distilled water, and adding reagents A and B as described above. The standard silica solution was prepared by fusing a weighed amount of finely-ground quartz with sodium carbonate in a platinum crucible. The cooled melt was dissolved in distilled water, neutralised with sulphuric acid, and diluted to known volume.

(vi) Units. Solubilities are expressed throughout as the concentration of the silica solution produced under the experimental conditions (mg. silica/100 ml. solution).

### (c) Discussion of Results

#### 1. The effect of various pretreatments on the solubility of siliceous dusts.

King (27) has shown the solubility of quartz dusts to be depressed at pH ca. 7, but not at markedly higher or lower pH, by addition of aluminium powder to the system. He concluded that this was due to formation of a protective layer of alumina on the quartz

surface, and correlated the variation in protective action on change of pH with the amphoteric properties of alumina.

The object of the following experiments was to investigate the action of various salts upon the solubility of silica. The silica dusts LAS(1) and RC(1) were pretreated by agitation under standard conditions with solutions of various salts, washed for 5 minutes, dried, and their subsequent solubilities in borate buffer solution determined. Since the period of washing was negligibly small compared with the subsequent solubility tests, it may be assumed that the former treatment made no significant contribution to the effects observed. Any contribution will, in any event, be constant throughout, all samples being washed for the same period of time. The effect of various pretreatments is shown in Tables 1-3.

It appears from Table 1 that pretreatment by solutions of iron and aluminium salts depresses the silica solubility; but, as may be seen from Table 2, pretreatment with tap water alone reduces the solubility almost as much as the salt solutions, and in some cases even more. Table 2 also shows that the solubility of the dust after pretreatment actually increases with increasing aluminium ion concentration; e.g., after pretreatment with M/80 aluminium sulphate solution the solubility was 0.60 mg./100 ml., while with M/10 aluminium sulphate the value was raised to 0.71 mg./100 ml. No correlation was found between the concentrations of the various salt solutions and their effects upon the solubility of the dust; but it

TABLE 1

Solubility of LAS(1) in borate buffer (pH 7.5) after 68 hrs. at 37°C;  
mass/liquid ratio, 6 g./60 ml.

(Pretreatment period, 17 hrs. at 37°C:mass/liquid ratio, 20 g./40 ml.)

<u>Pretreatment Solution</u>	<u>mg./100 ml.</u>
2.5% Ferrous ammonium sulphate	1.70
5.0% " " "	1.67
2.5% Aluminium sulphate	1.22
5.0% " " "	1.27
UNTREATED	2.40
	0.45
	0.48
	0.62
	0.73
	0.85
	0.34
	0.31
	0.35
UNPRECIPITATED	0.74
	1.76

TABLE 2

Solubility of RC(1) and LAS(1) in borate buffer (pH 7.5) after 48 hrs.  
at 37°C; mass/liquid ratio, 4 g./40 ml.

(Pretreatment period, 24 hrs. at 37°C; mass/liquid ratio, 10 g./40 ml.)

<u>Pretreatment solution</u>	<u>pH</u>	<u>RC(1)</u> <u>mg./100 ml.</u>	<u>LAS(1)</u> <u>mg./100 ml.</u>
M MgSO <sub>4</sub>	6.02	0.53	0.55
M/2 MgSO <sub>4</sub>	-	0.51	-
M Sr(NO <sub>3</sub> ) <sub>2</sub>	6.08	0.30	0.51
M/2 Sr(NO <sub>3</sub> ) <sub>2</sub>	-	0.29	-
M BaCl <sub>2</sub>	3.74	0.51	-
M/2 BaCl <sub>2</sub>	-	0.43	-
M/10 Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	3.49	-	0.71
M/20 "	3.62	-	0.67
M/40 "	3.73	-	0.66
M/80 "	3.85	-	0.60
Tap Water	6.34	0.31	0.63
<b>UNTREATED</b>	-	<b>0.74</b>	<b>1.38</b>

The solubility of RC(1) and LAS(1) in borate buffer (pH 7.5) after 48 hrs. at 37°C; mass/liquid ratio, 4 g./40 ml.

See also the discussion of Results, Section 5.

TABLE 3

Solubility of LAS(1)\* in borate buffer (pH 7.5) after 48 hrs. at 37°C;  
 mass/liquid ratio 4 g./40 ml.  
 (pretreatment period, 24 hrs. at 37°C; mass/liquid ratio, 4 g./40 ml.)

<u>Pretreatment solution</u>	<u>pH</u>	<u>mgs./100 ml.</u>
N/20 Acetic acid	3.02	1.15
" Propionic acid	3.12	1.10
" n-Butyric acid	3.05	1.20
" n-Valeric acid	3.08	1.12
" n-Caproic acid	3.07	1.03
" Sulphuric acid	1.50	1.23
" Hydrochloric acid	1.40	1.23
" Nitric acid	1.39	1.19
Distilled water	5.48	0.74
UNTREATED	-	1.07

\*Same LAS(1) dust as in Table 2, but examined 3 months after preparation. For reasons underlying the decrease in solubility (untreated), see Discussion of Results, Section 3, p. 33.

was observed that the solutions of highest pH depressed the solubility to the greatest extent.

Table 3 summarises the observed changes in solubility brought about by the pretreatment with solutions containing different anions. Pretreatments with organic acids all have approximately the same effect, the solubility of the pretreated dusts being substantially independent of progressively larger anions. The inorganic acids also produce similar results, but increase the solubility more than the organic acids. Depression in solubility might formally be ascribed to either (i) the building up of a barrier-layer of low solubility, or (ii) the removal of a layer of high solubility. The first of these effects could be produced by adsorption on the particle surfaces; but the results described above, coupled with the depression of solubility by distilled water alone, point to the pH of the pretreatment medium as the controlling factor, rather than to salt concentration as such. It follows, therefore, that under the conditions described, depression of silica dust solubility is not brought about by adsorption, which would be affected by concentration changes; and the experimental evidence which follows supports the alternative explanation - namely, the existence on siliceous dust particles of an outer layer of higher solubility than the interior.

## 2. Effect of pH on silica dust solubility.

Since the pH of the pretreatment solution appeared to be the

factor controlling the solubility of silica, its effect was further investigated by preparing a series of buffer solutions varying in pH over the range 2-11 and using these for pretreatment in the way already described. The buffers with pH 2-10 were prepared according to Clark (35) and that with pH 11 from the Universal buffer mixture of Frideaux and Ward (36).

The results of these experiments are shown in Fig. 1, where the three curves represent the variation of dust solubility in a borate buffer (pH 7.5) on changing the pH of the pretreatment solution, for Loch Aline sand dusts prepared in three different ways. The horizontal datum lines represent the solubility level of the various dusts before buffer treatment. The change in solubility brought about by treatment of the dust by a buffer solution at any given pH is therefore measured by the appropriate vertical distance from each datum line to its corresponding curve. The results may be summarised as follows.

(i) For dust LAS(5), prepared as in the Experimental section p.17 it is seen (Curve A) that pretreatment with acidic buffer solutions (pH<4) increases the solubility of the dust, the curve here lying above its datum line, whereas pretreatment with buffers of pH>4 decreases the solubility.

(ii) A similar effect is shown (Curve B) by a dust LAS(5)A prepared by treating a quantity of dust LAS(5) for 4 hours with cold concentrated hydrochloric acid. The datum line for LAS(5)A lies

LAS(S)B DATUM LINE

- △ LAS(S)
- LAS(S)A
- LAS(S)B

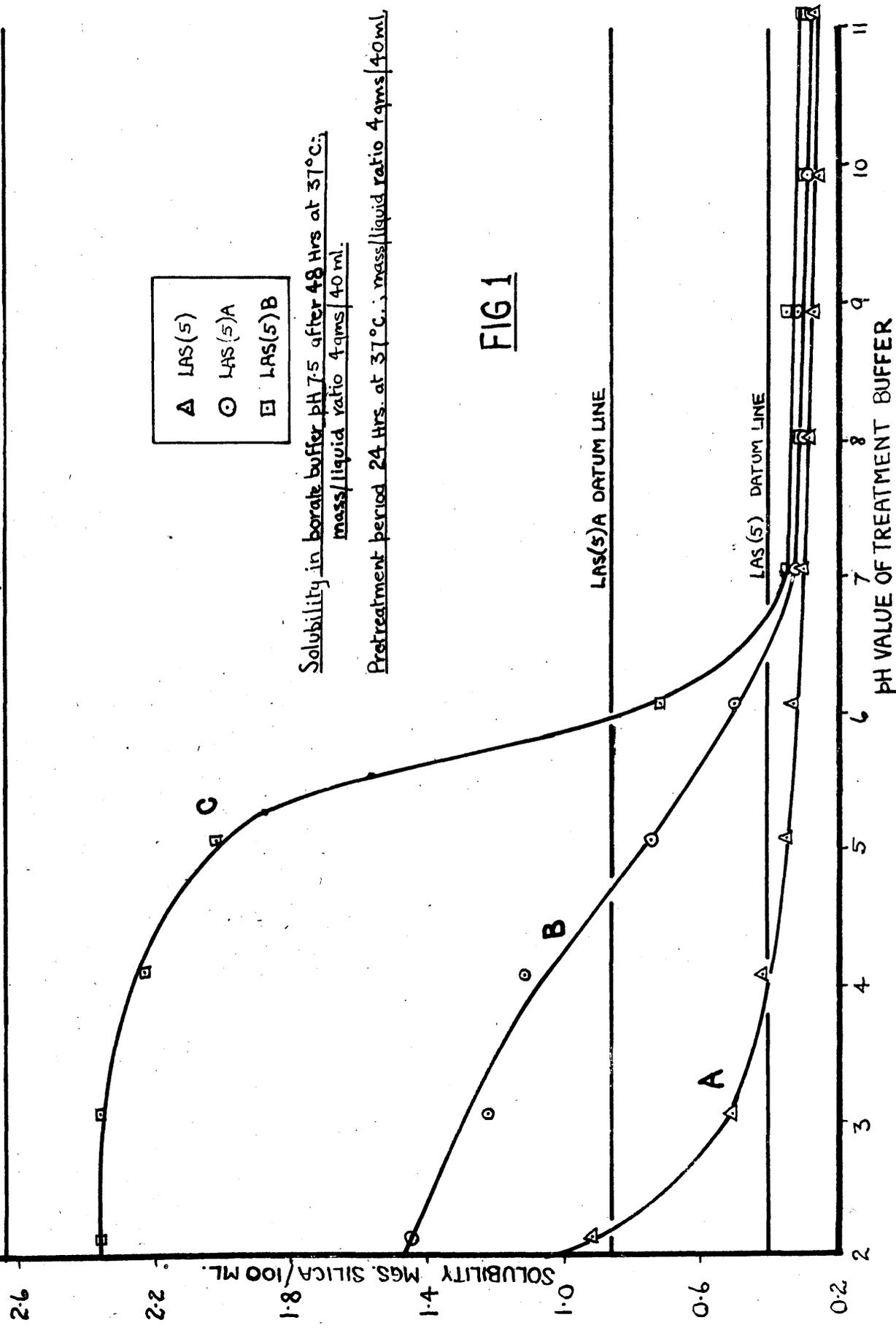
Solubility in borate buffer pH 7.5 after 48 Hrs at 31°C;  
mass/liquid ratio 4gms/40 ml.

Pretreatment period 24 Hrs. at 31°C.; mass/liquid ratio 4gms/40 ml.

FIG 1

LAS(S)A DATUM LINE

LAS(S) DATUM LINE



above that for LAS(5), showing that acid treatment during preparation of the dust has raised its solubility. Here, the more alkaline buffer treatments ( $\text{pH} > 5$ ) have depressed the solubility of the dust much more in absolute terms than for Curve A, but the final solubility is virtually the same for both dusts - ca. 0,3 mg./100 ml.

(iii) The dust LAS(5)B was prepared by treating a quantity of LAS(5) for 1 hour with hot and for 20 hours with cold concentrated hydrochloric acid; and this more vigorous treatment has raised still further the datum line corresponding to Curve C. Treatment of LAS(5)B with even the most strongly acid buffer has here brought about no increase in the solubility of the dust, the curve lying completely below its datum line, but alkaline buffer treatment ( $\text{pH} > 7$ ) has again depressed the solubility to the same minimum value - ca. 0.3 mg./100 ml.

### 3. Existence of a high-solubility layer on siliceous dusts.

The curves in Fig.1, and the earlier salt-treatment experiments, clearly suggest the existence of different solubility rates in the silica itself. It was, therefore, postulated that there exists on the surface of the silica particles a layer of silica which has a much higher solubility rate than that lying immediately beneath it. This high-solubility layer (hereafter designated the HS layer) is developed on Loch Aline sand surfaces by acid treatment and dispersed by the alkaline reagents employed.

The distances between the datum lines of Fig.1 show how the

concentrated hydrochloric acid treatment in the preparation of the dusts LAS(5)A and LAS(5)B has developed the HS layer, which is subsequently dispersed by alkaline buffer treatment, bringing all three dusts to a common solubility level. The flat portions of the curves (pH 7-11) represent complete dispersion of the HS layer, whereas the curved portions (pH<7) show the relative partial success of different buffer treatments in dispersing it. The intersection of each curve with its datum line may be regarded as the point of equilibrium between further development of the HS layer and its dispersion.

Based on this postulate, and in view of its value in explaining the solubility phenomena so far described, further experiments were devised to ascertain whether the existence of the HS layer could be demonstrated by extractive solubility methods - that is, by renewing the solvent at the end of each of a number of consecutive solution periods, so that during each such period the dust has substantially constant conditions for dispersion. If each dust particle were entirely homogeneous it should yield the same amount of silica into solution during each extraction period, assuming that all particles are so large that there is no possibility of the smaller ones being leached out entirely. To satisfy this requirement the dusts employed had all particles of diameter  $< 50 \mu$  removed by repeated sedimentation. All the particles of the dusts used were between 50 and  $400 \mu$  in diameter. Rock crystal dust RC(5) was prepared by

grinding selected crystals in an agate mortar, sedimenting from distilled water to obtain the desired particle size (50-250  $\mu$ ), and drying at 120°C.

Double-distilled water was the solvent, prepared with a tin condenser, collected in a glass jar, and stored in an Alkathene bottle. Agitation of the dust with the solvent was again carried out in Lusteroid tubes to avoid contact of the solution with glass. New calibration curves were prepared, using double-distilled water in place of borate buffer, since the change in solvent affects the development of the blue colour in the method of analysis described in the Experimental Section p.20 .

The results summarised in Table 4 show the dissolution of an HS layer in the 1st Solution Period. Particular care was taken to exclude all impurities, in order to avoid possible inactivation of the dust surface by gradual adsorption with resultant depression of the solubility. These results, obtained under stringent conditions of purity, coupled with the fact that no correlation was found between depression of solubility and salt concentration in the pretreatment solutions (Tables 1-3), support the present postulate - namely, that the decrease of solubility rate with time observed in extractive solubility experiments is due not to adsorption on the silica surfaces but, in fact, to the existence of a surface layer on the silica dust particles with a much higher solubility rate than that of the underlying material.

**TABLE 4**

**Extractive solubility of RC(5) in double-distilled water at 37°C;  
mass/liquid ratio, 4 g./40 ml.**

<u>Solution Period.</u>	<u>mg./100 ml.</u>
1st (24 hrs.)	0.30
2nd (24 " )	0.18
3rd (24 " )	0.16
4th (24 " )	0.14
5th (24 " )	0.10
6th (72 " )	0.29

As observed, from results obtained for the solubilities of the Loch Alinne sand dusts LAS(N)H and LAS(S)E over a period of two months, that the initial solubilities of these dusts in human lung solution decreased progressively with time of storage (Fig. 2).

LAS(N)H was prepared by sedimenting the natural Loch Alinne sand fine water to remove the small particles, followed by drying at 100°C. in an air oven. A portion of this dust was extracted with concentrated hydrochloric acid, washed with water, and similarly dried, to produ-

These conclusions were further supported by extractive solubility tests on Loch Aline sand dusts LAS(1) and LAS(3) and rock crystal dust RC(1) in borate buffer solutions. The results (Table 5) again show a high initial solubility rate corresponding to the dispersion of the outer surface of the dust particles.

It may be seen from Table 5 that Loch Aline sand dust LAS(3) which has been extracted with hydrochloric acid shows a higher initial solubility rate than the untreated dust, indicating development of the HS layer on the former. After the 1st Solution Period, however, both treated and untreated dusts exhibit the same solubility rates - an effect already noted in Fig.1, where the solubilities of LAS(5), LAS(5)A, and LAS(5)B are brought to a common level of ca. 0.3 mg./100 ml. by alkaline buffer treatment. This effect may be interpreted as complete removal of the HS layer.

It was observed, from results obtained for the solubilities of two Loch Aline sand dusts LAS(3)U and LAS(3)E over a period of two months, that the initial solubilities of these dusts in borate buffer solution decreased progressively with time of storage (Fig.2). LAS(3)U was prepared by sedimenting the natural Loch Aline sand from water to remove the small particles, followed by drying at 120°C. in an air oven. A portion of this dust was extracted with concentrated hydrochloric acid, washed with water, and similarly dried, to produce dust LAS(3)E. These dusts were stored in stoppered bottles at room temperature.

TABLE 5

Extractive solubility of LAS(3), RC(1), and LAS(1) in borate buffer (pH 7.5) at 37°C; mass/liquid ratio, 4 g./40 ml.

<u>Solution Period</u>	<u>RC(1):mg./100 ml.</u>	<u>LAS(3):mg./100 ml.</u>	
	<u>HCl extracted.</u>	<u>Untreated</u>	<u>HCl extracted</u>
1st (24 hrs.)	0.84	0.34	0.59
2nd (24 hrs.)	0.20	0.25	0.25
3rd (72 hrs.)	0.41	0.53	0.51
4th (72 hrs.)	0.32	0.39	0.35

<u>Solution Period</u>	<u>LAS(1):mg./100 ml.</u>
	<u>HCl extracted</u>
1st (24 hrs.)	0.95
2nd (24 hrs.)	0.29
3rd (24 hrs.)	0.21
4th (72 hrs.)	0.31
5th (72 hrs.)	0.24

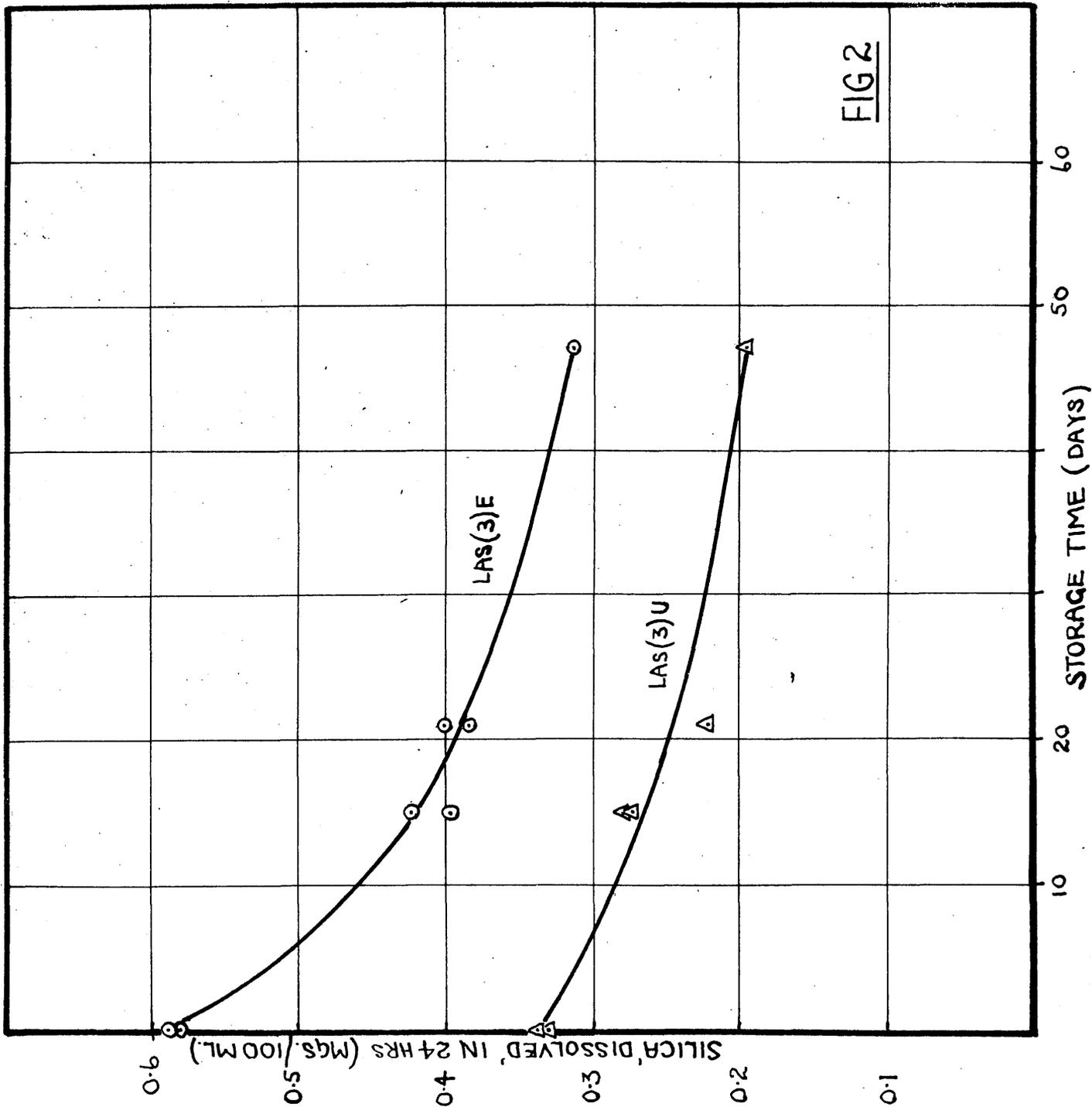


FIG 2

This decreasing solubility on storage may be explained by the gradual inactivation of the surface of the dust by adsorption of gases from the air; and it was at first thought that the high solubility rate of the surface of a dust might be due to reaction of the solvent with freshly formed surfaces which had not had time to become inactivated by adsorption of gases from the air. Attempts to regenerate the HS layer on material from which it had been removed by solution, might therefore be expected to yield some information on its nature. Dust from which the layer had been removed was dried or heated with the object of freeing the surface from adsorbed liquids or gases; but such treatment was found to have no effect in producing a new HS layer, as is shown by the results summarised in Tables 6 and 7.

Further information on the nature of the HS layer was, however, obtained from experiments on the effect of acid treatment on the solubilities of Loch Aline sand and rock crystal dusts (Tables 8 and 9).

Acid treatments were found to increase the initial solubility rate of Loch Aline sand, but to lower the initial solubility rate of rock crystal dusts (Tables 3, 5, 8 and 9).

To investigate this difference more fully, the following experiments were carried out to determine the effect of acid treatment on portions of these dusts from which the HS layer had been previously removed.

TABLE 6

Extractive solubility of LAS(1), LAS(3)U, and LAS(3)E in borate buffer (pH 7.5) at 37°C; mass/liquid ratio, 4 g./40 ml.

<u>Solution Period</u>	<u>LAS(1)</u> <u>mg./100 ml.</u>	<u>LAS(3)U</u> <u>mg./100 ml.</u>	<u>LAS(3)E</u> <u>mg./100 ml.</u>
1st (24 hrs.)	0.77	0.28	0.41
2nd (24 hrs.)	0.30	0.19	0.24
*3rd (24 hrs.)	0.20	0.17	0.18

---

\*Dust dried in silica crucibles in air-thermostat at 37°C for ca. 24 hrs. and heated for 1-5 hrs. at 625°C at end of 2nd Solution Period.

\*Dust dried in nitrocellulose at 37°C for 24 hrs. at end of 2nd Solution Period.

TABLE 7

Extractive solubility of LAS(3)U and LAS(3)E in borate buffer (pH 7.5) at 37°C; mass/liquid ratio, 4 g./40 ml.

Solution Period	<u>LAS(3)U</u> <u>mg./100 ml.</u>	<u>LAS(3)E</u> <u>mg./100 ml.</u>
1st (24 hrs.)	0.34	0.59
2nd (24 hrs.)	0.25	0.25
3rd (72 hrs.)	0.53	0.51
4th (72 hrs.)	0.39	0.35
5th (96 hrs.)	0.43	0.39
6th (96 hrs.)	0.35	0.34
*7th (96 hrs.)	0.26	0.26

---

\* Dust dried in air-thermostat at 37°C for ca. 24 hrs. at end of 6th Solution Period.

TABLE 8

Solubility of LAS(2) and RC(2) in borate buffer (pH 7.5) after 48 hrs. at 37°C; mass/liquid ratio, 4 g./40 ml.

(Pretreatment period 20 mins. at room temperature; mass/liquid ratio, 20 g./50 ml.)

<u>Pretreatment Solution.</u>	<u>LAS(2):mg./100 ml.</u>	<u>RC(2):mg./100 ml.</u>
Conc. HCl	0.62	0.37
Conc. HNO <sub>3</sub>	0.63	-
Conc. H <sub>2</sub> SO <sub>4</sub>	0.94	-
UNTREATED	0.48	0.67

**TABLE 9**

**Extractive solubility of RC(8) in borate buffer (pH 7.5) at 37°C.**

<u>Solution Period</u>	<u>RC(8):mg./100 ml.</u>	
	<u>Untreated</u>	<u>HCl extracted</u>
1st (48 hrs.)	0.71	0.55
2nd (89 hrs.)	0.46	0.42
3rd (48 hrs.)	0.16	0.15

After the first 48 hr. period the solubility rates of the rock crystal dust were increasing only very gradually, indicating that layers have been removed from the dust surface during the first period. The acid treatment is shown to have the effect of increasing the rate of solution of Loch Aline acid surfaces; on the other hand, the solubility of the rock crystal dust showed no measurable change, whereas the previous results (Tables 3, 5, 8 and 9) had indicated a decrease in solubility with acid treatment. The effect in Fig. 3 of this lowering effect was presumably due to the HCl having been removed during the first solution period.

Extractive solubility tests were carried out on two dusts, Loch Aline sand LAS(5), and rock crystal RC(8). The first solution period was of 25 days duration, and those following were each for shorter times varying from 3 to 14 days. The total amounts of silica which had been dissolved from the dusts at the end of each solution period were plotted against the time from the start of the tests.

At the end of the third period the dusts were washed free from buffer solution by repeated water sedimentation and each dust was agitated for 3 days at 37°C. with 40 ml. of 2N sulphuric acid. After this treatment the dusts were washed free from acid, borate buffer solvent was added, and the extractive solubility tests continued. The results are plotted in Fig. 3.

After the first solution period the solubility rates of the dusts are shown to be decreasing only very gradually, indicating that the HS layers have been removed from the dust surfaces during the first period. The acid treatment is shown to have the effect of increasing greatly the rate of solution of Loch Aline sand surfaces; on the other hand, the solubility of the rock crystal dust showed no measureable change, whereas the previous results (Tables 3, 5, 8 and 9) had indicated a decrease in solubility with acid treatment. The absence in Fig. 3 of this lowering effect was presumably due to the HS layer having been removed during the first solution period.

The increase in the solubility of the Loch Aline sand dust with acid treatment is in effect the production of a new HS layer which

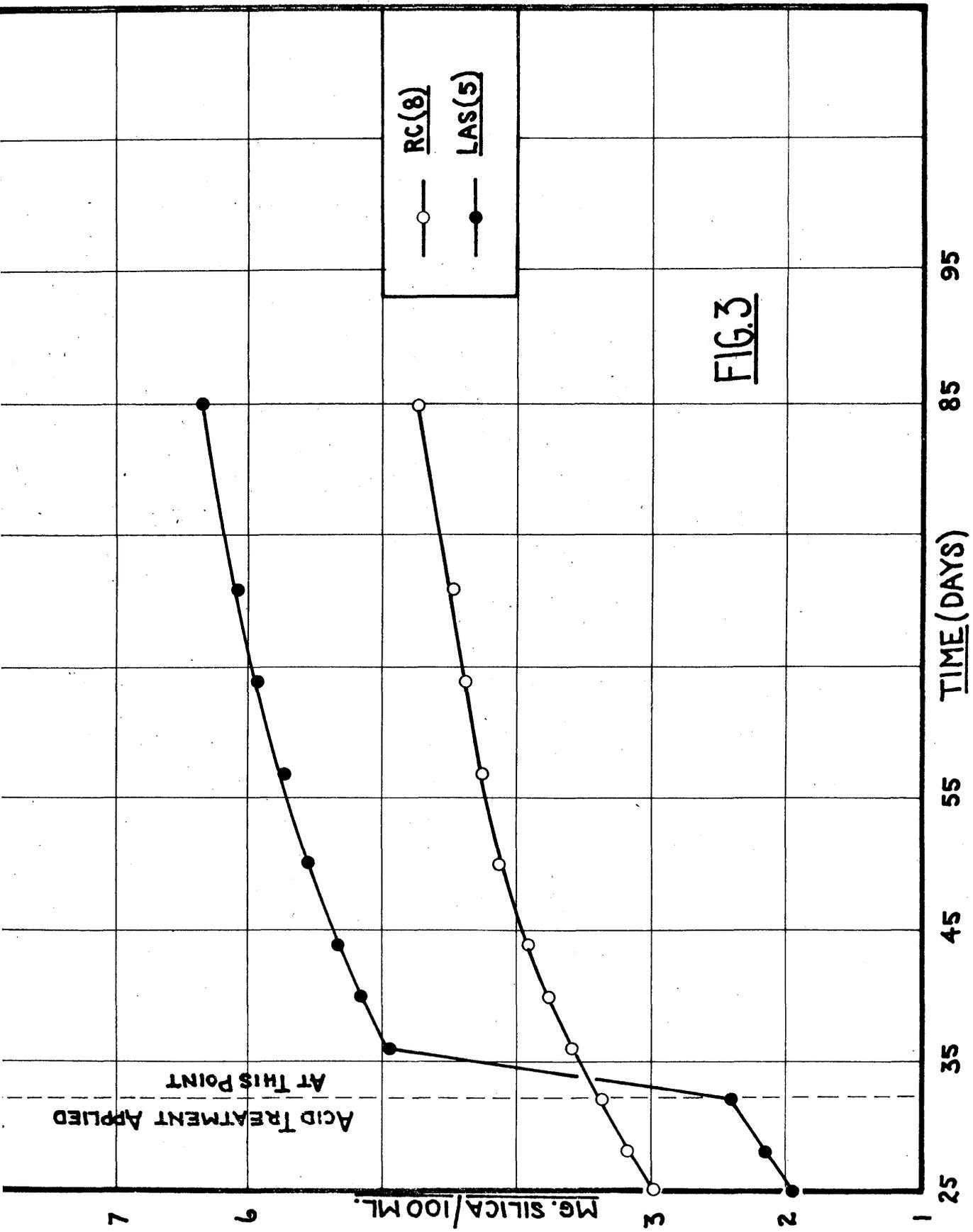


FIG. 3

ACID TREATMENT APPLIED AT THIS POINT

RC(8)  
LAS(5)

Mg. SILICA/100 ML. TIME (DAYS)

was completely dispersed during the fourth solution period. It is noted, however, that there is as yet no evidence that the regenerated HS layer and that existing on the original dust surfaces are identical in physical nature.

The natural Loch Aline sand, though of high silica content (99.8%), may nevertheless be regarded as relatively impure when compared with selected pieces of rock crystal, which is the purest obtainable form of crystalline quartz. The fact that analogous siliceous crystal surfaces may react quite differently to the same chemical treatment may be connected with the presence of minor traces of impurities in one of them, though this cannot be given categorically as the reason.

The effect of acid treatment on the solubility of another siliceous dust obtained from natural sources as a corollary to this last result was investigated. This silica dust, DRC, is produced commercially (37) by grinding rock of high silica content, from Coed Talon, North Wales; it has an average particle size of  $1\ \mu$  (calculated from specific surface area as measured by the Lea and Nurse (38) method) and contains ca. 7% of impurities (iron, aluminium, and magnesium, estimated as oxides).

The solvent used was Palitzsch's buffer solution (pH 7.4) prepared by mixing 200 ml. of M/20 sodium borate solution with 1800 ml. of M/5 boric acid, sodium chloride solution (12.404 g.  $H_3BO_3$  and 2.925 g. NaCl in 1 litre). This experiment was carried out at an

early stage of the present work. In all other experiments described in this work, it was found more convenient to use a simple borate buffer, free from sodium chloride (Experimental Section, p.19 ).

To prepare an acid-extracted sample of the dust for comparative solubility tests, 5 g. of dust was treated with boiling concentrated hydrochloric acid for 20 minutes; the suspension was then diluted and filtered through two thicknesses of filter paper (W.S.R. Balston, No. 1, 11 cm.). The dust which passed through the paper into the filtrate was neglected and the filtered material was washed repeatedly and dried at 100°C.

Since the particle size of this dust is much less than that of the others used in the present work, extractive solution tests were not employed because of the difficulty of renewing the solvent without loss of dust. 0.25 g. portions of untreated and acid-extracted DRG dusts were agitated for different periods at 37°C., each portion with 25 ml. of Palitzsch's buffer, and at the end of each period the amount of silica dissolved was estimated after filtration through a Ford Sterimat filter pad (Grade SB). The times normally allowed for development of the yellow and blue colours in the Molybdenum Blue method of silica analysis (Experimental Section, p. 20 ) were modified for the estimations in Palitzsch's buffer solution (Appendix p. 109) since the presence of chloride ion in the latter affects the rate of development of these colours. The modified development times used for the yellow and blue colours were 15 minutes and  $2\frac{1}{2}$  hours

respectively. The results are plotted in Fig. 4, which shows that acid treatment increased the solubility of the dust many times. The loss of a large number of small particles from the extracted dust during filtration, as mentioned above, serves to emphasise this effect, since their retention would presumably have increased the difference in the solubilities.

#### 4. Properties of the High-Solubility Layer.

(i) 'Dissolved', 'colloidal' and 'total' silica. - In the extractive solubility experiments it was noted that much colloidal silicic acid appeared as a turbidity during the first few solution periods. To investigate the origin of this material, and in particular its possible derivation from the HS layer, its total amount and rate of formation were determined by extractive solution in borate buffer at 37°C. It was first of all necessary to devise a method of distinguishing between dissolved and colloidal silica, and, indeed, to define these terms satisfactorily; and a convenient basis for this is provided by the work of King and McGeorge (22), who have shown:

- (a) That ultracentrifuging a silica dispersion does not sediment silica which reacts with ammonium molybdate reagent (used in the Molybdenum Blue colorimetric determination of silica), and
- (b) that ultrafiltration of silica solutions, by pressure through cellophane membranes, removes a proportion of

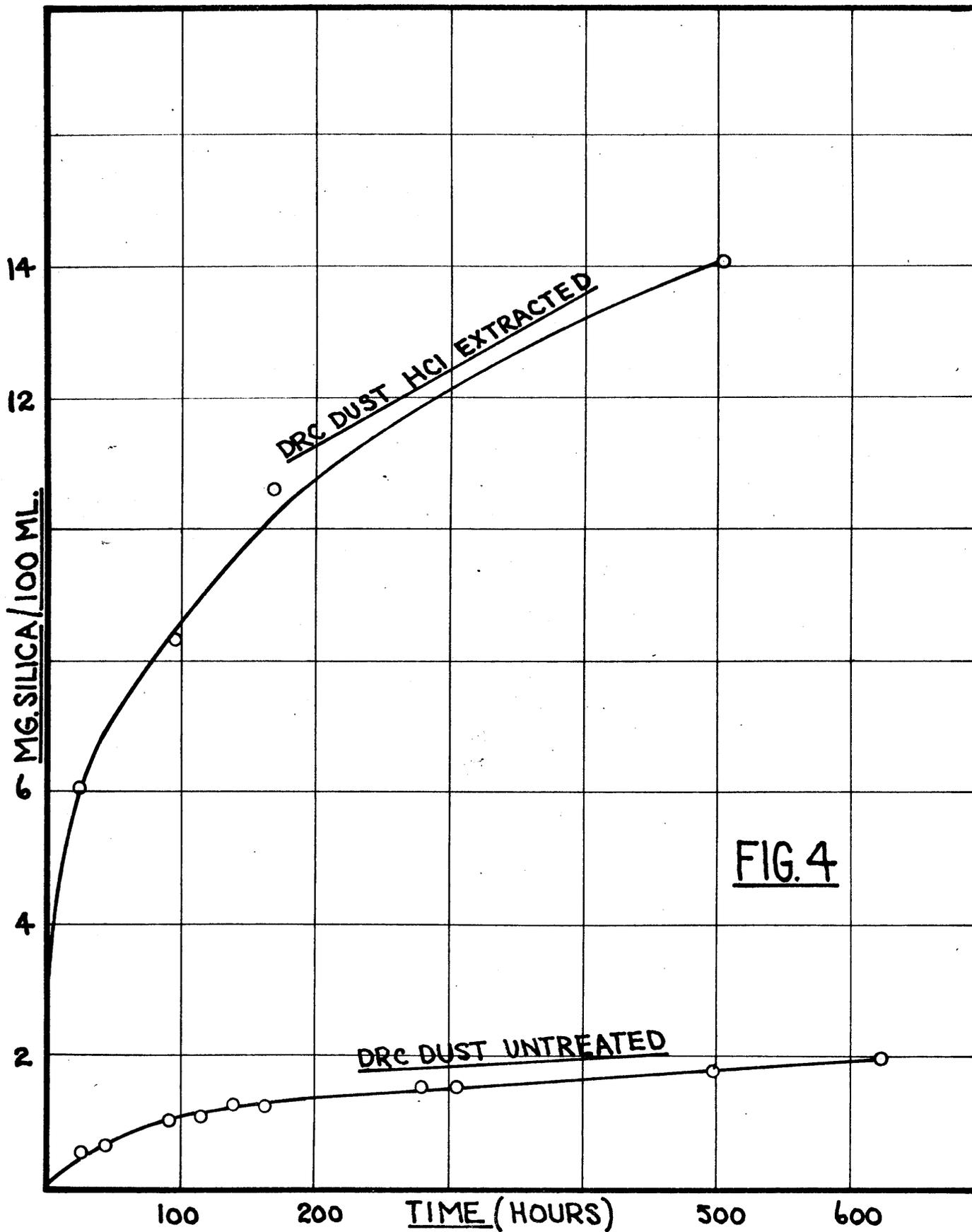


FIG. 4

the silica which reacts with ammonium molybdate.

This demonstrates that ammonium molybdate reacts with silica in true solution, and with very small particles of colloidal silica, but not with the larger particles which may be sedimented by ultracentrifugal methods.

It has now been observed that turbid colloidal suspensions of silica may be rendered crystal-clear to the naked eye by filtration through Ford Sterimat filter pads (Grade SB), and that the colloidal material thus removed is not "ammonium molybdate reactive" (hereafter contracted to AMR). Repeated passage of clear solutions of silica in borate buffer through these filter pads was found to have no effect on the AMR silica content of the solutions; and, since the pads permit a high rate of filtration, they may advantageously be used in separating fine solid particles, the technique being much simpler and faster than ultracentrifugal sedimentation.

In the following work, silica will be considered as dissolved if it is of sufficiently small particle size to react with the ammonium molybdate reagent under the analytical conditions previously described. The difference between total silica in a suspension and dissolved (AMR) silica provides a measure of colloidal silica. The following method has been developed for determination of total silica in borate buffer solutions, its basis being the conversion of all the silica in a dispersion into a form reactive with ammonium molybdate, followed by the colorimetric determination previously described.

5 ml. of the colloidal suspension of silicic acid in borate buffer solution is evaporated to dryness in a platinum crucible in an oven at 110°C. The residue, consisting of silica, boric acid and sodium borate, is heated gently at first to drive off water from the acid and sodium salt. The anhydrous material is then heated strongly over a Meker burner for 5 minutes, when the silica is dissolved by the molten sodium borate. The crucible is cooled and the anhydrous mass dissolved in about 10 ml. of distilled water. This solution is transferred to a measuring cylinder and made up to 43 ml. with distilled water. The silica solution thus obtained is crystal-clear to the naked eye and is then estimated by the colorimetric method. Calibration curves must, of course, be prepared using 5 ml. of borate buffer instead of 25 ml. as described previously.

(ii) Extractive solubility experiments. - The known effect of aluminium in depressing the solubility rate of silica dusts (18) was shown by extractive solubility tests carried out on two dusts, Loch Aline sand LAS(5), and rock crystal RC(8). A series of solution periods carried out in duplicate were interrupted after 57 days from the start of the tests and 2% aluminium metal turnings was added to one of the duplicates employed for each dust. After this addition the solubility tests were continued and the depressive effect on the solubilities of the addition of the metal is shown from the results in Fig. 5.

The solubilities of three siliceous dusts and the depressive

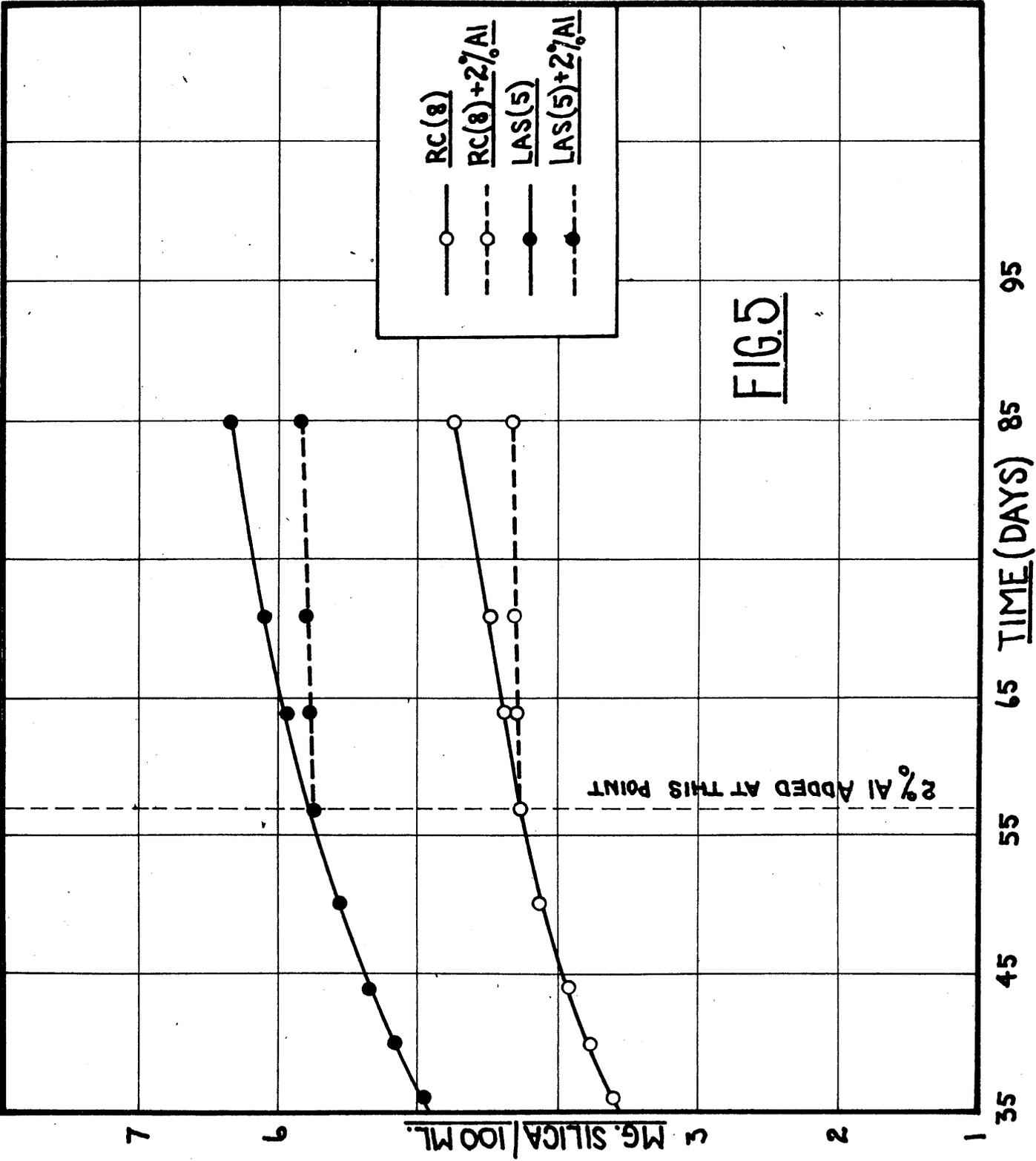


FIG. 5

effect of aluminium were studied in more detail by extractive solubility experiments carried out with rock crystal dust, RC(11)1; Loch Aline sand dust, LAS(5); and fused amorphous silica dust, VTL 2. The total and AMR silica contents of solutions were estimated after each of a series of solution periods; and in each case parallel tests were carried out with the addition to the dust of 2% of its weight of fine aluminium turnings (thickness ca. 0.025 mm.). The results are summarised in Figs. 6-9.

The total silica released into solution from all three dusts is much greater than the AMR silica, though the curve-gradients show that the final steady rates of solution do not differ greatly. The difference is due to the dispersion of a large amount of colloidal silica in the initial solution periods. This may be seen most clearly from Fig. 9, where the initial rate of production of colloidal silica is high, but has fallen after 15 days to a very low value. It seems highly probable that this initial high yield of colloidal silica is due to dissolution of the HS layer.

Addition of metallic aluminium showed similar effects with all three dusts, the limiting value of colloidal silica being reached more rapidly and its total amount reduced considerably. The effect of metallic aluminium on the balance between colloidal and AMR silica in a dispersion was investigated; and it was shown that when a dispersion containing both forms was shaken for 4 days with the metal turnings there was no alteration in the AMR silica content

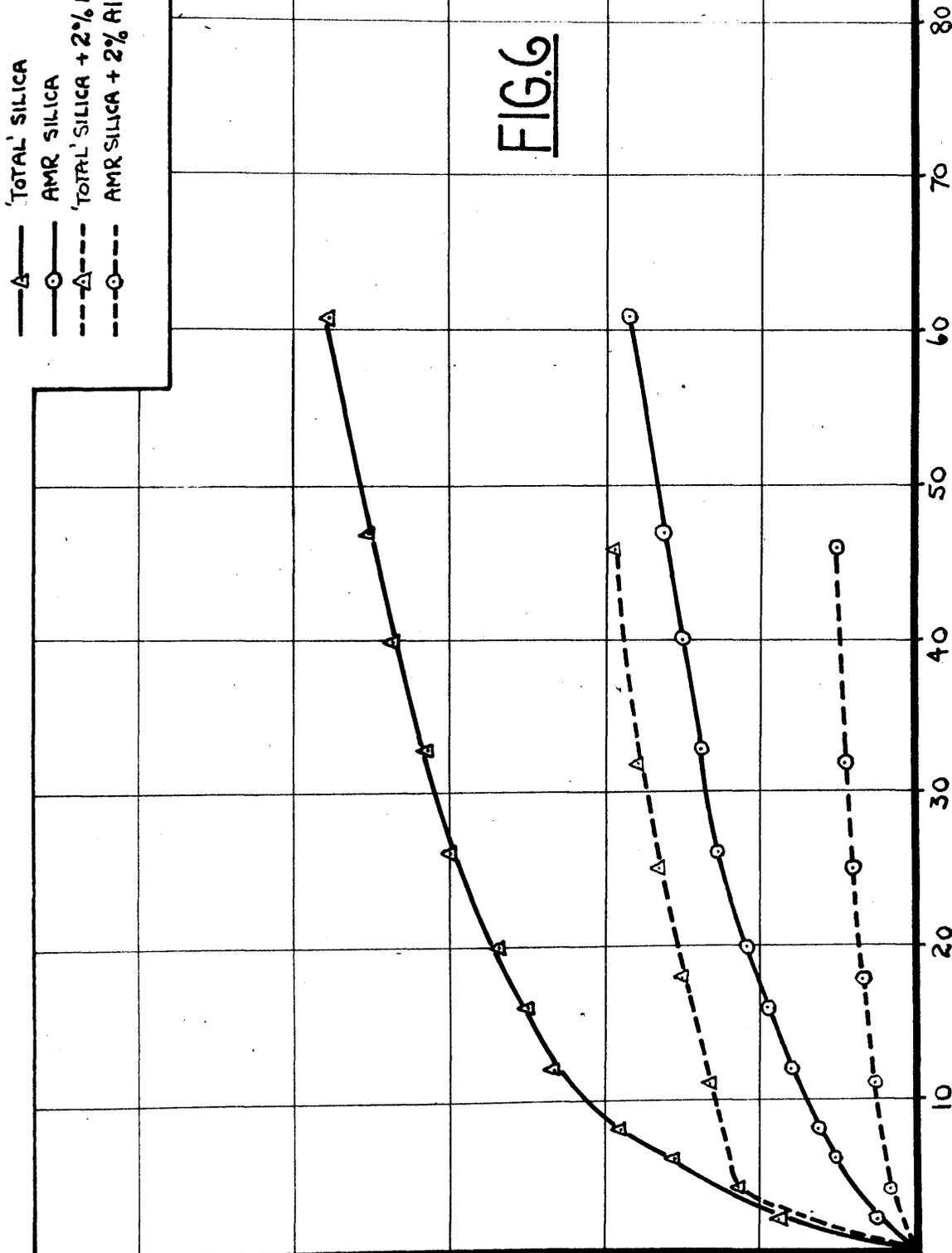
Extractive Solubility of  $RC(II)$  in borate buffer (pH 7.5) at  $37^{\circ}C$ .; mass/liquid ratio 4gms/40 ml.

- △— 'TOTAL' SILICA
- AMR SILICA
- - -△- - - 'TOTAL' SILICA + 2% Al.
- - -○- - - AMR SILICA + 2% Al.

MGS. SILICA/100 ML.

TIME (DAYS)

FIG. 6



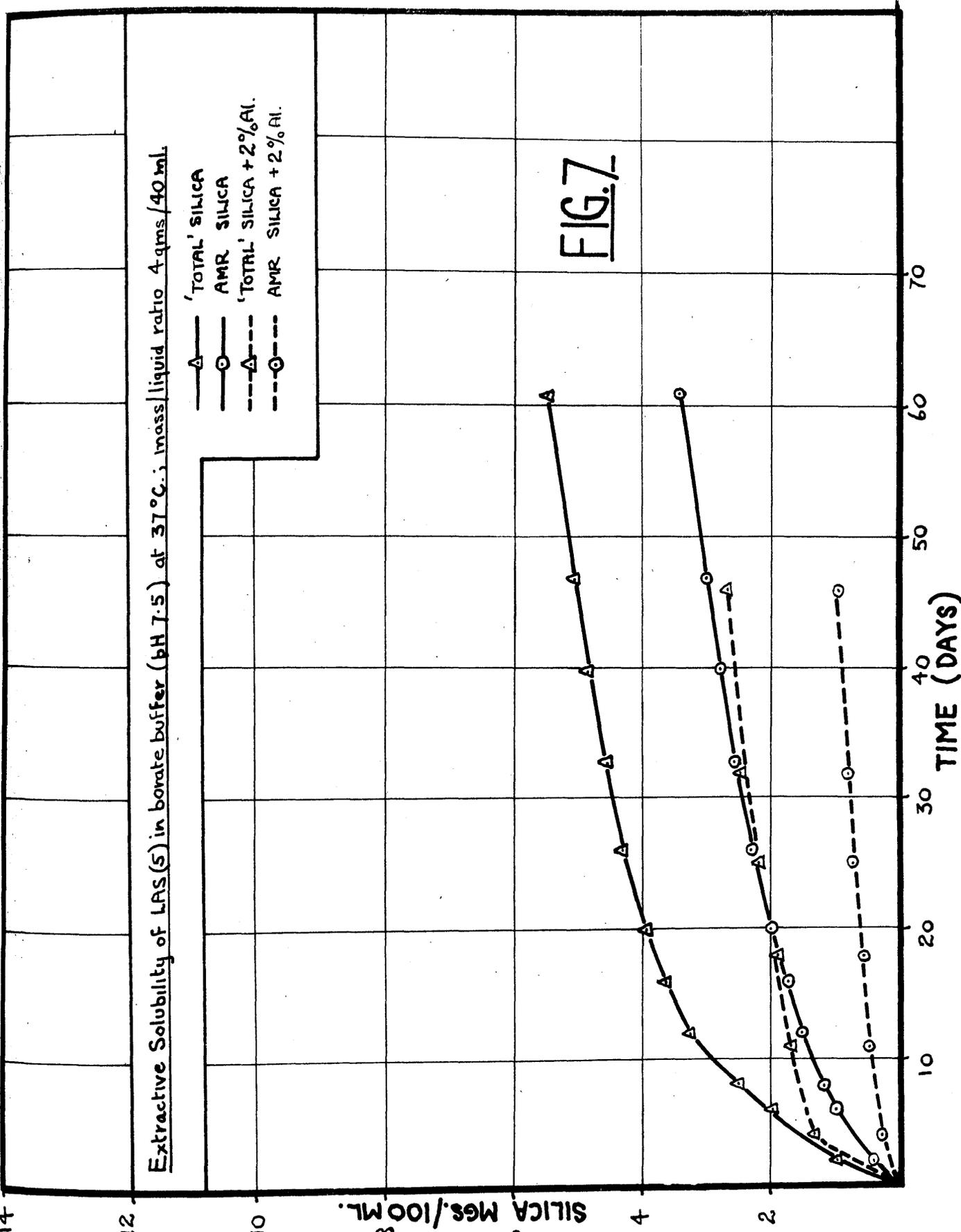
Extractive Solubility of LAS(S) in borate buffer (pH 7.5) at 37°C.; mass/liquid ratio 4.gms./40 ml.

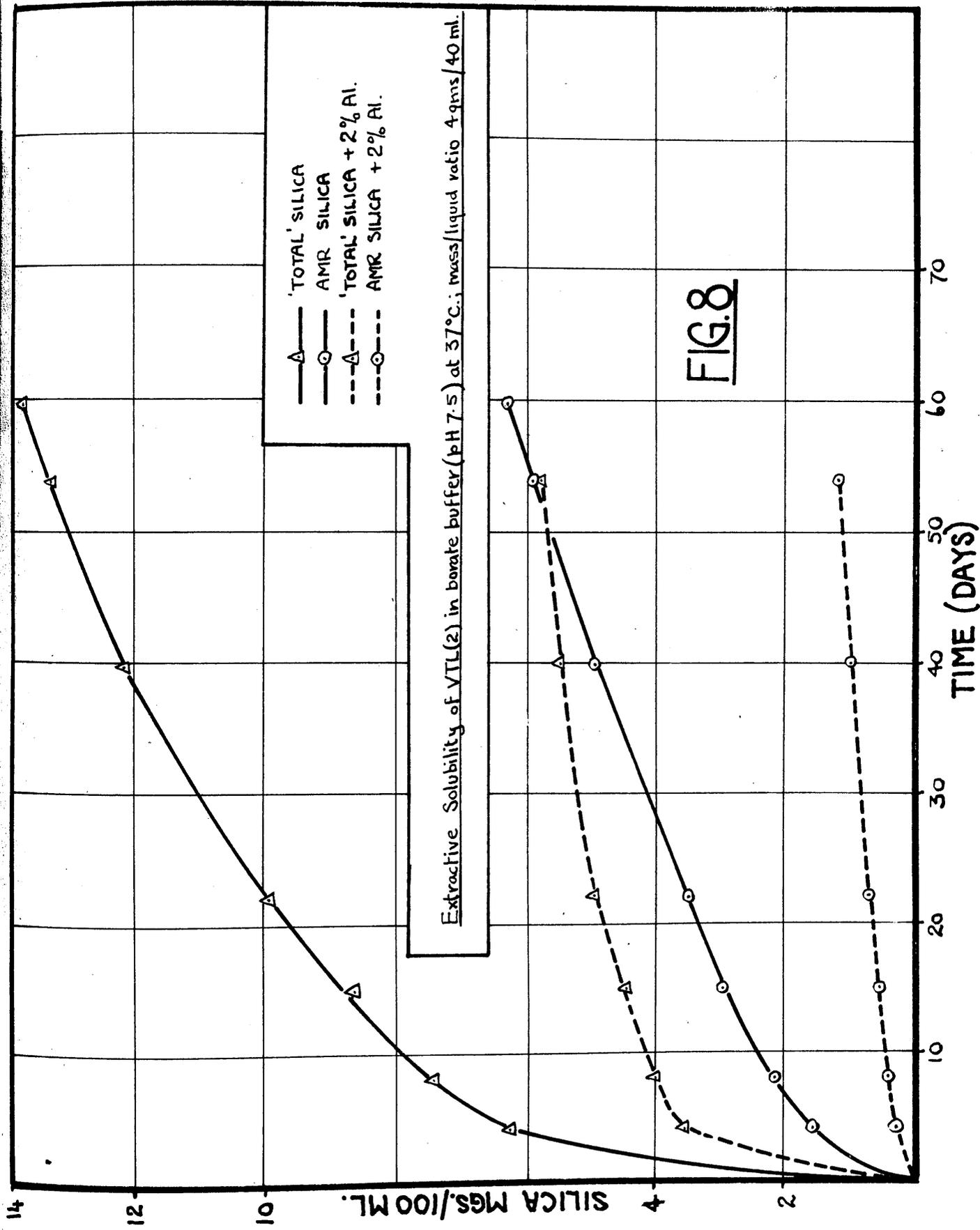
- △— 'TOTAL' SILICA
- AMR SILICA
- - -△- - - 'TOTAL' SILICA + 2%Al.
- - -○- - - AMR SILICA + 2%Al.

SILICA MGS./100 ML.

TIME (DAYS)

FIG. 7





- △ 'COLLOIDAL' SILICA RC(1)1
- △ 'COLLOIDAL' SILICA RC(1)1 + 2% Al
- 'COLLOIDAL' SILICA LAS(5)
- 'COLLOIDAL' SILICA LAS(5) + 2% Al
- 'COLLOIDAL' SILICA VTL(2)
- 'COLLOIDAL' SILICA VTL(2) + 2% Al

Extractive Solubilities in borate buffer (pH 7.5) at 37°C.; mass/liquid ratio 4 gms/40 ml.

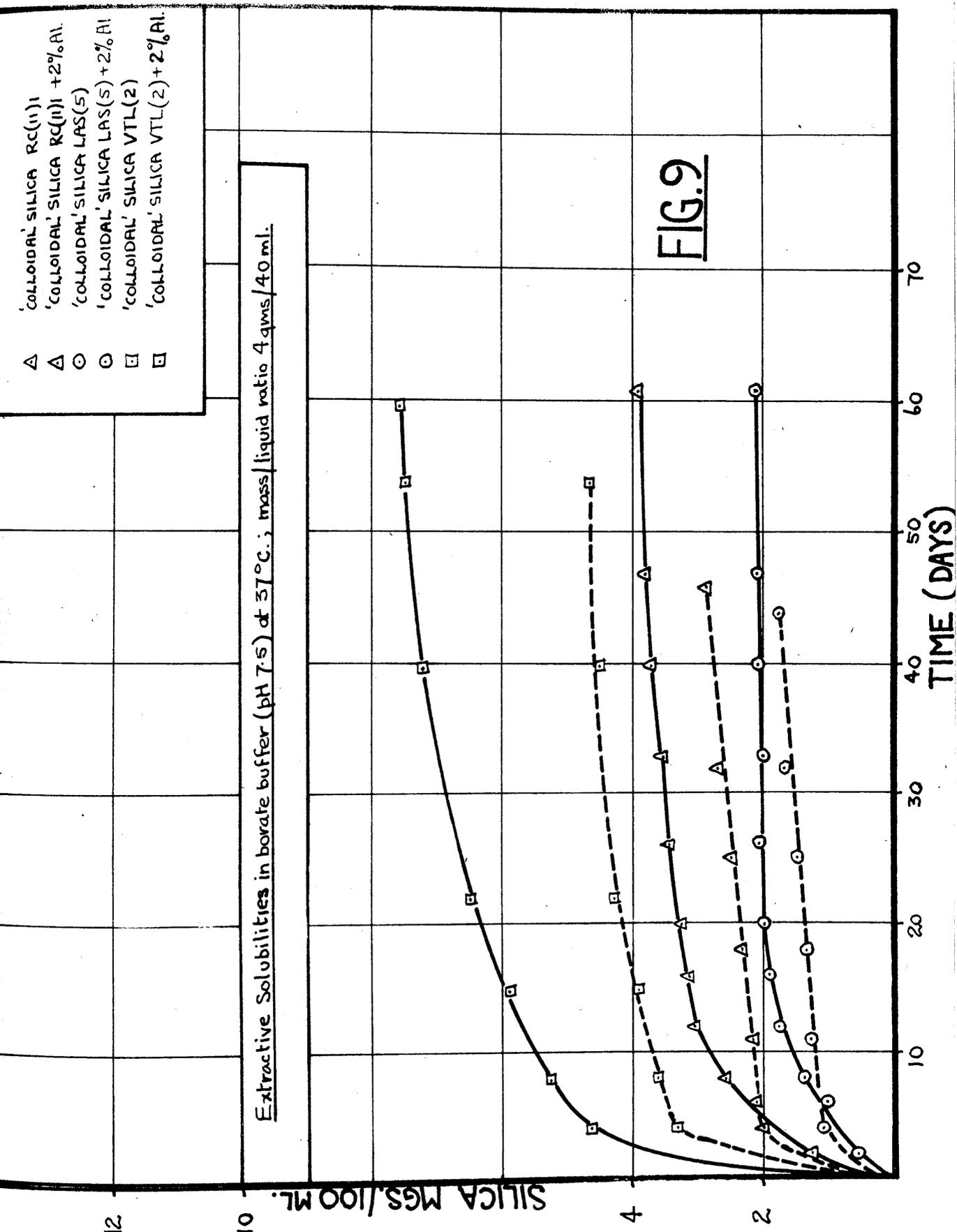


FIG. 9

attributable to the presence of the metal - in other words, that aluminium does not precipitate AMR silica as its colloidal modification. Further, since Figs. 6-9 show that addition of metallic aluminium to silica dusts prior to extractive solution in borate buffer, depresses the AMR silica and increases the proportion of colloidal silica produced, it may reasonably be concluded that the effect of the metal is a stabilisation of the colloidal silica dispersed from the dust particles, possibly by the mechanism suggested below.

For all three dusts the aluminium has brought about an immediate reduction in the AMR silica values, although at the end of 4 days it had not markedly reduced the total silica produced. This effect may be seen most clearly for rock crystal (Fig. 6). It may be explained by assuming the following mechanism of solution. The silica is released from the solid surface as colloidal silicic acid, which then breaks down to form AMR silica. The aluminium in solution is preferentially adsorbed on the colloidal silica, preventing its break-down into AMR silica; only when the adsorption of aluminium by colloidal silicic acid is complete is there appreciable adsorption at the solid dust particle surfaces. This effect therefore causes a time lag before the total silica depression is brought about.

(iii) Comparative solubilities for five siliceous dusts.-

Extractive solubility methods were further employed with the object of obtaining comparative solubility values for five siliceous dusts - rock crystal, RC(11)2; Loch Aline sand, LAS(6); Vitreosil, VTL(3);

olivine, OL(1); and orthoclase feldspar, OC(1). With the exception of LAS(6), which was not ground, the dusts were produced in an agate mortar and the 70-90 mesh B. S. S. fractions sedimented repeatedly from water to remove very small particles. All five dusts were found by microscopic examination to have average particle sizes of approximately 250  $\mu$ . Their extractive solubility values were determined in borate buffer, and parallel experiments were again carried out with the addition of 2% of aluminium turnings to each test. The concentration of silica in the solution at the end of each extractive solution period was added to the sum of the concentrations obtained for previous periods, and this overall value was tabulated against total time from the start of the tests. (Table 10).

From these results, a high initial solubility rate is again evident, indicating the presence of an HS layer on all five dusts. A similar total silica value is exhibited by all the dusts except Loch Aline sand LAS(6), for which it is markedly lower. The presence of metallic aluminium is shown to decrease the total and AMR silica values of all the dusts, and the colloidal silica values for all but olivine, the latter dust producing more colloidal silica after the addition of aluminium. No constant proportionality is apparent between the amounts of AMR, total, and colloidal silica yielded by the various dusts.

Investigations on the precise nature of the HS layer, and on its regeneration by various methods, are described in a subsequent part of the present work.

TABLE 10

Extractive solubilities of five siliceous dusts in borate buffer  
(pH 7.5) at 37°C; mass/liquid ratio, 4 g./40 ml.

(All results expressed as mg. silica/100 ml.)

(Results of tests with 2% aluminium shown in parenthesis)

<u>Time in Days.</u>	4	10	17	33	59
<u>'Total' Silica.</u>					
RC(11)2	4.55(3.6)	5.85(4.15)	6.28(4.22)	7.49(4.58)	8.78(5.66)
LAS(6)	1.52(1.13)	2.42(1.43)	2.83(1.53)	3.73(1.89)	4.70(2.21)
VTL(3)	4.16(2.21)	5.11(2.44)	5.66(2.57)	7.26(2.87)	8.55(3.21)
OC(1)	4.02(3.48)	5.12(4.03)	5.76(4.35)	7.03(4.92)	8.46(5.72)
OL(1)	4.75(5.0)	5.55(5.5)	5.90(5.73)	6.69(6.21)	7.79(7.21)
<u>AMR Silica.</u>					
RC(11)2	.64(.19)	1.06(.31)	1.42(.39)	2.10(.56)	2.90(.79)
LAS(6)	.50(.24)	1.04(.37)	1.44(.47)	2.16(.64)	3.04(.85)
VTL(3)	1.56(.26)	2.34(.39)	2.81(.48)	3.94(.67)	5.10(.95)
OC(1)	.83(.42)	1.72(.84)	2.32(1.16)	3.35(1.68)	4.61(2.38)
OL(1)	.99(.63)	1.39(.88)	1.63(1.02)	2.09(1.28)	2.65(1.68)
<u>'Colloidal' Silica.</u>					
RC(11)2	3.91(3.41)	4.79(3.84)	4.86(3.83)	5.39(4.02)	5.88(4.87)
LAS(6)	1.02(.89)	1.38(1.06)	1.39(1.06)	1.57(1.25)	1.66(1.36)
VTL(3)	2.60(1.95)	2.77(2.05)	2.85(2.09)	3.32(2.20)	3.45(2.26)
OC(1)	3.19(3.06)	3.40(3.19)	3.44(3.19)	3.68(3.24)	3.85(3.34)
OL(1)	3.76(4.37)	4.16(4.62)	4.27(4.71)	4.60(4.93)	5.14(5.53)

(d) Conclusions

1. The surface layer on dust particles prepared from five widely different siliceous materials (rock crystal; silica sand; fused amorphous silica; olivine; and orthoclase felspar) is found to have a much higher solubility rate than the material which lies immediately beneath it. A siliceous dust particle, therefore, may be considered as a relatively insoluble core covered by a layer which exhibits a higher solubility rate. The solubility rates of successive layers of the material are shown to decrease gradually, which suggests that the high-solubility layer (HS layer) on the surface is not discrete, but rather that there is a gradual and continuous change from the surface inwards towards the core.
  
2. For all dusts examined, the HS layer is removed by agitation in aqueous media buffered to pH 7.5. The initial solubility of rock crystal dust decreases on treatment with acid media, whereas that of the silica sand (from Loch Aline, Argyllshire) increases when thus treated. An increase in solubility was also observed on acid treatment of another silica dust of natural origin, but of somewhat lower purity.
  
3. After the HS layer has been removed from Loch Aline sand dusts, the initial high solubility may be regenerated by treatment with hydrochloric acid. The HS layer (original or regenerated) is more readily dispersed by alkaline than by acidic media. Acid treatment

of rock crystal dusts from which the HS layer had been removed has no effect on their solubilities.

4. Rock crystal dusts differ from Loch Aline sand dusts similarly treated, in that the initial high solubility is not regenerated by treatment with hydrochloric acid, and also, in that the original HS layer on rock crystal dusts is dispersed by acidic media.

5. During extractive solubility experiments, colloidal silicic acid is liberated from all five siliceous dusts examined; the amount is, however, appreciable only during the initial solution periods, indicating a connection with the dispersal of the HS layer.

6. The presence of metallic aluminium decreases the amounts of total and 'ammonium molybdate reactive' (AMR) silica liberated from the five dusts mentioned above, and decreases the amounts of colloidal silica dispersed in borate buffer solution from all but olivine, which yields more colloidal silica in the presence of aluminium. The proportion of colloidal silica in the material dispersed from all five dusts is, however, increased by the addition of aluminium to the systems.

7. Aluminium does not precipitate AMR silica from solution in the form of the colloidal modification, but probably acts as a stabilising agent in preventing the break-down of colloidal silica into the dissolved form.

PART 2Nature and Initial Production of the High-Solubility Layer.(a) Introduction

It has been shown in PART 1, that there exists on the surface of siliceous dust particles a layer which has a much higher solubility rate than the material forming the core of the particles. It was demonstrated by extractive solubility experiments that the greatest amount of silica was dissolved during the first solution period, and that during each succeeding period the amount decreased, indicating progressive removal of a layer of highly soluble material from the original dust particle surfaces.

The present section discusses the precise nature of the high-solubility layer (HS layer), and describes experimental work designed to confirm the suggestions put forward.

(b) Discussion

To interpret the high initial solubility rate exhibited by siliceous dust particle surfaces, three principal alternative mechanisms have to be considered.

1. Dispersion of a silica gel layer.

One obvious possibility is that the fresh crystal surfaces exposed during production of a dust by grinding might combine with atmospheric moisture to form a layer of hydrated silica on each dust particle. Upon subsequent contact with an aqueous medium such a layer would be expected to yield silica into solution at a high rate

until completely dispersed, the solvent then having reached the underlying core of crystalline silica.

Experimental evidence does not, however, support this view. It has been shown (PART 1, Figs. 6-9) that the HS layers on rock crystal, Loch Aline sand, and fused silica dusts have not been completely dispersed even after 14 days of continuous agitation with a borate buffer (pH 7.5). King and McGeorge (22), on the other hand, have shown that freshly precipitated silica gel reaches an equilibrium solubility value in ascitic fluid (pH 7.5), obtained from a case of congestive heart failure, within about 24 hours: and Lenher and Merrill (24) also found that gelatinous silica, in contact with conductivity water, reaches equilibrium in not more than 24 hours. Confirmatory evidence has now been obtained by the following method.

Commercial silica gel (4 g.) was agitated in a glass tube with 40 ml. of borate buffer (pH 7.5) at 37°C. At suitable intervals samples of the solution were withdrawn, filtered (hot) through a Ford Sterimat filter pad (Grade SB), and the silica content of the cooled filtrates determined by the Molybdenum Blue method employed throughout this work (PART 1, p. 20). The results are summarised in Table 11.

The fact that the equilibrium solubilities obtained by this method are higher than those reported by King and McGeorge (22) may be attributed to the absence from the borate buffer, of substances which in the ascitic body-fluid exerted a depressing effect on the solubility, or to a difference in the physical nature of the two silica gels, or to both of these factors. The slight observed

TABLE 11

Equilibrium Solubility of Silica Gel in Aqueous Media (expressed as mg. Silica/100 ml.)

<u>Time (hours) :-</u>	2	5	18	24	48	72	123	143
Solubility in ascitic fluid pH 7.5 (King and McGeorge (22) )	5.8	6.9	8.0	8.8	9.0	9.1	-	-
Solubility in conductivity water (Lenher and Merrill (24) )	-	-	-	42.8	42.4	42.8	-	-
Solubility in borate buffer, pH 7.5 (present work)	3.0	-	-	15.2	-	-	14.5	13.5

... these were presumably connected with a discrete layer, and ...  
 ... change of ... in the solubility ...  
 ... layer ...  
 ... gradual rather than a sudden decrease in the solubility ...  
 ... to indicate that the layer is not discrete, but that there  
 ... gradual and continuous change in the physical conditions of the

diminution of equilibrium solubility after 24 hours is most probably due to gradual aggregation of very small colloidal silica particles on prolonged agitation, which would lead to their progressively greater retention by the filter before colorimetric estimation of the filtrate. The very much higher results of Lenher and Merrill (24) are probably due to errors arising from their method of separating the solid and liquid phases before estimation (gravimetric) of the dissolved silica. Simple filtration was relied upon, so that finely-divided suspended particles would be determined as well as true dissolved silica. In all three sets of results, however, it is clear that equilibrium was reached in not more than about 24 hours: and it therefore appears that the HS layer consists of material much less readily dispersed by aqueous solvents than is silica gel.

This conclusion is further confirmed by the following considerations. A coating of silica gel on the dust particle surfaces would presumably constitute a discrete layer, and a sudden change of gradient in the solubility/time curves would be expected when the solvent had completely removed the gel layer and reached the less soluble crystal surfaces below. In fact, however, there is a gradual rather than a sudden decrease in the solubility rate, which seems to indicate that the layer is not discrete, but that there is a gradual and continuous change in the physical condition of the material from the surfaces inwards to the cores of the dust particles.

2. Gradual inactivation by adsorption on a crystalline surface.

The initial high solubility rate of dust particles might be explained alternatively by assuming the production of fresh and highly active crystal surfaces during production of the dusts by grinding. On this view, it would be anticipated that after contact of dust with solvent for some time, adsorption of substances from the solvent upon these fresh and active surfaces would bring about a gradual inactivation of the material, and hence a lowering of the solubility rate.

Again, however, this explanation of the nature of the high initial solubility is not supported by the experimental evidence. It was shown (PART 1, Tables 1 and 2, pp. 24 and 25) that the effects of salt-solution treatments upon the solubilities of the dusts were not connected with the salt concentrations employed; and it was, therefore, concluded that, since concentration changes of this kind have no effect, the mechanism is not dependent on adsorption but is in fact the dissolution of a highly soluble outer layer on the particles. This conclusion was supported by the demonstration (PART 1, Table 4, p. 32) of the high initial solubility effect with a rock crystal dust in double-distilled water, particular care having been taken to exclude from the solvent and dust, impurities which might have been possible adsorbates.

### 3. Dispersion of a Beilby layer.

It is considered that the most likely explanation of the nature

of the HS layer follows from the work of Beilby (39), who, after exhaustive microscopic examination of the effects of polishing on crystal surfaces, showed that such treatment produces a surface layer with physical properties different from those of the original crystalline material. Beilby postulated that during the process of polishing a thin surface layer of the crystal is melted and flows as a liquid, this transient fluid condition resulting in a layer of vitreous material like a skin upon the surface. As a result of experiments on the etching of polished surfaces he concluded that the surface skin has a solubility different from that of the normal crystalline form of the substance; and he demonstrated the production of this layer by polishing a large number of crystalline surfaces, mainly on metals but also on rock crystal. He suggested that the grinding of crystalline materials produced a layer on the surface of the dust particles similar to that which was shown to result from polishing; and he expressed the view that "the operations of cutting, filing, grinding or polishing produce on the surface of solids a thin film which is, in many respects, essentially different from the general body underneath it"...and..."the grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer crystalline fragments, but it involves the transformation of, at any rate, a part of the substance into the vitreous condition".

Beilby concluded that the 'polish layer' was amorphous; and more

recent evidence from X-ray work by Hamburger (40) has yielded more detailed information concerning the structure of such layers. Hamburger has shown that the polished surface films of crystalline materials consist of thin scales of levelled sub-microscopic crystallites, and that from the surface of such films inwards towards the core of the material the physical condition, structure, and texture show a gradual and continuous change through a transition layer. The condition of the polish layer, consisting of minute crystals in random orientation, was thus shown to blend into the single-crystal structure of the body of the material via the transition layer in which the crystallites become larger and more orderly in arrangement. This continuous change of structure may be connected with the gradual decrease of the solubility rate of siliceous dust particle surfaces observed during the present work (PART 1, Figs. 6-8).

Beilby suggested further that although the proportion of vitreous material produced by polishing was small for macro-crystals, the vitreous layer might well constitute a major fraction of the mass for dust particles of small dimensions and high specific surface. An observation bearing directly upon this hypothesis was made by Ray (41) during experiments on the heats of solution of various forms of silica in hydrofluoric acid. Ray showed that the heat of solution of quartz which had been ground for a long period in a mechanical agate mortar was greater than that of a quartz dust produced by a

short grinding treatment, and also that the heat of solution of vitreous silica was greater than that of either. He concluded that during the prolonged grinding treatment some of the quartz had been converted to the vitreous modification, and that this accounted for the greater heat of solution observed. From the difference between the heats of solution for the two quartz dusts Ray calculated that 31.2% of the quartz had been vitrified by the prolonged grinding. Such a transformation after prolonged grinding was also shown by Ray (42) to be accompanied by a change in the density of the quartz (silver sand), the value being reduced from 2.638 to 2.528 after grinding for 15 hours in a mechanical agate mortar. This reduction in the density indicated that 25.7% of the quartz had been vitrified, a result of the same order as that calculated from the heats of solution.

Ray's results have been discussed and criticised by Sosman (43), who concludes that the observed reduction in density was caused by some "unrecognised factor" and not by the effect of mechanical grinding. In support of this view Sosman quotes the work of Johnston and Adams (44), who obtained the following results for the density of quartz of different particle sizes:-

<u>Particle size.</u>	<u>d at 25°C.</u>
A 200 - 400 $\mu$	2.6469
B 140 - 170 $\mu$	2.6477
C 70 $\mu$ and below	2.6481
D 50 $\mu$	2.6489
E 20 $\mu$ down to limit of vision	2.6480

No reduction in density with decrease in particle size was observed by these workers, but it is noteworthy that although Johnston and Adams did not specify the period of grinding employed in the production of the dusts, there is nothing to indicate that it was prolonged, while it is the effect of prolonged grinding upon the density which was measured by Ray. The finest dust (E) examined by Johnston and Adams was obtained by sedimentation from water; no precautions designed to recover the very finest dust particles from the sedimentation liquid were recorded.

In view of these somewhat inconclusive results it was decided to attempt to confirm the results of Ray, and also to determine whether prolonged grinding has any effect upon the density of vitreous silica. It was thought that the latter experiment might confirm the idea that reduction in density is due to vitrification, since with fused silica no reduction due to this process could occur.

(c) Experimental

1. Materials: Source and preparation of dusts.

(i) Rock crystal dust (70 - 300  $\mu$ ) was prepared from large quartz crystals specially selected for their transparency and freedom from mineral contamination. These were ground by hand in an agate mortar, and a dust prepared by repeated sedimentation from water to ensure complete removal of finer particles. On analysis it showed 99.92% silica.

(ii) Vitreous silica dust (300-600  $\mu$ ) was prepared from Transparent Vitreosil (28), containing 99.8% silica. This was ground in a steel roller mill, sieved, and the 50-70 mesh B.S.S. fraction sedimented from water. On microscopic examination of the particles of this dust, occasional air-bubble occlusions were observed.

## 2. Method of density determination.

The densities were measured by means of a glass bottle pycnometer with a ground-glass stopper (Fig. 10). To promote complete wetting of the dust surfaces, liquid and dust were brought into contact under vacuum conditions. Distilled water in the bulb of the apparatus was de-aerated by opening stopcock A to the vacuum pump for 30 minutes, while the air was removed from the density bottle by the side arm B. When this was complete the density bottle was half filled with the de-aerated water via stopcock C, and then reconnected through B to the vacuum pump for 20 minutes. The bottle was then detached from the rubber tubing and completely filled with the de-aerated water. The densities were measured at 18°C., 0.5-1.0 g. of the dust being used for each determination. Results are reported to three decimal places; and it is estimated that the experimental error inherent in the method is not greater than ca.  $\pm 0.25\%$  of the measured density.

The densities of quartz, and vitreous silica were determined

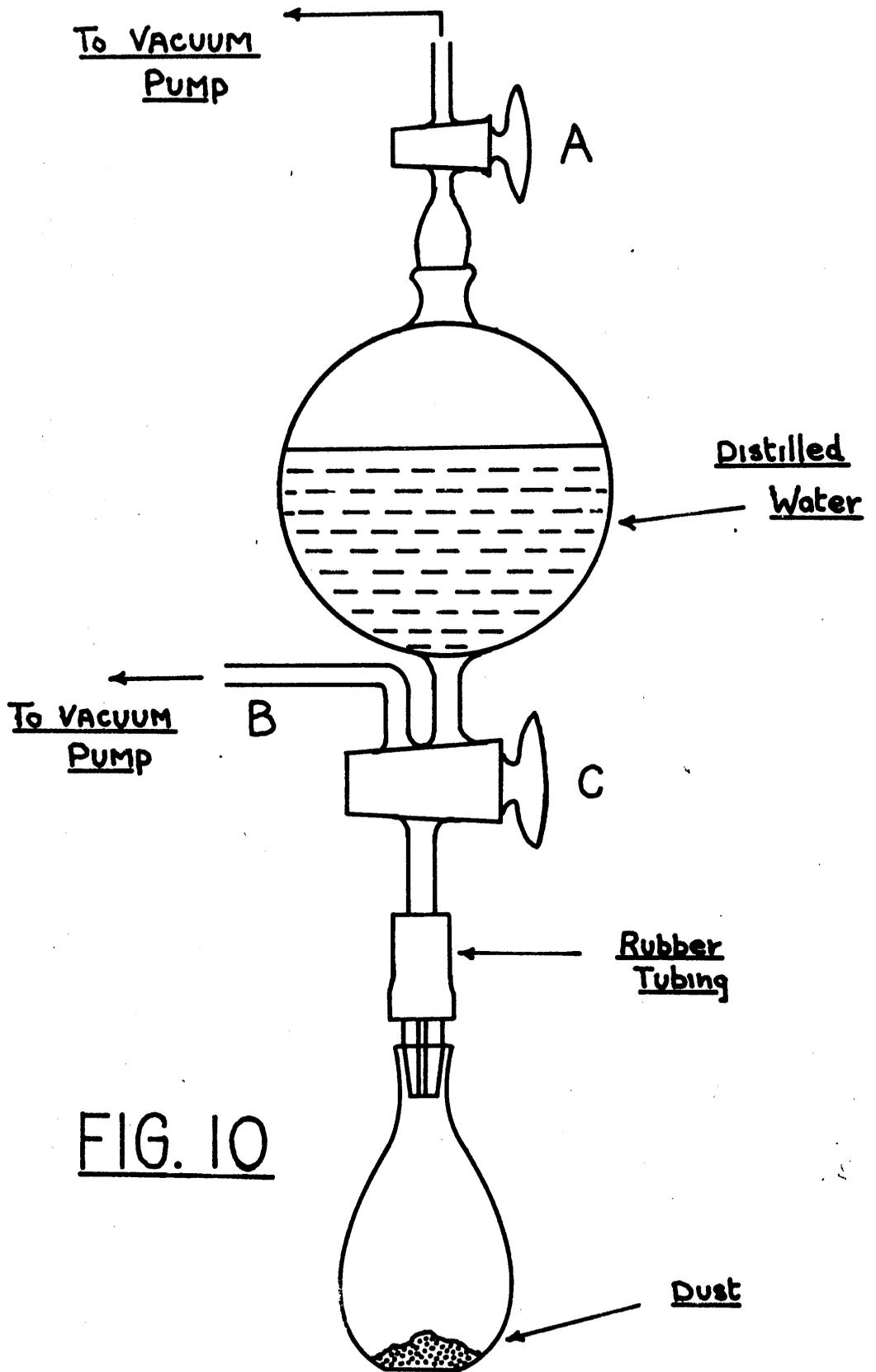


FIG. 10

before and after various grinding treatments in an agate mortar; and the density of the agate mortar itself was determined by weighing and direct displacement of water.

### 3. Contamination of dust by agate.

It was thought likely that during grinding in the mechanical agate mortar a certain amount of agate might be removed by abrasion, and thus contaminate the dust produced. To test this possibility, the following experiment was carried out, suggested by the known relative hardness of alumina, quartz, and agate (9, 7, and 6, respectively, on Mohs' scale). 3.5 g. of fused alumina (99.7% alumina) was ground in the agate mortar, and the amount of silica in the resulting dust was determined after various periods of grinding, by evaporation with hydrofluoric acid. Contamination of the alumina dust by abraded agate was clearly confirmed by the results shown in Table 12.

### 4. Examination of dusts for quartz and cristobalite.

In view of the high surface-temperatures which have been shown by Bowden and Hughes (45) to be produced during grinding and polishing processes, it was considered possible that cristobalite and tridymite might be formed during prolonged grinding of quartz, and that any reduction in the density of the quartz might be due in part to development of these modifications, as well as to the possible production of vitreous silica.

**TABLE 12****Silica Contamination of Alumina Dust ground in an Agate Mortar**

<u>Period of grinding.</u>	<u>Silica content of dust.</u>
4 hours	5.3%
18 hours	7.2%

The density of quartz was found to be decreased (from 2.650) by a prolonged grinding treatment (18 hours) in an agate mortar.

After grinding fused alumina in an agate mortar for periods of 4 and 18 hours, it was found that the resulting dusts were contaminated with 5.3% and 7.2% respectively of silica, removed from the agate pestle by abrasion during the grinding.

The observed reduction in density of quartz cannot, however, be wholly explained by assuming a similar contamination of the agate from the mortar, though this is probably a contributing factor.

Quartz and vitreous silica dusts were therefore examined before and after grinding to ascertain qualitatively the modifications of silica present. Tests were performed by the differential thermal analysis method described by Grimshaw, Heaton, and Roberts (46); and, since the formation of tridymite normally follows that of cristobalite (47) it was considered sufficient to examine the ground dusts for quartz and cristobalite only. The results are shown in Table 13; and they indicate no formation of cristobalite from quartz, or of either quartz or cristobalite from vitreous silica, under the conditions of grinding employed.

(d) Summary

1. The density of quartz was found to be decreased (from 2.648 to 2.550) by a prolonged grinding treatment (17 hours) in an agate mortar.
2. After grinding fused alumina in an agate mortar for periods of 4 and 18 hours, it was found that the resulting dusts were contaminated with 5.3% and 7.2% respectively of silica, removed from the mortar and pestle by abrasion during the grinding.
3. The observed reduction in density of quartz cannot, however, be wholly explained by assuming a similar contamination of the quartz by agate from the mortar, though this is probably a contributory factor, since the final density of the dust (2.550) is lower than that of the agate itself (2.586).

TABLE 13

Densities of Quartz, Vitreous Silica, and Agate, with Silica Modifications detected by Differential Thermal Analysis.

<u>Material examined.</u>	<u>Silica modifications present.</u>	<u>Density at 18°C.</u>	<u>Estimated experimental error.</u>
1. <u>Quartz (rock crystal) dust</u> (70-300 $\mu$ )			
Original	Quartz present; no cristobalite.	2. 648 (2. 649)*	$\pm 0. 21\%$
Ground for 5 minutes to pass 200- mesh B. S. S. (70 $\mu$ and below)		2. 647	$\pm 0. 21\%$
Ground for 17 hours	Quartz present; no cristobalite.	2. 550	$\pm 0. 12\%$
2. <u>Vitreous silica dust</u> (300-600 $\mu$ )			
Original	No quartz or cristobalite.	2. 201 (2. 203)*	$\pm 0. 14\%$
Ground for 17 hours	No quartz or cristobalite.	2. 230	$\pm 0. 25\%$
3. <u>Agate mortar</u>			
		2. 586	$\pm 0. 20\%$

(\* Figures in brackets after Sosman (43) ).

4. No cristobalite could be detected in the quartz dust after prolonged grinding. The density reduction is therefore attributed to partial conversion of the quartz to the vitreous condition, not to another crystalline modification of silica.

5. No measurable change in density was observed in quartz submitted to only a short period of hand-grinding (5 minutes) in an agate mortar, reducing the quartz dust (70-300  $\mu$ ) to pass 200 mesh B.S.S. (70  $\mu$  and below).

6. The density of vitreous silica was found to be increased (from 2.201 to 2.230) by a prolonged grinding treatment (17 hours) in an agate mortar.

7. No quartz or cristobalite could be detected in the vitreous silica dust after prolonged grinding. The observed increase in density is not, therefore, attributed to production of a silica modification of higher density by crystallisation of the vitreous material, but to (a) contamination of the dust by agate ground from the mortar, and (b) opening of the air bubbles noted microscopically in the original vitreous material.

(e) Conclusions

The above results fully confirm Ray's observation that

prolonged grinding reduces the density of quartz. In addition, the results obtained by differential thermal analysis support the conclusions of Ray and of Beilby that during the grinding of a quartz dust a considerable amount of vitreous silica is formed. It therefore seems highly probable that the HS layer on siliceous dust particle surfaces arises through physical vitrification of crystalline surfaces brought about by mechanical disturbance (polishing, grinding, etc.).

#### Acknowledgment

The writer gratefully records his thanks to his colleague Mr. P.B. Dempster for carrying out the differential thermal analysis measurements summarised in Table 13.

... sand, and vitreous silica) were interrupted after the HS lay  
been removed by solvent, and the dusts were each submitted i  
polishing treatment. The solution tests were then resumed,  
ascertain whether this treatment had regenerated an HS layer  
dust surfaces.

#### 2. Materials: Source and preparation of dusts.

(i) Rock crystal dust (240-650  $\mu$ ) was produced by grind

PART 3Removal and Regeneration of the HS Layer(a) Introduction

The evidence developed in the foregoing section (PART 2) supports the postulate that the HS layer is similar in nature to the Beilby layer. The work now to be described was designed to test this concept, and in particular to determine whether the HS layer could be regenerated on the surface of dust particles from which it had previously been removed by solvents, by submitting such particles to a purely mechanical polishing process. A positive result in this experiment would clearly go far towards establishing the identity of the HS and Beilby layers.

(b) Experimental1. General.

Solubility/time curves for three dusts (rock crystal, Loch Aline sand, and vitreous silica) were interrupted after the HS layers had been removed by solvent, and the dusts were each submitted to a polishing treatment. The solution tests were then resumed, to ascertain whether this treatment had regenerated an HS layer on the dust surfaces.

2. Materials: Source and preparation of dusts.

(i) Rock crystal dust (240-660  $\mu$ ) was produced by grinding quartz crystals (99.92% silica: specially selected for transparency

and freedom from mineral inclusions) in an agate mortar. All particles less than 240  $\mu$  in diameter were removed by repeated sedimentation from water.

(ii) Loch Aline sand dust (200-520  $\mu$ ) was obtained by separating the desired particle-size range from a quantity of natural silica sand (99.8% silica) from Loch Aline, Argyllshire, by sieving and water-sedimentation. No grinding was employed.

(iii) Vitreous silica dust (200-700  $\mu$ ) was produced by grinding Transparent Vitreosil (99.8% silica) in a steel roller-mill. The dust was then extracted with hydrochloric acid to eliminate traces of iron contamination, and the desired particle-size range was again obtained by water-sedimentation, all particles below 200  $\mu$  being removed.

The particle-size range of all the above dusts was measured microscopically, using a calibrated graticule.

### 3. Removal of the HS layer

A 4 g. sample of each of the three dusts (rock crystal, Loch Aline sand, and vitreous silica) was agitated with 40 ml. of borate buffer (pH 7.5) in an air thermostat at 37°C. for a number of consecutive solution periods. At the end of each period, the amounts of 'ammonium molybdate reactive' (AMR) and total silica yielded into the solvent were determined as previously described (PART I, pp. 20 and 45); the solvent was then renewed so that the dust

had constant conditions for dissolution during each successive solution period.

The amount of silica found to have been yielded into solution by the dust during a solution period was added to the sum of amounts determined for previous periods, and the resulting value was plotted against the time from the start of the tests.

The results of this continued process of leaching the dust particle surfaces with successive quantities of fresh solvent show the initial high solubility rate of the particles, followed by a gradual decrease in the rate of solution until an almost constant rate is reached. This constant condition was reached by all three dusts after about 20-30 days of agitation with the solvent, and it was assumed that by then the HS layer had been completely removed from the dust particle surfaces.

After removal of the HS layer the dusts were submitted to a polishing treatment, and the solubility tests were then continued.

#### 4. Polishing agents

The following two polishing agents were employed.

(i) Rock crystal dust (75  $\mu$  and below), produced by grinding selected crystals of quartz in an agate mortar to pass 200 mesh B.S.S.

(ii) Silicon carbide dust (60  $\mu$  and below), manufactured commercially as a fine grinding powder for metals (48).

## 5. Polishing Treatment

After the above treatment, the 4 g. portions of dust were washed free from traces of the borate buffer solvent by five separate sedimentations from fresh quantities of distilled water, and were then dried at 37°C. (Such drying has been shown (PART 1, pp. 36 and 37) to have no effect in regenerating a high solubility rate after removal of the HS layer).

The 4 g. quantities of dry dust were each mixed with 5 g. of polishing agent in 2 oz. glass bottles, closed with screw-cap plastic lids, and rotated at 50 r.p.m. for a number of days. The particle size of the dusts used as polishing agents was much smaller than that of the particles to be polished, the intention being that during agitation of the mixture the surfaces of the larger particles would be subjected continuously to the mild abrasive action of the smaller particles passing over them.

At the end of the polishing treatment the original dust was separated from the polishing agent, either by repeated sedimentation from water (ca. 30 separations), or by washing the mixture for 10 minutes on a 90 mesh B.S.S. with a jet of water, the original dust being retained on the sieve. Microscopic examination of the dusts thus recovered revealed no trace of residual polishing agent, indicating that a complete separation had been achieved.

The dusts so treated were then subjected to a further series of solution periods in borate buffer, to determine the effect of the

polishing treatment upon their solubilities.

The results for rock crystal, Loch Aline sand, and vitreous silica dusts are shown in Figs. 11, 12, and 13; and it is clear that for each dust the polishing process has regenerated an HS layer.

It is at first sight surprising that the polishing treatment should generate on vitreous silica particles a surface layer differing in physical properties from the underlying core. The latter is of fused and amorphous material, and the evidence summarised up to this point strongly suggests that the HS layer is also vitreous in nature, so that there is no immediately obvious reason why they should differ in solubility. A complete explanation must clearly await further evidence; but it is at least possible that the core and the HS layer differ slightly in the extent to which they approach a truly amorphous condition devoid of any organised structure. The massive fused silica from which the dust was prepared contains, in all probability, random incipient crystallites, formed during slow cooling; whereas the surface micro-layer of vitreous material, being formed and cooled much more rapidly, might be expected to approach more nearly a truly amorphous condition. Further evidence on this point is described in the following section (PART 4) after an investigation of adsorption phenomena at the HS layer.

(c) Summary

1. The solubility rates exhibited by all three dusts were initially

Rock Crystal (240-660 $\mu$ )

—○— 'TOTAL'

- -○- - 'TOTAL' AFTER  
POLISHING  
AMR

—●— AMR AFTER  
POLISHING

6 DAYS POLISHING WITH  
ROCK CRYSTAL POLISHING  
AGENT ; SEPARATED BY  
WATER SEDIMENTATION

CURVES A-B INDICATE  
CONTROL EXPTS.  
(UNPOLISHED DUST)

FIG. II

POLISHING TREATMENT APPLIED  
AT THIS POINT

12

10

MG. SILICA/100 ML

4

2

10

20

30

40

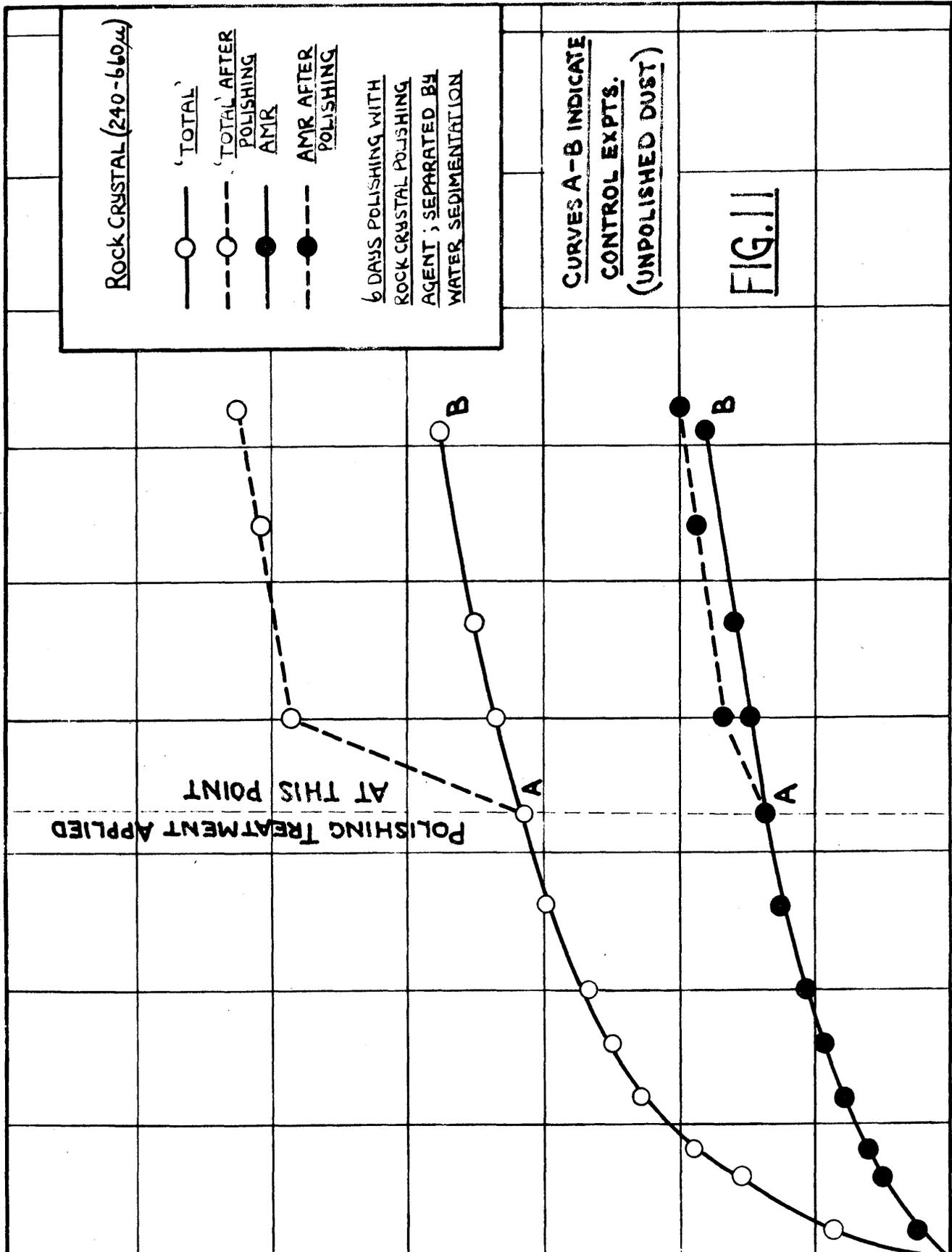
50

60

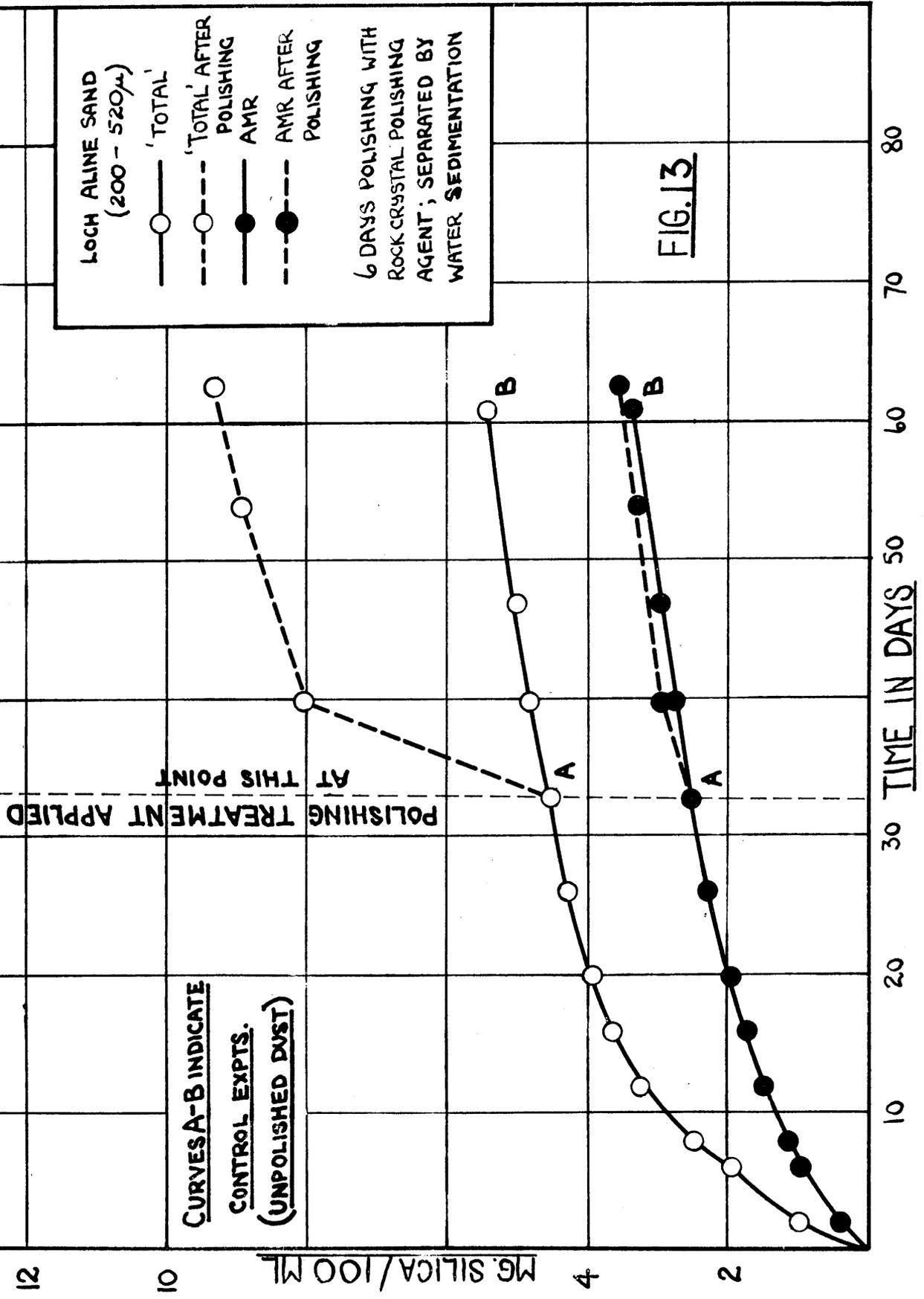
70

80

TIME IN DAYS







high, and then gradually decreased to a low and almost constant rate after about 30 days of agitation with the solvent. It is considered that this constant rate corresponds to complete removal of the high-solubility (HS) layer.

2. The effect of polishing quartz (rock crystal and Loch Aline sand) or vitreous silica surfaces which were free from an HS layer was to increase many times the rate of solution of these surfaces. The increase was similar for dusts prepared from each of the above three substances. The increase in the total silica was much greater than that of the 'ammonium molybdate reactive' silica showing that the silica liberated into solution was mainly in the colloidal form. This high rate of production of colloidal material is similar to that observed during the initial solubility periods of an untreated dust, the period of dissolution of the HS layer being characterised by the production of a high proportion of colloidal material. It is concluded, therefore, that the effect of polishing has been to regenerate an HS layer on the dust surfaces.

3. Figs. 11, 12, and 13 show that in all three cases the new HS layers have been rapidly dispersed by subsequent agitation with the solvent, the solubility/time curves quickly regaining their previous gradient. This may be due to the mild quality of the abrasive action in the polishing treatment, and would seem to indicate that only a very thin layer on the surface has been affected.

(d) Conclusions

Since the HS layer is shown to be regenerated by purely mechanical treatment a close similarity is established between the HS layer and the polish layer of Beilby. It seems most likely, therefore, that the HS layer arises through surface flow on dust particle surfaces, produced by mechanical disturbance during the grinding process and is similar in nature to that shown to be produced during polishing.

but by measuring the amount of adsorption of a dyestuff, methylene blue, on these dusts before and after removal of the HS layer from the dust particle surfaces.

Apart from an interest in the possible importance of the adsorptive processes, it was considered that since the adsorption of substances from the body fluids by dust particles lodged in the lung has been suggested as an important factor in the silicosis reaction, any effect of the HS layer upon adsorptive processes would be some indication of the possible importance of this layer in the pathological reactions resulting in a silicotic condition of the lung.

PART 4Effect of the HS layer on Adsorption at Siliceous Dust Surfaces.(a) Introduction

Since the presence of the HS layer on siliceous dust surfaces was shown in PART 1 to have a controlling influence on their solubility rates in various solvents, it was considered likely that this layer might have some appreciable effect on adsorption processes at dust particle surfaces.

The following experimental work was intended therefore to determine whether the presence of HS layers on the surfaces of three siliceous dusts, (rock crystal, Loch Aline sand and vitreous silica) has any effect upon their adsorptive properties. This was carried out by measuring the amount of adsorption of a dyestuff, methylene blue, on these dusts before and after removal of the HS layers from the dust particle surfaces.

Apart from an interest in the possible importance of the layer in adsorptive processes, it was considered that since the adsorption of substances from the body fluids by dust particles lodged in the lung has been suggested as an important factor in the silicotic reaction, any effect of the HS layer upon adsorptive processes might be some indication of the possible importance of this layer in the pathological reactions resulting in a silicotic condition of lung tissue.

Two dusts of similar size distributions were prepared from each

of three siliceous materials, the two dusts in each case differing only in that the HS layer had been removed from one of them.

Adsorption experiments were then carried out to determine the effect of the removal of the HS layer on the adsorptive properties of these dusts.

(b) Experimental

1. Choice of Adsorbate

It was decided to use a dyestuff as adsorbate since small amounts of these substances in solution may be estimated conveniently by a colorimetric technique. A number of dyes therefore, (a few from each of the main classes of dyestuffs) were tested on a Loch Aline sand dust as a preliminary experiment in order to find the most suitable dye for the adsorption tests to follow. The method of testing the relative adsorptive properties of these dyes was as follows:-

Approximately 0.01 g. of each dye was dissolved in 10 ml. of water, and 1 g. of the Loch Aline sand dust was added. After the dust and dye solution had been in contact for 30 minutes with intermittent agitation, the dust was washed by sedimentation four times from fresh quantities of water. The intensity of colour imparted to the dust was then estimated visually and the results of the tests are shown in Table 14.

It is shown that only the basic dyes have any appreciable

TABLE 14

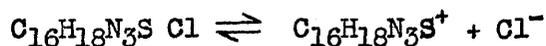
<u>Class</u>	<u>Name</u>	<u>Adsorption</u>
<u>Direct Cotton Dyes</u>	Chorantine Fast Yellow 2RL	Nil
	Chlorazol Fast Scarlet 4BS	Nil
	Chlorazol Sky Blue FFS	Nil
<u>Acid Dyes</u>	Keton Fast Yellow 4BL	Nil
	Napthalene Orange RDS	Nil
	Alizarin Sapphire Blue G	Nil
	Azo Geranine 2GS	Nil
	Solway Blue BNS	Nil
	Lissamine Fast Yellow	Nil
<u>Basic Dyes</u>	Methylene Blue (B.P. Quality)	Strong
	Malachite Green	Strong
	Acridine Orange	Strong
	Magenta	Strong
	Rhodamine	Strong
<u>Sulphur Dyes</u>	Methyl Violet	Strong
	Thionol Indigo Blue 4R200	Nil
	Thionol Olive R300	Nil
	Sulphol Claret 2RL	Nil
	Thionol Brilliant Green 3BS	Nil
	Sulphol Brilliant Blue RL	Nil
	Sulphol Brilliant Green SG	Nil
<u>Vat Dyes</u>	Caledon Jade Green XN300	Nil

Note: The dyes listed above with the exception of Methylene Blue were of "Technical" quality.

affinity for the silica surfaces. The choice of an adsorbate was, therefore, confined to the basic dye class. Methylene blue was finally chosen from that group since it could be most readily obtained in an almost pure state as the B.P. quality.

## 2. The Mechanism of Adsorption of Basic Dyes on Silica

The colour of basic dyes is connected with the positively charged part of the molecule when in solution, e.g. methylene blue ionises thus:-



This would seem to indicate that the adsorption is of an ionic character and that the dye is attracted to the silica surfaces by virtue of its positive charge in solution.

Tests were therefore carried out to determine if the particles of the dusts used in the present work were negatively charged in water suspension. The method employed was similar to that described by Findlay (49) for demonstrating the electrophoresis of colloidal suspensoid sols; the procedure was as follows:-

About 0.5 g. of Loch Aline sand was finely ground in an agate mortar and suspended in distilled water. The suspension was then introduced into the U-tube shown in Plate 1 by means of a funnel connected to the bottom by a length of rubber tubing. The level of the suspension in the U-tube was raised till about 1 mm. of the

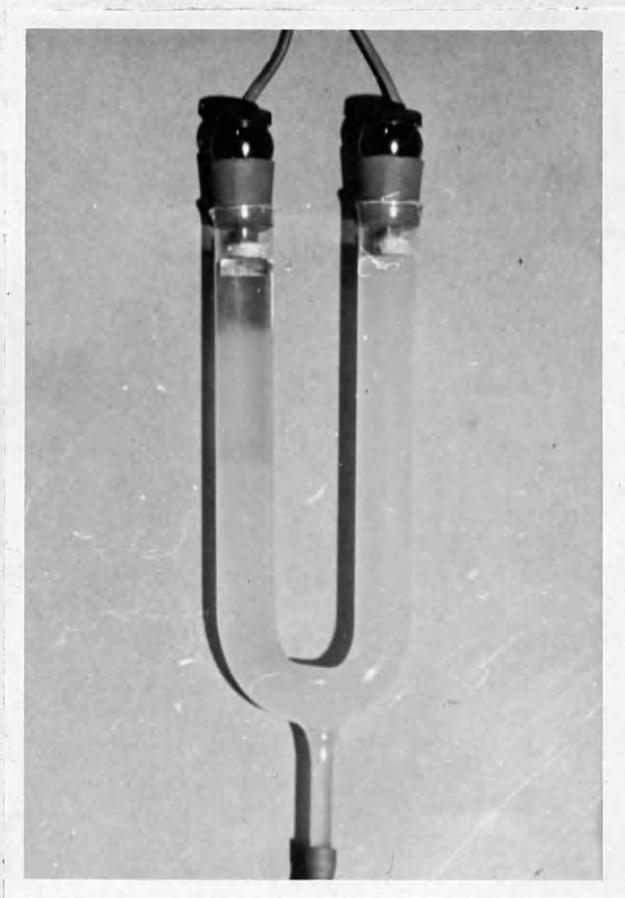


PLATE 1

electrode plates was covered. A direct current of 240 volts was applied across the electrodes and the tube was placed in a position as free as possible from vibration. After 20 minutes a definite migration of the dust particles was observed. Plate 1 shows the test after this condition had been reached; the repulsion of the dust by the negative electrode on the left of the photograph is visible. The charges on the electrodes were determined by reference to a standard accumulator cell. This procedure was then repeated with rock crystal and vitreous silica dusts. It was found that the three dusts tested - Loch Aline sand (under  $1 \mu$ ), rock crystal (under  $5 \mu$ ), and vitreous silica (under  $5 \mu$ ) - were all repelled by the negative electrode, showing that they are negatively charged in water suspension. From these results, therefore, it was concluded that the preferential adsorption by silica of dyestuffs of the basic group is due to their being positively charged in solution and attracted to the negatively charged silica surfaces.

### 3. Materials

#### (i) Preparation of silica dusts

A rock crystal dust (125-200  $\mu$ ) was prepared by reducing large quartz crystals (1-2 cm.) in a steel jaw-crusher and subjecting the product to further reduction in a steel roller mill. The dust was then sieved and the 70-90 mesh B.S.S. fraction obtained was extracted twice for 5 minute periods with concentrated hydrochloric

acid to remove iron picked up during the grinding process. It was observed that the amount of iron contamination was much less in the larger sieve fractions; the iron impurity, being of small particle size, was concentrated in the dust fraction below 200 mesh. After acid treatment the 70-90 mesh fraction was sedimented 10 times from water in order to remove traces of the acid and all particles smaller than 125  $\mu$ ; the dust was then dried at 120°C.

A Loch Aline sand dust (125-475  $\mu$ ) was prepared by repeated sedimentation from water (ca. 20 separations) of a quantity of the natural sand to remove all the particles smaller than 125  $\mu$ . The sedimentations were carried out in a plastic bucket to avoid possible contamination of the dust by contact with a metal container, and the dust was dried at 120°C.

A vitreous silica dust (125-200  $\mu$ ) was produced by reducing a quantity of Transparent Vitreosil (28) (99.8% silica) in a steel roller mill. The product was then sieved and the 70-90 mesh B.S.S. fraction was acid treated, washed repeatedly with water, and dried, similarly to the rock crystal dust described above.

The particle size ranges of all the above dusts were determined microscopically by using a calibrated graticule.

(ii) Preparation of silica dusts without HS layers

Removal of the HS layers from the surfaces of portions of the three silica dusts described above was accomplished by dissolving off

the outer layers of the dust particles in suitable solvents. The rock crystal and vitreous silica dusts were treated with 40% hydrofluoric acid (Analar quality) for 10 minutes and 5 minutes respectively. The shorter time period was employed for the vitreous silica dust since its reaction with the acid is much more vigorous than that of rock crystal. The treatments were carried out in an Alkathene beaker; and, at the end of the treatment period the dissolution of the silica was stopped by dilution of the acid with a large volume of water. The dusts were sedimented 10 times from fresh volumes of water to remove all traces of the acid and were then dried at 120°C.

The solubilities of the dusts in borate buffer solution before and after hydrofluoric acid treatment were determined, by the methods previously described (PART 1, pp. 20 and 45), to ensure that the acid treatment had been effective in removing the HS layers; the results are shown in Table 15. It was found that the untreated dusts gave high total silica results indicating a comparatively rapid liberation of colloidal silica into the solvent, a process which, it was concluded (p. 51), was connected with the dissolution of the HS layer. After hydrofluoric acid treatment the dusts exhibit a much lower rate of production of colloidal silica and the total and AMR solubility values are considerably reduced, indicating that the HS layers have been removed.

Since acid treatment had been shown to increase the solubility

TABLE 15

Solubilities in mg./100 ml. after 8 days in borate buffer pH 7.5 at 37°C; mass/liquid ration 4 g./40 ml.

	<u>Total</u>	<u>AMR</u>	<u>Colloidal</u>
<u>Rock crystal dust (125-200 <math>\mu</math>)</u>			
Untreated	10.25	1.26	8.99
After HF treatment	1.14	0.76	0.38
<u>Vitreous silica dust (125-200 <math>\mu</math>)</u>			
Untreated	9.75	2.60	7.15
After HF treatment	1.80	1.42	0.38

The above results show that the presence of the HF layer in the dust causes a low colloidal silica value. Substantially, values of HF treated silica figures indicating HF layer had been treated.

(iii) Purity of Methylene blue (tetramethylthionine chlori  
 $C_{16}H_{18}N_3ClS \cdot 3H_2O$

The dye used in the following tests was of B.P. quality following specifications from the British Pharmacopoeia (1948) relate to its purity:-

As - Not more than 10 p.p.m.

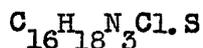
Fb - Not more than 50 p.p.m.

rate of Loch Aline sand dusts (PART 1, Table 8, p. 38) and the HS layer had been shown to be removed by treatment with solvents of pH values 7 and over (PART 1, Fig.1, pp. 28-29) it was decided to remove the HS layer from a portion of the Loch Aline sand dust by agitation with borate buffer solution (pH 7.5). 4 g. quantities of the dust were each agitated in Lusteroid tubes with 40 ml. of the buffer for 24 days at 37°C. The dust was then washed free from the buffer and dried at 120°C. The solubilities of the Loch Aline sand dust before and after treatment were determined to ensure that the HS layer had been removed; these results are shown in Table 16. The solubility figures for the untreated dust show the high rate of production of colloidal silica connected with the presence of the HS layer while after treatment the dust shows a low colloidal silica value and substantially reduced AMR and total silica figures indicating that the HS layer had been removed.

(iii) Purity of Methylene blue (tetramethylthionine chloride,  
 $C_{16}H_{18}N_3Cl \cdot 3H_2O$ )

The dye used in the following tests was of B.P. quality and the following specifications from the British Pharmacopoeia (1948, p. 346) relate to its purity:-

- As - Not more than 10 p.p.m.
- Pb - Not more than 50 p.p.m.
- Zn - A sensitive test for this metal, which should be absent, is specified.



- Not less than 80.0%

TABLE 16

Solubilities in mg./100 ml. after 6 days in borate buffer pH 7.5;  
mass/liquid ratio 4 g./40 ml.

	<u>Total</u>	<u>AMR</u>	<u>Colloidal</u>
<u>Loch Aline sand dust (125-475 <math>\mu</math>)</u>			
Untreated	1.95	0.95	1.00
After buffer treatment	0.37	0.34	0.03

The percentage of  $C_{16}H_{18}N_3Cl.S$  in the dye used was estimated by a volumetric method as follows:-

About 0.4 g. of the dye, accurately weighed into a flask was dissolved in 25 ml. of water and 10 ml. of concentrated hydrochloric acid; the air in the flask was displaced with carbon dioxide, a stream of which was maintained through the flask during the test. 50 ml. of approximately N/10 titanous chloride solution was added, (previously standardised with ferric ammonium sulphate solution) and the mixture boiled gently for 10 minutes. The solution was cooled and the excess titanous chloride titrated with N/10 ferric ammonium sulphate using 5 ml. of 10% ammonium thiocyanate solution as indicator, this being added towards the end of the titration. A blank was carried out omitting the dye and from the difference between the two tests the volume of titanous chloride solution required to reduce the dye was obtained. Each ml. of N/10 titanous chloride solution is equivalent to 0.01600 g. of  $C_{16}H_{18}N_3Cl.S$ . The methylene blue dye was found to contain 83%  $C_{16}H_{18}N_3Cl.S$ .

#### 4. Method

##### (i) Solution of the adsorbate

The methylene blue solution for the adsorption experiments was prepared by dissolving a weighed amount of the dyestuff (0.0570 g.) in water and diluting the solution till it gave a reading between 40 and 50 units on the scale of an EEL colorimeter using a red Ilford

filter No. 608. It was necessary to use a solution of such a concentration that it would give a reading upon the most accurate portion of the logarithmic colorimeter scale. The dilution required to bring the dye solution to this suitable concentration was noted (final volume 16 litres) and the concentration of dye present was then calculated as follows:-

$$0.0570 \times \frac{83}{100} \times \frac{1}{16} = .00296 \text{ g. } C_{16}H_{18}N_3Cl.S/\text{litre.}$$

A number of solutions with a range of known dye concentrations was prepared by diluting portions of the original solution; and by measuring their colour intensities with the colorimeter, it was shown that the concentration of methylene blue in solution varied linearly with the colorimeter reading. By measurement from this graph it was found that a drop in the colorimeter reading of 20 divisions was equivalent to a reduction of the dye concentration by 1.25 mg.  $C_{16}H_{18}N_3Cl.S/\text{litre.}$

To reduce, therefore, the colorimeter reading of 10 ml. of dye solution by 1 division required the removal of,

$$\begin{aligned} \frac{1.25}{20 \times 100} &= 6.25 \times 10^{-4} \text{ mg. } C \ H \ N \ Cl. \ S \\ &= \frac{6.25 \times 10}{319.9} \text{ Gm. Moles } C_{16}H_{18}N_3Cl.S \\ &= 0.195 \times 10^{-8} \text{ Gm. Moles } C_{16}H_{18}N_3Cl.S \end{aligned}$$

$$(\text{Mol. Wt. of } C_{16}H_{18}N_3Cl.S = 319.9).$$

#### (ii) Adsorption Procedure

A portion of the dust to be examined was accurately weighed into a glass colorimeter tube and 10 ml. of the methylene blue

solution was run in from a burette. The tube was closed with a cork coated with paraffin wax. 1 g. quantities of the rock crystal and vitreous silica dusts were used in these tests while 0.25 g. portions of the Loch Aline sand dusts were employed since it was found that the natural sand had a greater affinity for the dye.

At a number of measured time intervals from the time of contact of dust and solution, the colour intensity of the solution was read on the colorimeter. The design of the colorimeter, shown in Fig. 14, rendered possible a direct reading of the intensity of the solution without separating it from the dust. The dusts, from which all particles below  $125 \mu$  had been removed, settled rapidly to the bottom of the tube and did not interfere with the light beam passing through the supernatant liquid. The dusts were shaken with the solution at the end of each reading. A blank test was carried out simultaneously, omitting the dust, the difference in the colorimeter readings of the two being a measure of the adsorption by the dust. The difference in the colorimeter readings of the test and blank at the end of each time interval was multiplied by the factor previously calculated 0.195, to obtain the amounts of methylene blue adsorbed ( $\text{Gm. Moles} \times 10^{-8}$ ); and the resulting values were plotted against time.

Adsorption tests were carried out on the three dusts, rock crystal, Loch Aline sand, and vitreous silica, with and without their HS layers, and the results are shown graphically in Figs, 15, 16, and

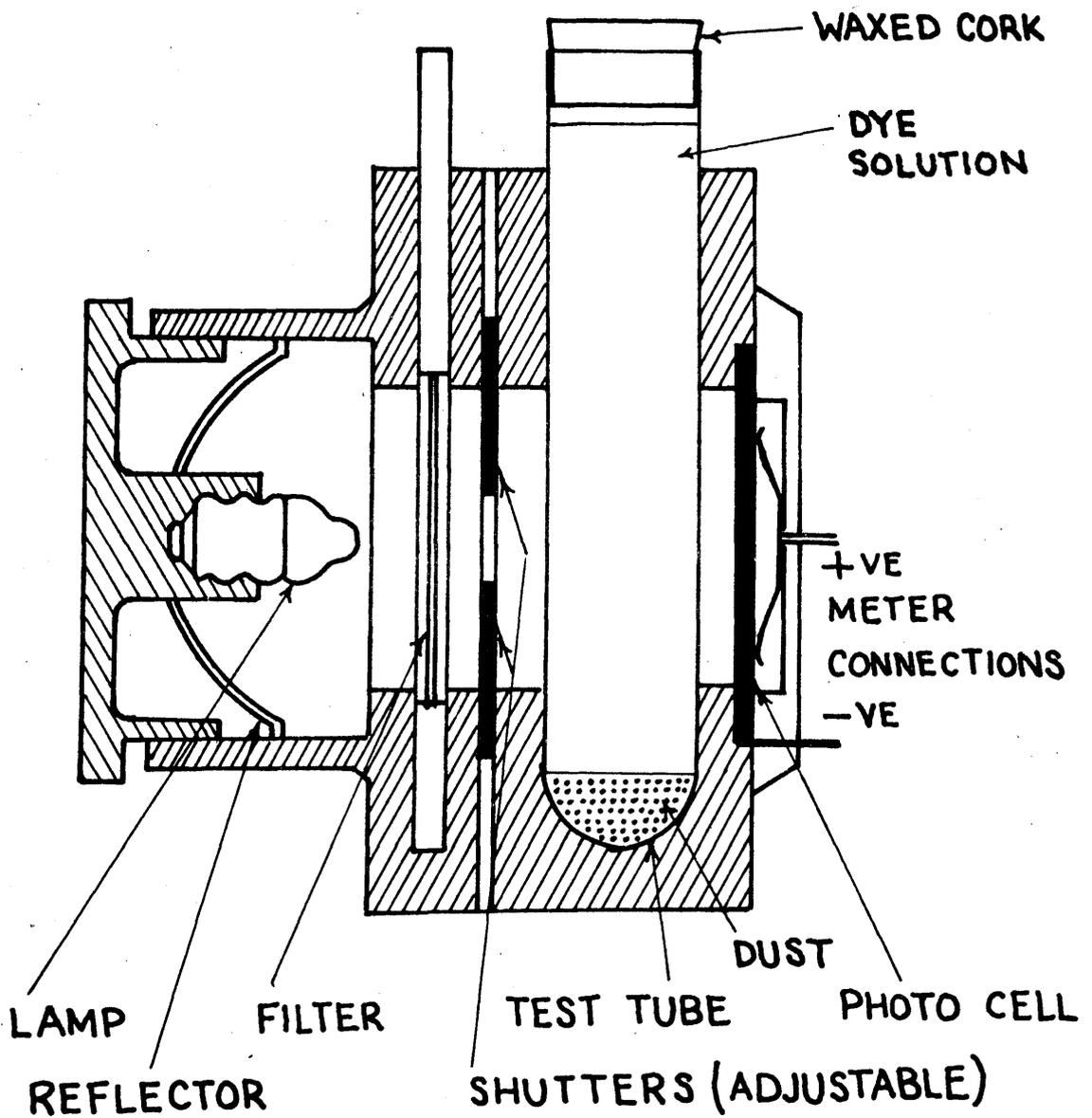


FIG. 14

17.

(c) Conclusions

1. General

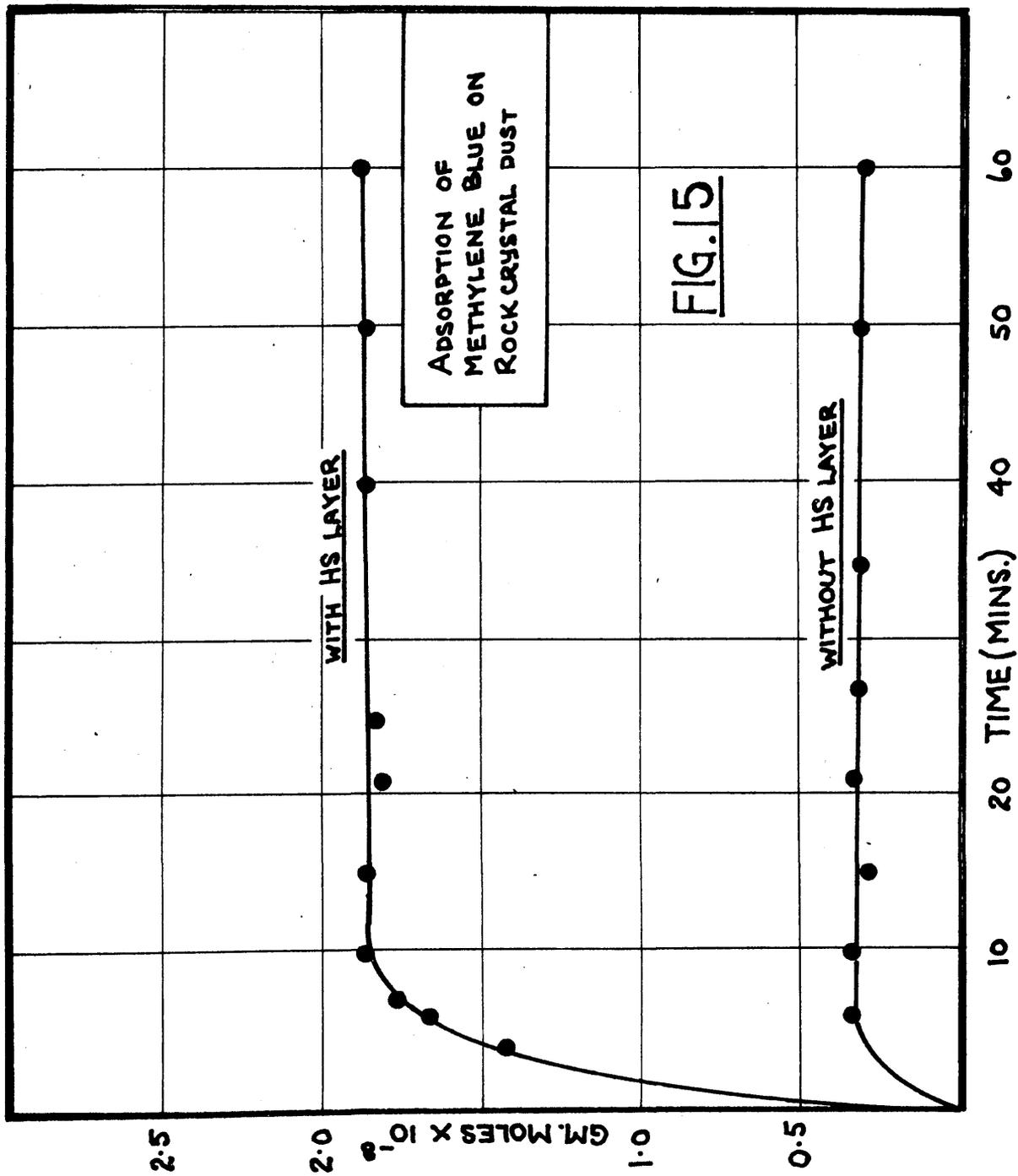
All the dusts have established an equilibrium condition with the dye solution fairly rapidly, this being most marked for rock crystal and vitreous silica dusts, the Loch Aline sand being the slowest of the three in reaching equilibrium.

2. Dusts with HS layers

Of the three dusts the Loch Aline sand showed the greatest affinity for methylene blue; rock crystal came next, and the vitreous silica adsorbed the least amount of the dye. The large differences in the amounts adsorbed cannot be due to differences in the specific surface areas of the dusts since the three have particle size ranges of the same order. The relatively high affinity of Loch Aline sand for the dyestuff would seem to indicate that the activity of the surface in adsorption processes is not connected with its solubility since the Loch Aline sand dust in PART 1 (Table 10, p. 49), has been shown to have a markedly lower solubility than rock crystal or vitreous silica dusts.

3. Dusts without HS layers

The removal of the layer from the rock crystal dust has the effect of decreasing considerably the amount of adsorption which takes



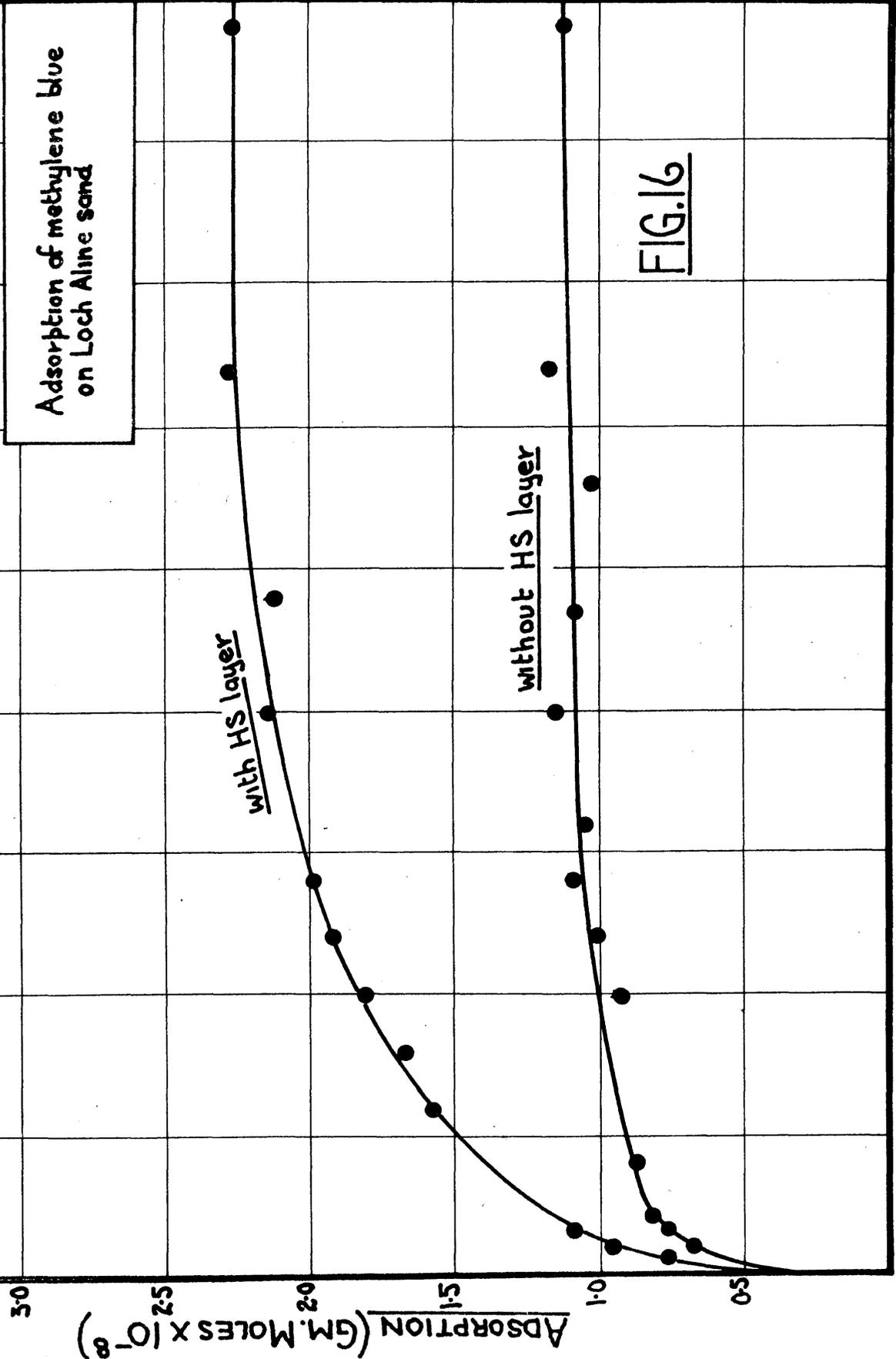
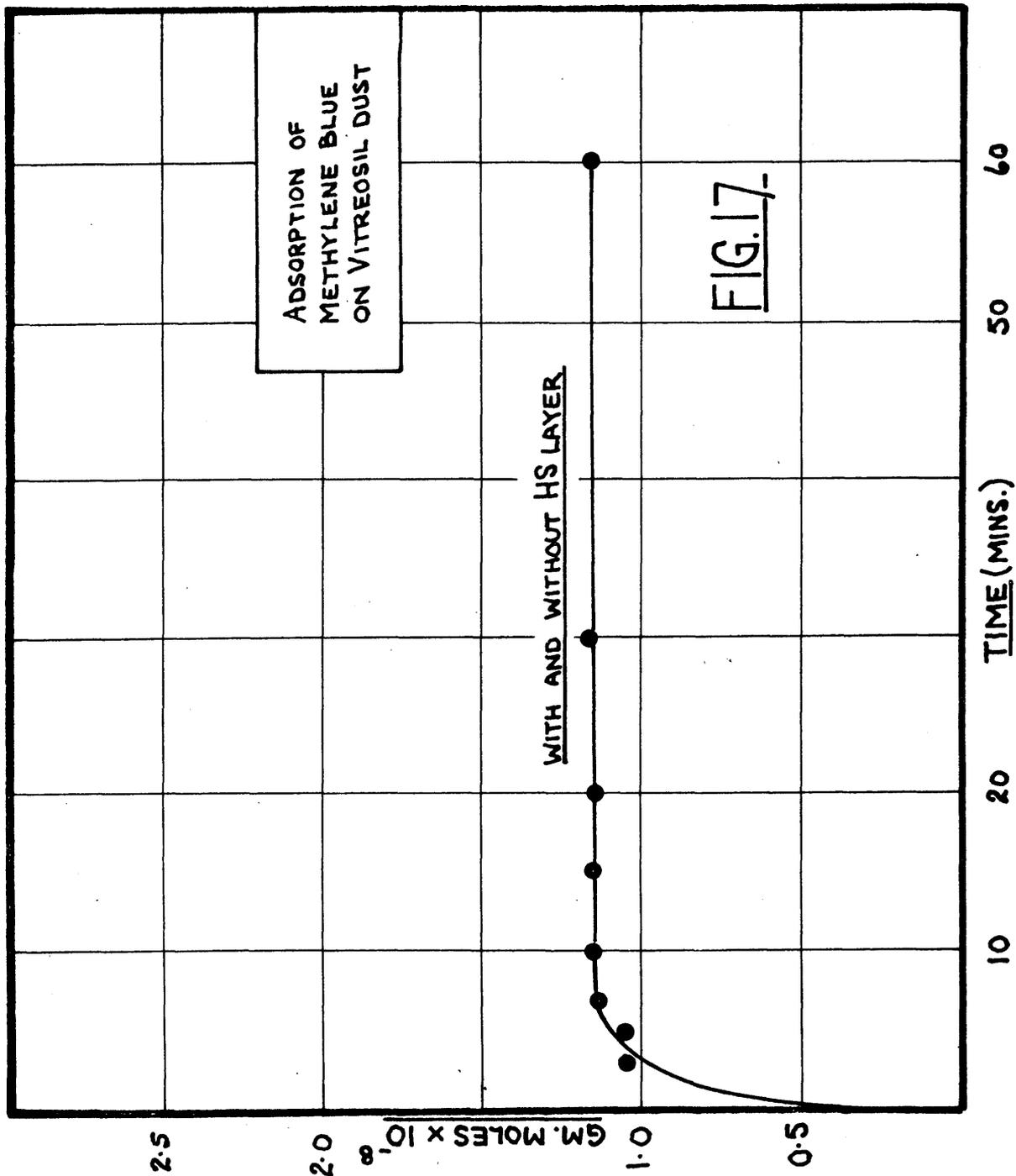


FIG. 16

25 50 75 150 175 200



place at the dust surfaces, the equilibrium adsorption value being reduced to less than one-fifth of its amount when the HS layer is present. The amount adsorbed by the Loch Aline sand dust is reduced similarly, on removal of the HS layer, to about half its former value.

Removal of the layer from the vitreous silica dust however causes no measurable change in the affinity of the dust for the dyestuff and in Fig. 17 the graphs for the two vitreous dusts with and without the layer are coincident and are plotted as the one curve.

There is apparently no obvious connection between the solubility exhibited by a dust and its adsorptive properties, since all three dusts showed a high solubility rate before removal of the HS layer but only two (rock crystal and Loch Aline sand) showed lower affinities for the dyestuff after this layer had been removed.

In the two cases where the adsorptive properties have been decreased this may be explained by postulating that the HS layer has a higher affinity for the dye than the crystal faces beneath the layer. In the case of the vitreous silica dust the removal of the layer has not altered the affinity of the surface for the dye but has altered radically its solution potential. There is therefore a similarity in nature between vitreous silica and the HS layer as far as adsorptive processes are concerned while there is considerable contrast in their properties from the aspect of their solubilities.

The similarity in the adsorptive powers of the two vitreous

silica dusts may be due to there being no radical change brought about in the physical condition of the surface by the removal of the HS layer since it has been concluded (PART 2, pp. 58 and 67) that this layer is of a microcrystalline character bordering on the amorphous state; while, on the other hand, the large difference in the adsorptive properties brought about by the removal of the HS layers from the rock crystal and Loch Aline sand surfaces may be due to a definite change in the surface condition by exposing the fully developed crystalline surfaces beneath the layer.

It is well known that the incident radiation had been cut off by the removal of the HS layer.

These phenomena are generally explained by the theory of internal photoelectric effect, according to which certain electrons in the molecules of the substance being irradiated are displaced to metastable levels by energy from the incident radiation; their return to normal levels requires the release of energy which takes the form of light waves and so produces fluorescence or phosphorescence.

The effect of exposure of quartz and vitreous silica to radiation has been studied by Smith (20) and Quinn (50) and

PART 5The effect of X-ray irradiation on the solubility of siliceous dusts(a) Introduction

Some extraordinary results were obtained from an investigation of the effect of X-ray irradiation on the solubility of siliceous dusts; the reasons for initiating this work are outlined below.

A large number of substances when irradiated by light have been observed themselves to emit light waves. The re-emission of light under the stimulating influence of incident radiation is called fluorescence. When the incident radiation ceases the light emission from the substance may end and this is the case generally for gases and liquids. In solids, however, an after-glow may persist for long periods after the incident radiation had been cut off and this is known as phosphorescence.

These phenomena are generally explained by the theory of internal photoelectric effect, according to which certain electrons in the molecules of the substance being irradiated are displaced from their orbits to metastable levels by energy from the incident radiation; their return to normal levels requires the release of energy which takes the form of light waves and so produces fluorescence or phosphorescence.

The effect of exposure of quartz and vitreous silica to radium radiation has been studied by Beilby (39) and Choong (50) and was shown to produce fluorescence and phosphorescence in both materials,

and at the same time to have the effect of colouring these substances.

Beilby, after exposing a polished lens of rock crystal for four days to the  $\beta$ - and  $\gamma$ - radiation from radium, observed a patch of dark brown colouration where the rays had entered the crystal. On removal from the radiation the coloured patch showed a faint phosphorescence which disappeared after 6 weeks at ordinary temperature. On heating to 100°C. after this time the phosphorescence was revived and the crystal glowed very brightly; on raising the temperature to 250°C. the glow became still more intense, then ceased altogether. After this treatment the brown colouration was found to have disappeared.

After studying the effects of heat in producing revived phosphorescence (thermophosphorescence) in a number of other substances (among which were calcspar; potash glass; flint glass; potassium chloride, bromide and iodide), Beilby suggested that, on the application of heat, the increase in intensity followed by fatiguing of the phosphorescence was due to increased thermal agitation bringing about a faster neutralisation of an ionised condition set up in the material by exposure to the radium radiation.

At each temperature the phosphorescing substance discharges energy till it reaches an equilibrium condition and on raising the temperature to a new value, equilibrium is again reached by a further emission of light. The storage of energy from the incident radiation therefore depends upon the ability of the substance

irradiated to insulate internally the separation of charges brought about within the material. This is in agreement with the known properties of substances generally, since gases and liquids, the molecules of which are relatively mobile, show only very short-lived phosphorescence; whereas longer periods of after-glow are shown by viscous liquids and solid materials.

Choong (50) has made a systematic study of the coloration and luminescence produced by radium rays ( $\beta$  and  $\gamma$ ) on four types of quartz, (colourless, rose, citrine and smoky) in both their crystalline and vitreous conditions. He found that:-

1. All four crystalline varieties turn to a shade of black after radiation; the persistence of the colour on subsequent heat treatment depending on the variety of the quartz.
2. The four vitreous varieties are changed to a violet colour by irradiation.
3. By exposure to these rays the crystalline and vitreous forms of all four types of quartz exhibit fluorescence and phosphorescence.
4. By heating all the radiated forms the colouration and phosphorescence do not disappear simultaneously, phosphorescence being the more persistent.

Choong also showed that by employing X-rays in place of the radium radiation exactly similar colour, fluorescent, and phosphorescent effects were obtained with the crystalline and vitreous forms of these four types of quartz.

In view of these physical changes which have been shown to be brought about by exposure to radium and X-rays the following series of experiments was carried out to determine if exposure of a siliceous dust to one of these radiations (X-rays) has any effect upon the solubility of the dust.

In the diagnosis of silicosis X-ray photographs of the patient's lungs are regularly taken, the mineral deposits in the lung tissues being visible on the plates as white spots. In this way the progress of the disease may be followed. Since it is widely held that the pathogenicity of a dust depends upon its solubility, it was considered to be of some importance to determine whether exposure of siliceous dusts to X-rays had any effect upon their solubilities.

(b) Experimental

1. Materials

A Loch Aline sand dust (200-520  $\mu$ ) was prepared by sedimenting a quantity of the natural sand repeatedly from water to remove all the particles smaller than 200  $\mu$ . The resulting dust was dried at 120°C.

A rock crystal dust (240-660  $\mu$ ) was obtained by reducing quartz crystals (0.5-1 cm. size) in a jaw crusher and further in a steel roller mill. The product was sieved and the 50-70 mesh B.S.S. fraction extracted with concentrated hydrochloric acid to remove iron impurity introduced in the crushing process; the dust was then dried at 120°C.

Five other dusts were prepared as described in PART 1, p. 17 from the following siliceous materials; rock crystal, Loch Aline sand, Vitreosil, olivine and orthoclase felspar; all had average particle sizes of approximately 250  $\mu$ .

## 2. Solubility Determinations

The total and AMR solubilities of the various dusts in borate buffer solution pH 7.5 at 37°C. were measured as described previously (PART 1, pp. 20 and 45) using 4 g. portions of the dusts with 40 ml. of buffer.

## 3. X-ray Exposures

The 4 g. portions of the dusts used in the solubility tests were irradiated with X-rays by enclosing the dust at the bottom of a Lusteroid tube with a circle of filter paper and supporting the tube horizontally with the dust 15 cm. from the target of an X-ray set (Metropolitan Vickers, Raymax). A tungsten target was used to supply the radiation for all exposures; unfiltered radiation was employed, (inherent tube filtration - 0.035 mm. Al) while the tube voltage and current were 70 K.V. and 10 m.a. respectively. All the exposures were carried out at room temperature while the solubilities were measured at 37°C. This rise in temperature was intended to promote thermophosphorescence by emission of the energy stored during the irradiation period. In all the tests the dusts were subject to this rise in temperature after irradiation.

(c) Results

The effects of X-ray exposure on the solubilities of two dusts Loch Aline sand (200-520  $\mu$ ) and rock crystal (240-660  $\mu$ ) were determined by exposing them to the X-rays for periods of 6 and 12 minutes and measuring their solubilities after treatment. Controls in each case were employed, omitting the radiation treatment. The results are shown in Table 17.

The solubility of the Loch Aline sand dust was increases slightly by the 6 minute exposure while doubling the X-ray dosage produced a further small increase. The solubility of the rock crystal dust showed no change which could be regarded as outside the experimental error involved in the method of silica determination. In view of the slight but definite increase in the case of Loch Aline sand it was considered possible that the relatively high rate of solution during the dispersion of the HS layer from these dusts might be masking a small effect due to the radiation treatment. It was decided therefore to test the effect of radiation treatment upon dust surfaces having low solubility rates, i. e. on dusts from which the HS layer had been removed as completely as possible.

Dusts of five siliceous materials, rock crystal, Loch Aline sand, Vitreosil, olivine and orthoclase felspar, of similar average particle sizes (250  $\mu$ ) were submitted to a series of extractive solution periods and their rates of solution were followed by analysis. Extractive solubility curves were obtained by plotting

TABLE 17

Solubilities in mg./100 ml. after 5 days in borate buffer pH 7.5 at 37°C; mass liquid ratio 4 g./40 ml.

<u>X-ray Treatment</u>	<u>Loch Aline sand dust (200-520 <math>\mu</math>)</u>	
	<u>AMR</u>	<u>Total</u>
Nil	.59	2.17
6 Minutes	.66	2.26
12 Minutes	.67	2.35

<u>Rock crystal dust (240-660 <math>\mu</math>)</u>		
Nil	.81	3.70
12 Minutes	.79	3.60

the control group was given the same amount of dust as the first treatment of similar duration to the first. The points of the scale have been located and shown on the graphs (Figs. 1-5), while the letters attached to the arrows indicate the treatment applied (W = Washing, D = Drying, and X = X-ray).

#### (d) Discussion of Results

The radiation treatments of the five dusts are shown to effect upon their total silica curves while little change is

the total amount of silica dissolved from the dust at the end of each solution period against the time from the start of the tests. After 59 days the slopes of the total and AMR silica curves, shown in Figs. 18-22, had been reduced considerably and were assuming fairly constant values; it was assumed then that the HS layers had been removed from the dust surfaces. The 4 g. portions of the dusts used in the solubility tests were then washed free from the borate buffer solvent by five sedimentations from distilled water and dried at 37°C. Each dust was then exposed to X-ray irradiation for 6 mins.; the dosage was measured and found to be approximately 4,300 Roentgens. After this treatment borate buffer solvent was added and the solubility tests continued. As a control these tests were later interrupted again and the dusts were washed in the same manner as before, and dried at 37°C., while the radiation treatment was omitted. Following the control procedure the dusts were exposed to a second X-ray treatment of similar duration to the first. The points at which the dusts have been treated are shown on the graphs (Figs. 18-22) by arrows, while the letters attached to the arrows indicate the type of treatment applied (W = Washing, D = Drying, and X = X-ray exposure).

#### (d) Discussion of Results

The radiation treatments of the five dusts are shown to have most effect upon their total silica curves while little change has been generally brought about in the AMR silica values.

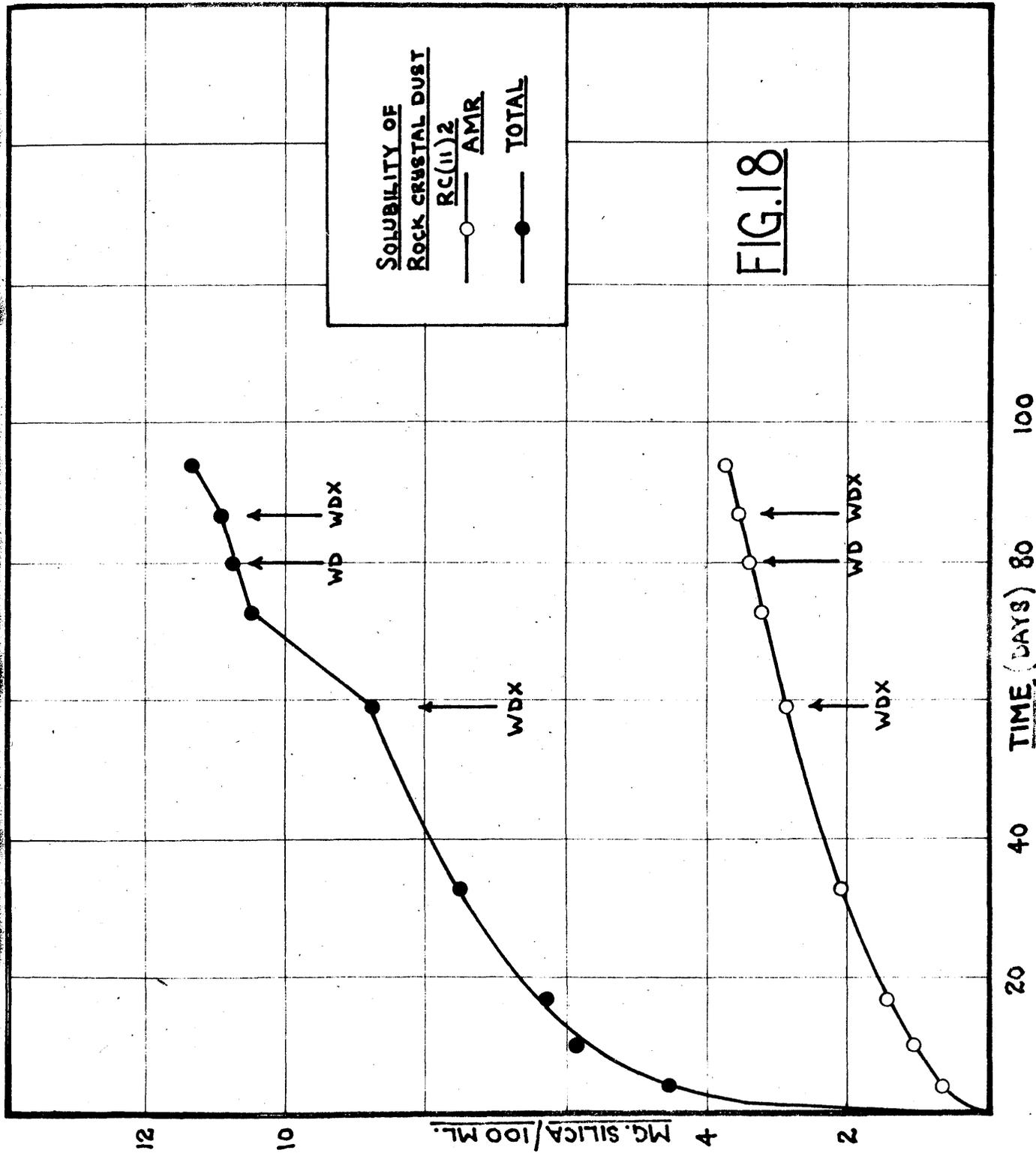
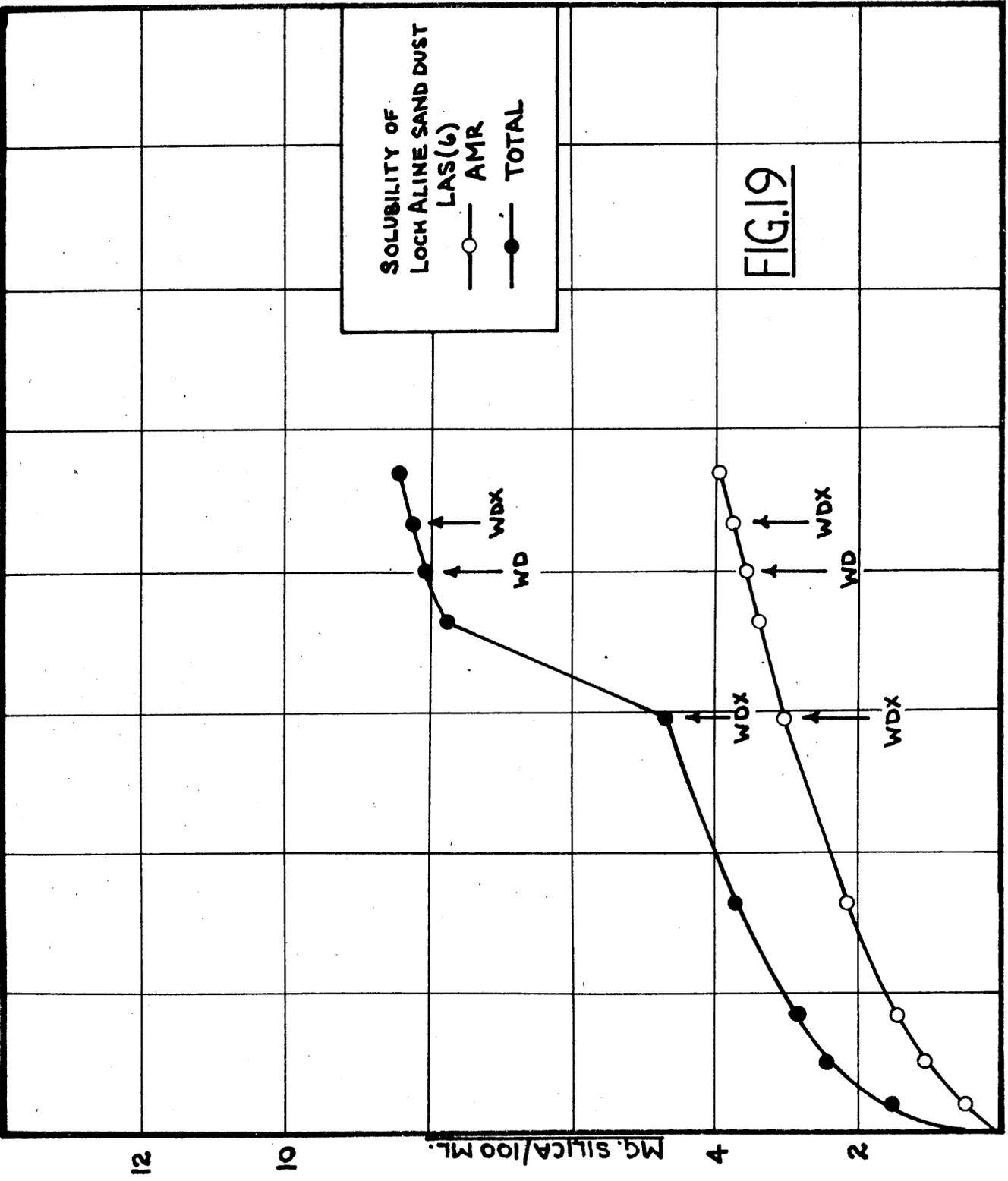


FIG.18



**FIG.19**

20 40 TIME (DAYS) 80 100

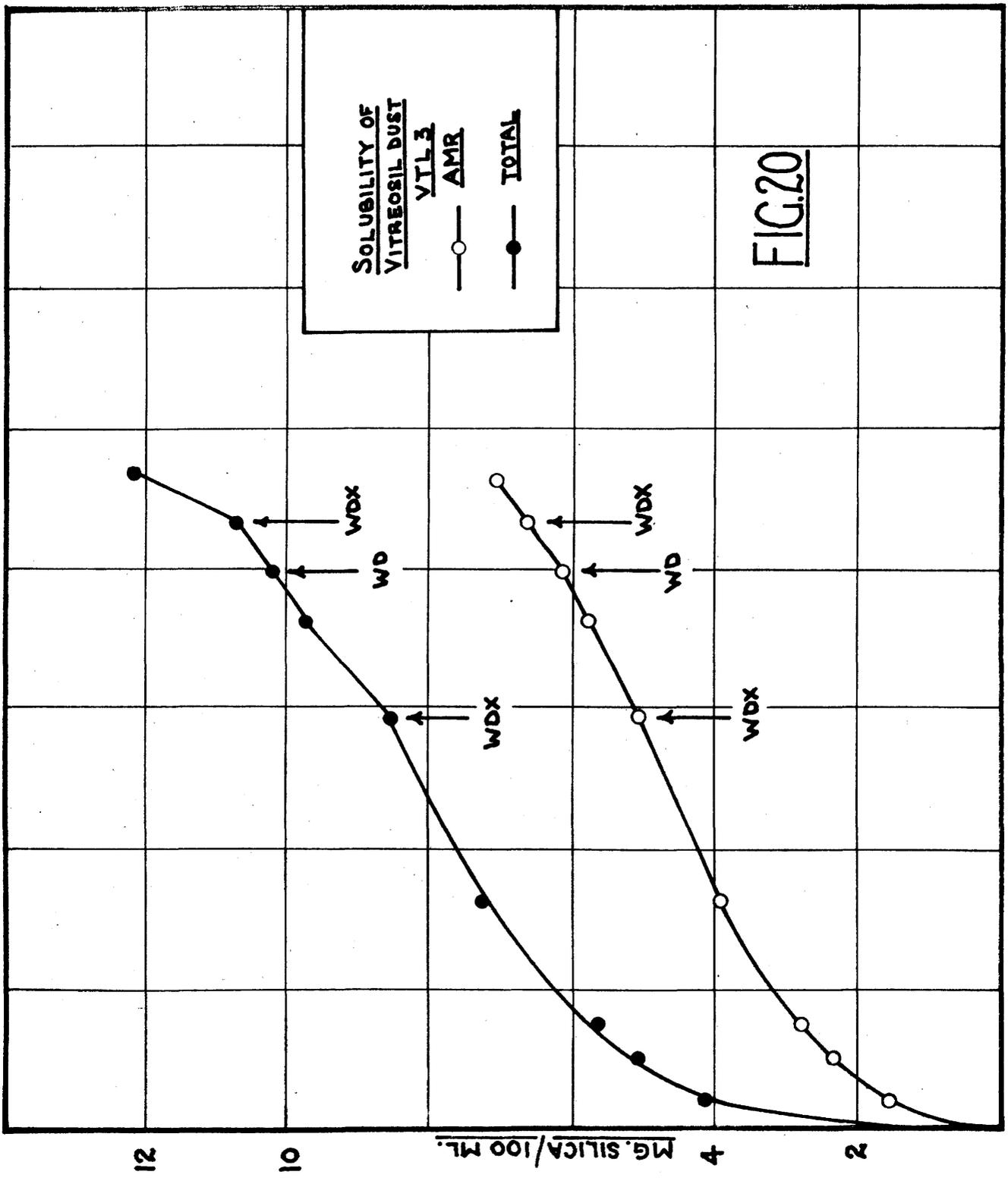
12

10

MG. SILICA/100 ML.

4

2



**FIG. 20**

TIME (DAYS)

MG. SILICA/100 ML.

12

10

4

2

20

40

80

100

WDX

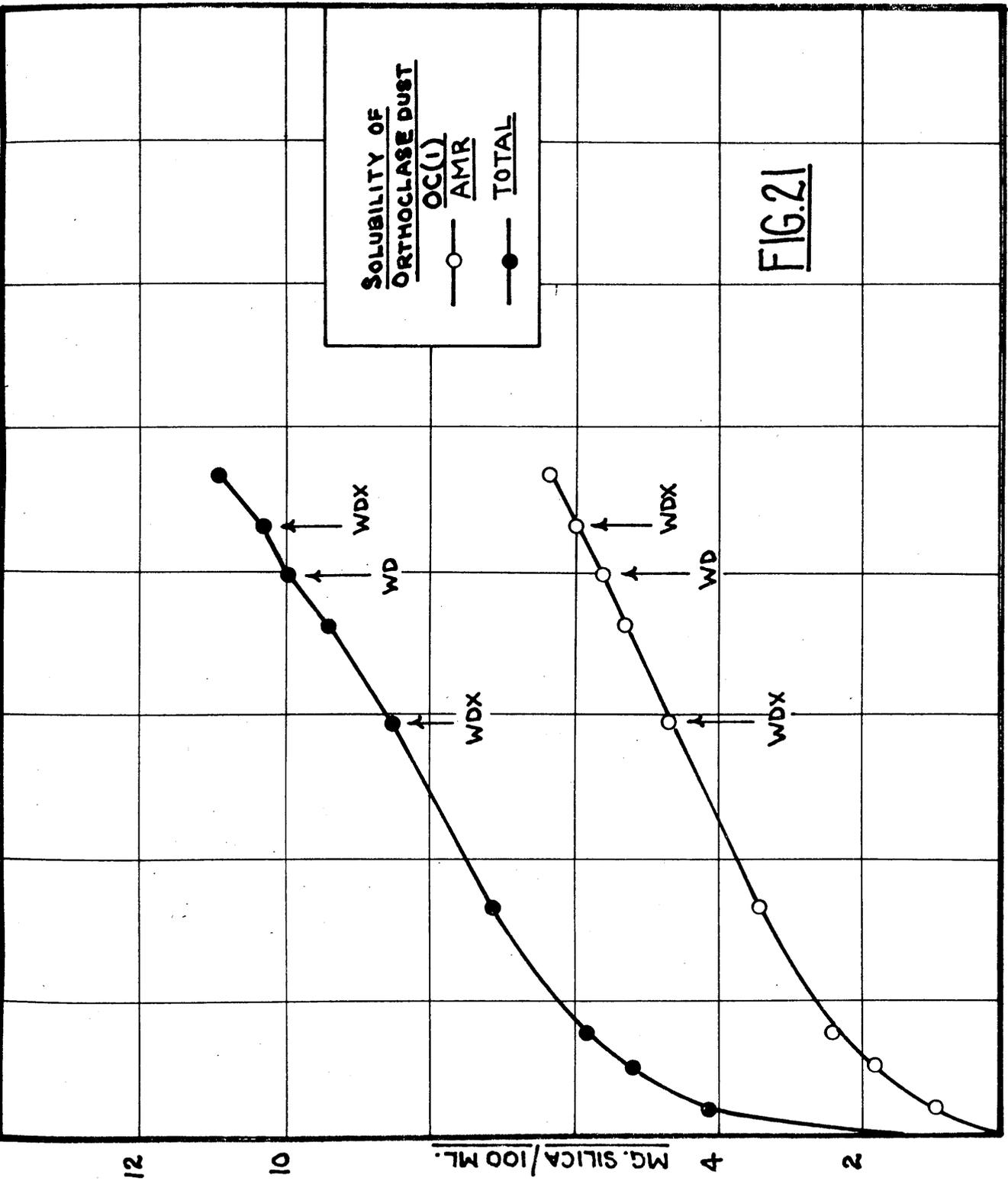
WD

WDX

WDX

WD

WDX



**FIG. 2.1**

100  
80  
40  
20  
TIME (DAYS)

12  
10  
MG. SILICA / 100 ML.  
4  
2

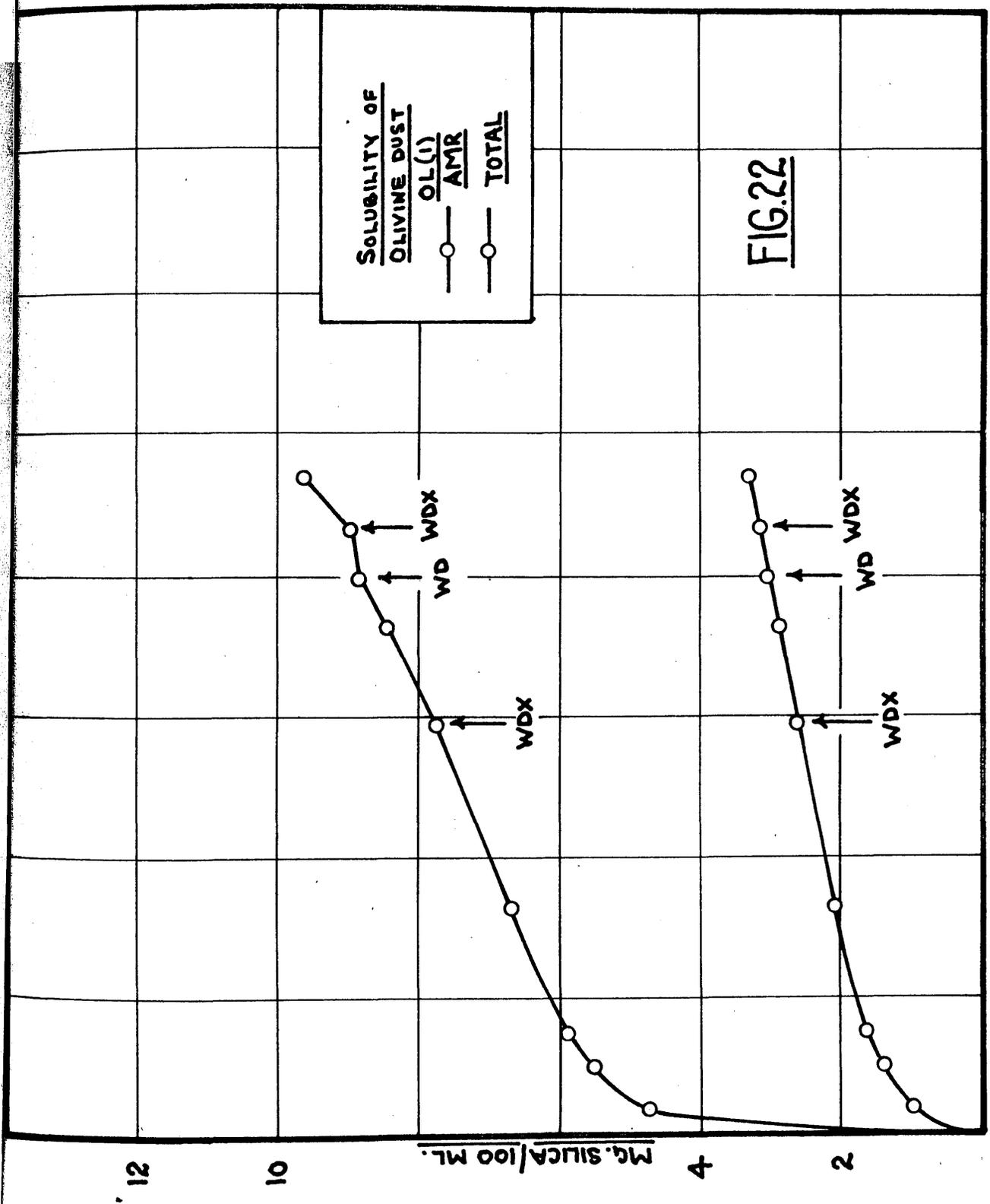


FIG. 22

SOLUBILITY OF OLIVINE DUST

$\frac{OL(1)}{AMR}$

TOTAL

MG. SILICA/100 ML.

TIME (DAYS)

12

10

4

2

20

40

80

100

The washing and drying control treatments have no effect in increasing the solubility rates of the dusts, (this has been shown previously for Loch Aline sand in PART 1, Table 7, p.37) and so where increases have been observed these are attributed to the effect of the X-ray irradiation.

#### 1st Irradiation Treatment

After the first X-ray exposure all five dusts exhibited an increased rate of solution shown by the greater slopes of their total silica curves; this was most marked for the Loch Aline sand, rock crystal and Vitreosil dusts. With the exception of the latter dust the AMR silica curves were not affected by the first X-ray exposure and therefore the increases in the total silica values by the irradiation treatment are due to increased rates of production of colloidal silica. A slight increase in the rate of solution of AMR silica from the Vitreosil dust was brought about by the first X-ray exposure, but since this increase is not sufficiently large to account for the higher value reached by the corresponding total silica curve the higher solubility is therefore due mainly to a larger amount of colloidal silica being formed and to a lesser extent, an increase in the amount of dissolved silica.

#### 2nd Irradiation Treatment

The second X-ray exposure produced large increases in the total silica solubility rates of the rock crystal and Vitreosil dusts; and smaller increases for the orthoclase and olivine dusts; while the Loch

Aline sand showed no measurable change.

The AMR silica curves for all the dusts except Vitreosil, again showed no change on X-ray irradiation; so that the increases in the total solubilities were again due to the production of colloidal silica at a greater rate. The vitreous silica AMR value was increased but not sufficiently to account for the rise in the corresponding total silica curve indicating that, similar to the effect of the first exposure, the increase in solubility was due mainly to the dispersion of colloidal silica and to a lesser extent the production of more dissolved silica.

(e) Conclusions

1. Dusts with HS layers

X-ray irradiation of a Loch Aline sand dust was found to increase slightly its solubility in borate buffer solution while similar treatment had no measurable effect upon the solubility of a rock crystal dust.

2. Dusts with HS layers

X-ray irradiation of five siliceous dusts (rock crystal, Loch Aline sand, Vitreosil, orthoclase and olivine) from which the HS layers had been removed, was found to increase their solubility rates, the additional silica yielded into solution due to the irradiation treatment, was mainly in the colloidal form although a small part of the increase in the solubility rate of the Vitreosil dust was due to

dissolved (AMR) silica.

The Loch Aline sand dust after first exposure showed the largest increase in solubility, while after a second irradiation treatment no change in its solubility was observed. This may be due to the effect having been fatigued by the first exposure. The dusts containing the largest amounts of silica (rock crystal, Loch Aline sand and Vitreosil) showed the greatest changes in their solubility rates due to X-ray exposure while the silicate mineral dusts (olivine and orthoclase feldspar) showed smaller changes on irradiation treatment.

#### Acknowledgment

The author gratefully records his thanks to Mr. T.S. Wylie (Physics Dept., Royal Technical College) for carrying out the X-ray irradiation treatments.

Specialist reports on the physiological effects of dusts, and a detailed account of the results of the present work, are to be published in the Journal of the Royal Society of Medicine, and are being prepared for publication by the Royal Society of Medicine. The present work has been carried out in the Department of Physiology of the Royal Society of Medicine, and is being published in the Journal of the Royal Society of Medicine.

Regarding the general validity of the solubility theory of silicosis, it follows that the HS layer is most likely to be

PART 6Discussion of Results and Suggestions for Future Work(a) The HS layer

The most important result arising from the present work is the demonstration of the existence of the HS layer on siliceous dust particle surfaces. This phenomenon has not hitherto been investigated and it is considered that the establishing of the presence of this layer contributes to a clearer understanding of the solution mechanism of dust particles.

It has been shown that the HS layer has special properties in that its dissolution results in the production of relatively large amounts of colloidal silica while the solution of the crystal surfaces lying beneath the layer yield much less silica in this form. It is suggested, therefore, that when dust particles trapped in the lung come into contact with the lung fluids, and during the initial dissolution period when the HS layer is dispersed, such a rapid production of colloidal silica, similar to that observed in vitro during the present work, may have an important bearing on the initiation of the physiological changes resulting in the silicotic condition of the lung tissue.

Assuming the general validity of the solubility theory of silicosis, it follows that the HS layer is most likely to have a major role in the disease mechanism since its presence has been found throughout the investigation to have a controlling effect

upon the solubility values obtained for all the siliceous dust tested.

It is therefore suggested that a complementary investigation in the medical field would be of value to determine the part played by the HS layer in the initiation and development of silicosis. This might be achieved by preparing quartz dusts of similar particle size, with and without HS layers, and analysing the tissue changes effected by similar doses of each after their subcutaneous injection into mice.

(b) The nature of the HS layer

By investigating the changes brought about in the density of quartz by prolonged grinding treatment, and by coupling the results with an examination of the dusts for other silica modifications (cristobalite and tridymite), it was concluded that prolonged grinding of quartz converts a portion of it to the vitreous state.

This result would seem to indicate that a very fine dust of pure quartz cannot be produced by grinding, since this process necessarily entails the conversion of some of it to the vitreous form.

It is suggested that when the grinding process is of short duration only a thin surface layer of the crystalline particles is converted to the vitreous state. It is postulated that this change is similar in nature to the production of the Beilby layer brought about by polishing. A polishing treatment has been shown to regenerate the HS layer on dust surfaces from which the original layer had been previously removed, and it is therefore suggested that

the HS layer is similar in nature to the Beilby layer and is produced on the dust particle surfaces by the grinding treatment during their formation.

Beilby (39) has shown that the surface layer produced by polishing is a general phenomenon and has demonstrated its formation on a large number of materials both crystalline and amorphous. It may follow that initial high solubility rates, similar to those exhibited by the siliceous dusts tested in the present work, may be exhibited by dust particles of other materials. This hypothesis was not tested, the investigation being confined entirely to siliceous materials, although this is considered to be a promising subject for further work.

(c) The effect of the HS layer on adsorptive processes

Following the establishing of the existence of the HS layer on siliceous dust surfaces, the work was extended with the object of ascertaining the importance of this layer in adsorption mechanisms. Since adsorption is a surface effect it was considered most likely that the presence of such a layer might well have a major role in adsorptive processes.

This was borne out in finding that the removal of the HS layer from quartz dust surfaces decreases greatly the affinity of these surfaces for a basic dyestuff (methylene blue).

Further work showed that no measurable change was effected, in the affinity of a fused silica dust for methylene blue, by removal of

its HS layer. This difference in the behaviour of crystalline and vitreous silica dusts, it is suggested, is an indication that the HS layer and vitreous silica have some common factor in their physical nature such that the removal of the layer from the vitreous silica dust does not alter the affinity of its surfaces for the dyestuff.

It is also suggested that the large differences in the adsorptions on the quartz dusts with and without their HS layers are due to the layer being of radically different physical nature from the crystalline structure of quartz.

This postulate is apparently in full agreement with the experimental results obtained from the adsorption tests. However, when this is examined again in the light of the solubility results, an apparent contradiction appears. If it is assumed that the high solubility rate of the HS layer on quartz dusts is due to its being of different physical nature from quartz, then it would seem to follow that the vitreous silica dust should show no high initial solubility rate if the HS layer and vitreous silica are similar in nature. An HS layer has, however, been shown to be present on vitreous silica as well as quartz dusts. This would appear to indicate that the solubilities of these dust surfaces and their adsorptive properties are not controlled by the same aspect of the physical natures of their surfaces, making it possible to alter the surfaces in such a way as to affect greatly their rates of solution without changing their adsorptive properties.

Beilby (39) suggested that the polish layer on crystalline substances was amorphous, and other workers (40) have shown since that from the amorphous surface of the layer inwards, the degree of crystallinity increases gradually, and finally blends with the single crystal structure of the body of the material. Beilby showed that a polish layer is developed on amorphous as well as on crystalline surfaces by polishing, and that such a layer has quite different properties from those of the body of the material. It would seem, therefore, that the difference in nature of the polish layer on an amorphous solid and the body of the material must be subtle, yet nevertheless fundamental enough to produce a marked contrast in their properties. The results obtained in the present work indicate such a subtle difference in the nature of the HS layer and the physical condition of vitreous silica both exhibiting similar adsorptive properties but markedly different solubility rates.

The role of the HS layer in adsorption processes might be further investigated with a view to determining its possible importance in the pathological changes characteristic of silicosis. Such work might profitably be directed to the effect of the HS layer on the adsorption by silica dust particles of organic constituents of body fluids, e.g. proteins, since such adsorptive processes have been suggested (12) as possible causes of the destruction of lung tissue.

(d) The effect of X-ray irradiation on the solubility of Siliceous dusts

The results obtained in the present work show that X-ray irradiation can effect large changes in the solubility rates of siliceous dusts. The tests were designed mainly to establish the existence or absence of any effect by such irradiation treatment, since, as far as could be ascertained, no previous work has been carried out on this subject.

It has been found that the solubilities of five siliceous dusts (rock crystal, Loch Aline sand, Vitreosil, orthoclase feldspar, and olivine) from which the HS layers had previously been removed, are increased by X-ray irradiation treatment, and that the additional silica yielded into solution is mainly in the colloidal form. A slight increase was observed in the solubility of a Loch Aline sand dust, having its HS layer intact, after exposure to X-rays, while similar treatment was found to produce no measurable change in the solubility of a rock crystal dust with its HS layer.

While the present work has established the presence of an effect upon the solubility by X-ray irradiation, sufficient evidence is not available to allow postulation as to the mechanism of the effect. It is considered that further study might profitably be directed to the reasons for such changes together with an investigation from the medical point of view into the possible hazards which might arise from such effects.

APPENDIXIntroduction

To preserve the flow in presentation of the main body of the work, two experimental sections have been included in the APPENDIX.

Section 1 describes a preliminary investigation of the Molybdenum Blue method of silica analysis and the resulting modifications to this method for its use in solubility experiments; the final standard procedure which was developed and used throughout for solubility tests is described in PART 1, p. 20.

Section 2 describes a field investigation which was carried out at Plean Colliery, Stirlingshire, and which is complementary to the work described in PART 2, on the effect of prolonged grinding on quartz.

with a solution of sodium silicate in which was neutralising the excess sodium carbonate with hydrochloric acid diluting the solution to a measured volume. Two sets of standards in the method were also prepared separately.

Calibration curves were then obtained using the three solutions according to the method of Harrison & Storr as follows:

Reagents

3% sodium molybdate in N. H<sub>2</sub>SO<sub>4</sub>

Section 1An Investigation of the Molybdenum Blue Method of Silica Estimation

The Molybdenum Blue colorimetric method of silica analysis as described by Harrison and Storr (33) was investigated and it was developed for use in determining the amount of silica in buffer solutions. This method was chosen since it is a fast method and may be used to determine extremely small amounts of silica in solution.

The Molybdenum Blue method depends upon the formation of a yellow silico-molybdic acid complex when ammonium molybdate is added to silica solutions. This yellow colouration is reduced by addition of quinol and sodium sulphite to Molybdenum Blue and under standard conditions the intensity of the blue colour produced may be measured colorimetrically and calibrated with the amount of silica in the original solution. The method was tested by preparing separately three standard silica solutions by fusing weighed amounts of quartz with sodium carbonate (Analar quality) in a platinum crucible and dissolving the resulting sodium silicate in distilled water, neutralising the excess sodium carbonate with hydrochloric acid and diluting the solution to a measured volume. Two sets of reagents used in the method were also prepared separately.

Calibration curves were then obtained using the three standard solutions according to the method of Harrison & Storr as follows:-

Reagents

5% ammonium molybdate in N.  $H_2SO_4$

5% quinol solution containing 1 ml. N.  $H_2SO_4$  in 100 ml. of solution.

20% sodium sulphite solution.

The reagents were all prepared with distilled water.

#### Method

A volume of silica solution to be analysed is measured into a graduated 50 ml. flask and 2 ml. of the ammonium molybdate solution added; the yellow colour produced is allowed to develop for a fixed time (not less than 2 mins.) and 2 ml. of quinol solution and 3 ml. of the sodium sulphite solution are then added; the solution is then diluted to 50 ml. with distilled water and the blue colour produced is allowed to develop for a fixed period (not less than 15 mins.) before reading the intensity of colour on a Spekker Photoelectric Absorptiometer using an Ilford red filter No. 608.

The results obtained using the three standard silica solutions are shown in Table 18. These results show failure to duplicate accurately points on a calibration curve. Since the procedure had been closely standardised, the only factor which had not been controlled was the amount of hydrochloric acid used in neutralising the excess sodium carbonate in the preparation of the standard solutions. Two more silica solutions of known concentration were therefore prepared except that sulphuric acid was used in place of hydrochloric. It was found using these solutions that the blue colour intensities produced with a series of different amounts of silica could be reproduced accurately; the results are shown in Table 19.

TABLE 18

<u>Mg. Silica</u>	<u>Spekker readings using three standard silica solutions</u>		
0.1	.113	.182	.181
0.2	.210	.334	.345
0.3	.324	.490	.517
0.4	.429	.645	.695
0.5	.539	.800	.885

(Yellow and blue colour developments, 2 and 20 mins. respectively)

was interfering with the test. It was found that the amount of silica to be excluded to prevent the appearance of a blue colour was

**TABLE 19**

By using the following amounts of silica in the test solutions

<u>Mg. Silica</u>	<u>Spekker readings using two standard silica solutions</u>	
0.1	.134	.132
0.2	.272	.267
0.3	.406	.415
0.4	.507	.577
0.5	.726	.735

Experiments on phosphoric acid, iron, calcium and magnesium were possible to give similar results. It was found that in the long run it is possible to use a buffer solution

**(Yellow and blue colour developments, 2 and 20 mins. respectively)**

Interference with the Molybdenum Blue test of analysis (33) is a dearth of buffer solutions with pH values in the normal range which do not contain phosphate.

A Clark and Lobb (51) phosphate buffer containing dissolved silica was tested with the analysis reagents and no blue colour was obtained the resulting solution being coloured yellow.

Palitzsch's buffer solution was prepared by mixing 200 ml. M/20 sodium borate solution (19.108 g.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ /litre) 1300 ml. of M/5 boric acid, sodium chloride solution (12.404 and 2.925 g. NaCl in 1 litre). This buffer did not interfere the production of the blue colour but since it contains a

It was concluded that the presence of chloride ions in the solutions was interfering with the rate of development of the colours and must be excluded to preserve the accuracy of the method as defined above.

By using the two different sets of reagents it was found possible to obtain reproducible results and points on the calibration curve could be duplicated accurately using different sets of reagents prepared separately.

Since the method of analysis was intended for use in solubility experiments on siliceous dusts, and since it was desired as far as possible to simulate in these solution tests, the conditions pertaining in the lung, it was decided to use a buffer solution within the pH range 7.3 - 7.5, the pH of body fluids (30). The presence of phosphate interferes with the Molybdenum Blue method of analysis (33) and there is a dearth of buffer solutions with pH values in the physiological range which do not contain phosphate.

A Clark and Lubs (51) phosphate buffer containing dissolved silica was tested with the analysis reagents and no blue colour was obtained the resulting solution being coloured yellow.

Palitzch's buffer solution was prepared by mixing 200 ml. of M/20 sodium borate solution (19.108 g.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$ /litre) with 1800 ml. of M/5 boric acid, sodium chloride solution (12.404 g.  $\text{H}_3\text{BO}_3$  and 2.925 g.  $\text{NaCl}$  in 1 litre). This buffer did not interfere with the production of the blue colour, but, since it contains chloride ions which had been previously shown to affect the method of analysis,

the following tests were carried out to determine the effect of Palitzsch's buffer solution upon the rate of development of the molybdenum blue colour. The reagents were added as described above to solutions of known silica concentration with and without the presence of the buffer; the results (Table 20) show that the presence of buffer increases the intensity of the blue colour produced.

Further tests (Table 21) showed that an increase in the amount of buffer in the solution to be analysed produces molybdenum blue colours of higher intensity. It was also found that, with 10 ml. of Palitzsch's buffer solution present and after a blue development time of 20 mins., the intensity of the colour was still changing fairly rapidly; this is shown from the results in Table 22. The rate of change of intensity is less with the lower silica concentrations.

The effect of variation of the yellow colour development time was also investigated in the presence of 2 ml. of buffer solution and the results in Table 23 show that as this development time is increased the intensity of the resulting blue colour is higher. A long blue colour development time was employed in these tests so that any errors arising from reading the intensity of one solution before another would be negligible compared to the total time.

The results of Tables 22 and 23 emphasise the necessity for strict observance of standard development times and it was found that when this was done reproducible results were obtained in the presence of Palitzsch's buffer solution when the same amount of this

TABLE 20

<u>Mg. Silica</u>	<u>Palitzsch's buffer present</u>	<u>Spekker readings</u>
0.1	Nil	.115
0.1	9 ml.	.137
0.2	Nil	.225
0.2	18 ml.	.268

(Yellow and blue colour developments, 2 and 20 mins. respectively)

TABLE 21

<u>Mg. Silica</u>	<u>Palitzsch's buffer</u>	<u>Spekker reading</u>
<u>Mg. Silica</u>	<u>Palitzsch's buffer present</u>	<u>Spekker reading</u>
0.1	Nil	.122
0.2	10 ml.	.138
0.3	20 ml.	.151
0.4	30 ml.	.170

(Yellow and blue colour developments, 2 and 20 mins. respectively)

0.5	10 ml.	.187
0.6	10 ml.	.178
0.7	10 ml.	.193

(Yellow colour development, 2 mins.; blue colour development, 20 mins. shown in parentheses)

TABLE 22

<u>Mg. Silica</u>	<u>Palitzsch's buffer present</u>	<u>Spekker reading</u>	
		<u>(25-30 mins.)</u>	<u>(45-50 mins.)</u>
0.1	10 ml.	.132	.131
0.2	10 ml.	.257	.260
0.3	10 ml.	.375	.393
0.4	10 ml.	.505	.542
0.5		<u>(15-20 mins.)</u>	<u>(25-30 mins.)</u>
0.5	10 ml.	.605	.627
0.6	10 ml.	.722	.762
0.7	10 ml.	.878	.911

(Yellow colour development, 2 mins.; blue colour developments are shown in parenthesis.)

TABLE 23

<u>Mg. Silica</u>	<u>Palitzsch's buffer present</u>	<u>Yellow colour development (mins.)</u>	<u>Blue colour development (hours)</u>	<u>Spekker reading</u>
0.2	2 ml.	0.5	19	.495
0.2	2 ml.	1	19	.502
0.2	2 ml.	2	19	.514
0.2	2 ml.	4	19	.537
0.2	2 ml.	8	19	.540

concluded that this is the standard case which should be used as a standard when estimating the silica concentrations of a series of solutions.

It was found that a series of 12 solutions with different amounts of silica each in 10 ml. of Palitzsch's buffer solution could be estimated accurately at the same time by lengthening the yellow colour development time from 2 to 18 mins. and using a blue colour development period of 2½ hours. With these as standard development times the solubility of a fine siliceous dust D80 in Palitzsch's buffer solution was measured as previously described (PART I). In further experiments, however, it was found more convenient

buffer was present in each of the tests.

When a large number of tests were to be carried out at the same time the difficulty of adding the reagents simultaneously to a series of solutions and the higher rate of colour development initiated by the presence of the buffer combined to decrease the accuracy of the method.

The optimum blue development time for estimating the silica content of 10 ml. of Palitzsch's buffer was found by reading the intensity of the blue colour produced by 0.2 mg. of silica (2 mins. yellow development) after different blue development periods. The results in Table 24 show that after  $2\frac{1}{2}$  hours blue colour development, the intensity of the colour is increasing only very slowly and it was concluded that this is the shortest time which should be taken as a standard when estimating the silica concentrations of a series of solutions.

It was found that a series of 12 solutions with different amounts of silica each in 10 ml. of Palitzsch's buffer solution could be estimated accurately at the same time by lengthening the yellow colour development time from 2 to 15 mins. and using a blue colour development period of  $2\frac{1}{2}$  hours. With these as standard development times the solubility of a fine siliceous dust DRC in Palitzsch's buffer solution was measured as previously described (PART 1, p. 41). In further experiments, however, it was found more convenient to use a borate buffer without chloride, since shorter development times could be employed. The technique of the method was improved by:-

TABLE 24

<u>Blue Colour Development time (Mins.)</u>	<u>Spekker Reading</u>	<u>Increase in Spekker Reading per 5 Minute Interval</u>
5	.239	.032
10	.271	.019
16	.290	.015
20	.305	.013
25	.318	.014
30	.332	.009
34.5	.341	.009
52	.372	.007
61.5	.386	.004
71.5	.394	.005
81.5	.405	.005
91	.416	.003
145.5	.444	.001
155.5	.446	.001
160.5	.447	.001
207	.457	.0002

(i) Using only one solution for developing the molybdenum blue colour this containing both quinol and sodium sulphite.

(ii) Eliminating the errors in development time arising from the individual addition of the reagents to a series of solutions for estimation, by using a rack with a series of equally spaced tubes into which the reagents were previously measured and from which they could be poured simultaneously into equally spaced tubes containing the silica solutions.

(iii) Eliminating the different conditions set up in each solution due to the time required to dilute a number of them individually to exactly 50 ml., by previously diluting the silica solutions (to 43 ml.) so that on the addition of the reagents (7 ml.) the final volume was 50 ml.

(iv) Providing similar and simultaneous agitation after addition of the reagents for the whole series of solutions to be estimated, by means of a number of equally spaced spatulas bolted to a holder.

A standardised method incorporating these improvements is described fully in PART I, p. 20, this method was used for all the solubility tests with the exception of those on the DRC siliceous dust already mentioned.

## Section 2

### The Temperatures reached by Drilling Bits in Mining Operations

#### (a) Introduction

In view of the high surface temperatures which are known to be produced during polishing and grinding processes, and having regard to the changes in crystal structure of the silica lattice which result from heating, it was considered that an estimation of the temperatures reached by bits during drilling operations would give an indication of possible polymorphic changes which might be brought about in the crystalline particles of the dusts produced. It was considered that any such changes in the crystalline structure of airborne silica dust particles might be of some significance in the causation of silicosis among drill operators who are exposed to heavy concentrations of airborne dust.

#### (b) Experimental

##### 1. General

The tests were divided into two sections according to the hardness of the material which was to be drilled, (i) coal and soft rock, and (ii) hard rock.

Rotary drills are used in coal and soft rock, while for brushing operations in hard rock percussive drills are employed.

##### 2. Temperature measurement

The methods devised for measuring the temperatures of the bits

used in these two drilling procedures are as follows:-

(i) Rotary Drilling

A number of rotary bits were prepared, each with four 'temperature spots', as shown in Fig. 23, these consist of a hole  $3/32$ " diameter x  $1/4$ " deep near the cutting face of the bit. At the bottom of the hole is a cube of alloy previously prepared and of known melting point, the side measurement of the cube being slightly less than  $3/32$ ". On top of the cube is packed a plug of steel wool, the hole being finally closed with a copper plug.

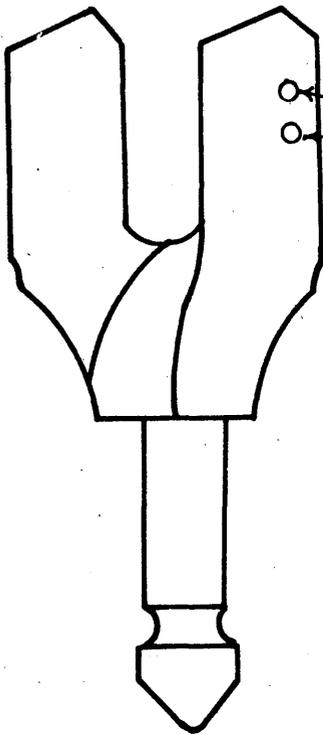
The four 'temperature spots' in each bit contained alloy cubes of different melting points the four making a series over the temperature range expected to be reached by the bit when in use.

After the prepared bits had been used in a drilling operation the alloy cubes were examined to ascertain which ones had fused and in this way the highest temperature reached by the bit was determined.

(ii) Percussive Drilling

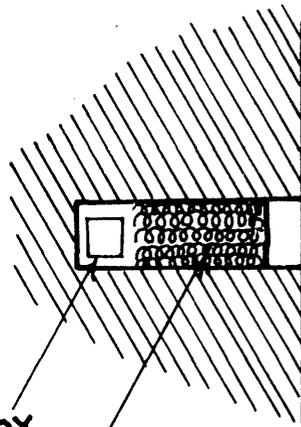
The use of 'temperature spots' in the percussive bits was found to be impracticable since the powerful percussive action caused deformation of the alloy cubes by their continuous agitation inside the 'temperature spot' holes. A means was therefore devised to measure the temperature of the percussive bits by a thermocouple.

The percussive drill shanks have a hole ca.  $1/4$ " diameter running throughout their length; this central channel may be used to



'TEMPERATURE SPOTS'

ELEVATION

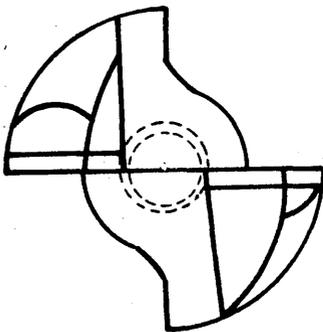


ALLOY  
CUBE

STEEL WOOL

COPPER  
PLUG

SECTION OF  
'TEMPERATURE SPOT'



PLAN

ROTARY BIT

FIG. 23

carry a stream of water to the drill head with the object of laying the dust produced during the drilling operation. This procedure is known as 'wet drilling'.

The drills are worked by compressed air and a blast of air directed through the central channel may be used to clear the hole at the end of the drilling operation to facilitate withdrawal of the drill shank. The temperatures of the bits were measured during 'dry drilling', so that the results would indicate the highest temperatures which the bit was likely to reach in operation.

This central channel offered a most convenient situation for thermocouple leads. The drill, in addition to its percussive action, rotates slowly (20 r.p.m.) during operation, and a method was required to pick up the current from the thermocouple leads since these would rotate with the drill shank.

Details of the device which was designed for this purpose are shown in Fig. 24. The current 'Pick-Up' is held on the drill shank between two steel springs which are kept under compression by the two brass clamping rings. The main body of the 'Pick-Up' is built of ebonite and consists of two rings (A) fixed to a central core (B) which revolve with the drill shank. A central ebonite portion (C), which bears on the surface of the core (B), remains stationary when the drill shank is revolving. The thermocouple (chromel/alumel) junction is mounted in a brass bush inside the drilling bit and the ends of the thermocouple are led through the central channel

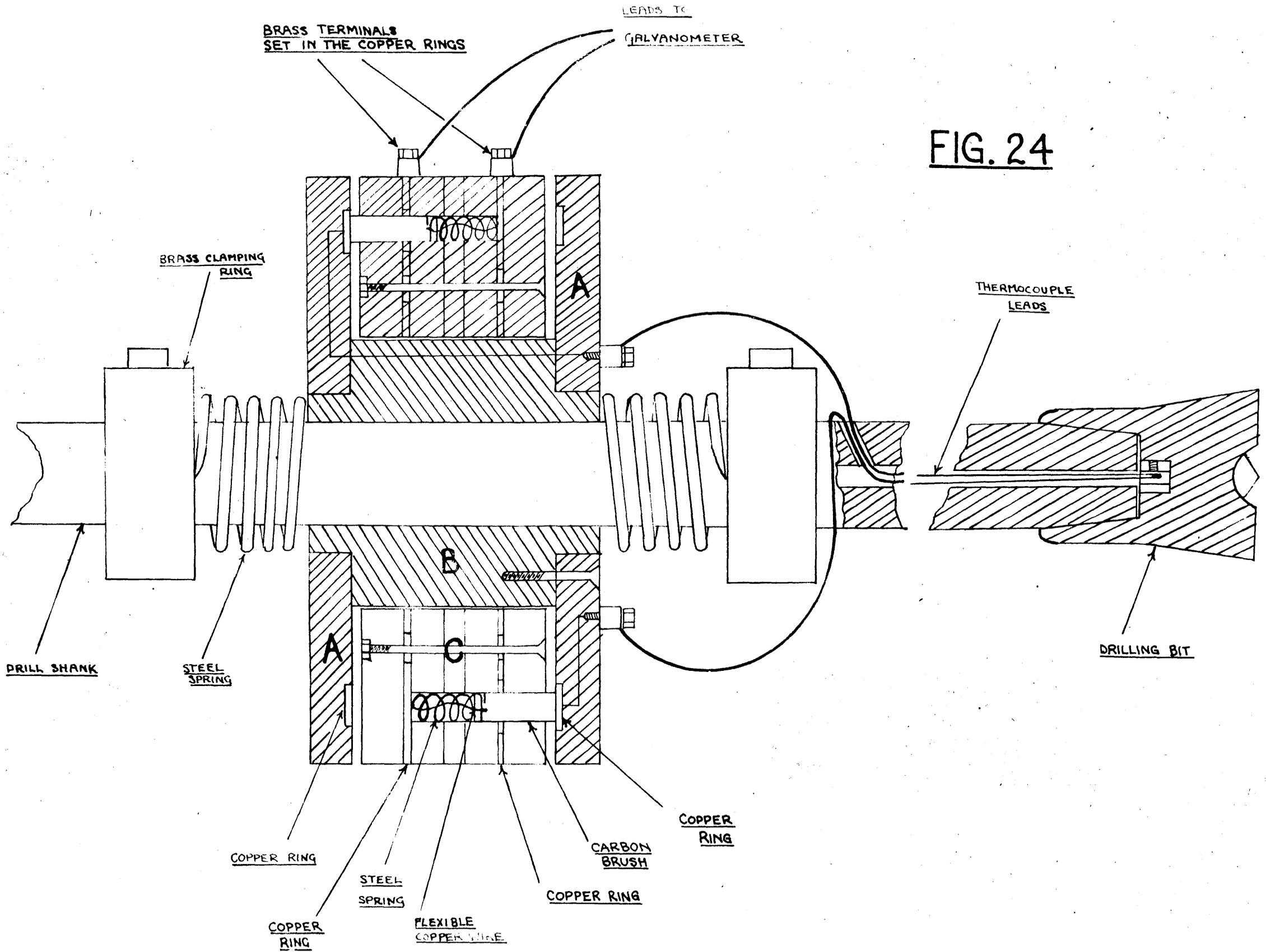


FIG. 24

of the shank and are brought outside the shank at a suitable point near the 'Pick-Up' for connection to the terminals set in the ebonite ring (A). The thermocouple potential is thus connected to the copper rings set in (A) and is picked up from these rings by the carbon brushes which are in electrical contact with the copper rings set in the central portion (C). The current is then led from the outer periphery of (C) to the galvanometer.

The 'Pick-Up' was made by Mr. A. Clunie and staff (Tech. Chem. Dept. (Workshops), Royal Technical College).

### (iii) Procedure

Tests using the 'temperature spots' for rotary drilling and the 'Pick-Up' for percussive operations were carried out at Plean Colliery, Stirlingshire, in conjunction with Mr. W.H.S. Massie (Tech. Chem. Dept., Royal Technical College).

### (c) Results

The highest temperatures reached by rotary bits in coal (Mohs' Hardness,  $2\frac{1}{2}$ ) was found to be ca.  $70^{\circ}\text{C}$ . and in soft rock (Mohs' Hardness, 2) ca.  $100^{\circ}\text{C}$ .

The percussive drills in the hardest sandstone rocks (Mohs' Hardness,  $6\frac{1}{2}$ ) reached ca.  $120^{\circ}\text{C}$ .

### (d) Conclusions

The temperatures observed were considerably below that required

for the transformation of quartz to cristobalite and tridymite (870°C.). It is noted however in percussive drilling of the hardest rocks, that, although the bit as a whole was not raised to a temperature near that required for conversion, incandescent sparks were observed at the start of drilling and it may therefore be assumed that extremely small amounts of the rock were being raised to temperatures above 870°C.

It was concluded that no change in the crystalline structure of airborne quartz dust particles produced in drilling operations, could be brought about by the temperatures reached by the drilling bits.

- (12) *Am. J. Hyg.*, 1922, 10, 111.
- (13) *Am. J. Hyg.*, 1923, 11, 111.
- (14) *Am. J. Hyg.*, 1923, 11, 111.
- (15) *Am. J. Hyg.*, 1923, 11, 111.
- (16) *Arch. Gewerbepath. Geol.*, 1935, 3, 1.
- (17) *Beitr. path. Anat.*, 1935, 96, 442.
- (18) *King, E.J., Occup. Med.*, 1947, 4, 30.
- (19) *Parry, J.J., Robson, W.D., and Levin, H.A. Genet. and Dev.*

REFERENCES

- (1) National Coal Board, Report and Accounts for 1948, p. 29  
(H.M.S.O., 1949).
- (2) Dimerbrock, cited by Collis, E.L., Pneumokoniosis with Special  
Reference to Dust Phthisis, (H.M.S.O., 1915).
- (3) Peacock, T.B., Trans. Path. Soc. London, 1861, 12, 36.
- (4) Greenhow, E.H., Trans. Path. Soc. London, 1865, 16, 59.
- (5) Haldane, J.S., Colliery Guardian, 1915, 110, 1181.
- (6) Lanza, A.J., Trans. Coll. Physicians Philadelphia, 1918, 40, 270.
- (7) Gye, W.E., and Kettle, E.H., Brit. J. Exptl. Pathol., 1922, 5, 241.
- (8) Gardner, L.U., Am. Rev. Tuberc., 1923, 7, 344.
- (9) Sayers, R.R., Bur. Mines, Tech. Paper, 372; Chem. News, 1925,  
131, 353.
- (10) Heffernan, P., J. Ind. Hyg., 1926, 8, 481.
- (11) Kettle, E.H., J. Ind. Hyg., 1926, 8, 491.
- (12) Heffernan, P., Tubercle, 1929, 11, 61.
- (13) Kettle, E.H., J. Path. and Bact., 1932, 35, 395.
- (14) Policard, A., Presse med., 1933, 41, 89.
- (15) Siegmund, H., Arch. Gewerbepath. Gewerbehyg., 1935, 6, 1.
- (16) Geise, W., Beitr. path. Anat., 1935, 94, 442.
- (17) King, E.J., Occup. Med., 1947, 4, 26.
- (18) Denny, J.J., Robson, W.D., and Irwin, D.A., Canad. med. Ass. J.,  
1937, 37, 1; 1939, 40, 213.
- (19) Belt, T.H., and King, E.J., J. Path. Bact., 1943, 55, 69.
- (20) King, E.J., Wright, B.M., Ray, S.C., and Harrison, C.V., Brit.  
J. industr. Med., 1950, 7, 27.
- (21) Briscoe, H.V.A., and Holt, P.F., Nature, 1949, 163, 334.
- (22) King, E.J., and McGeorge, M., Biochem. J., 1938, 32, 417.

- (23) Whitehouse, A. G. R., J. Indust. Hyg., 19, 138.
- (24) Lenher, V. and Merrill, H., J. Amer. Chem. Soc., 37, 2630.
- (25) Isaacs, L., Bull. Soc. Chim. biol., 1924, 6, 656.
- (26) King, E. J., Biochem. J., 1939, 33, 944.
- (27) King, E. J., Medical Research Council, Special Report Series No. 250,  
(H. M. S. O., 1945).
- (28) Supplied by The Thermal Syndicate Ltd., Wallsend, Northumberland.
- (29) Supplied by Mr. W. R. Flett, Economic Geology Section, Royal  
Technical College, Glasgow.
- (30) Amor, A. J., "The Chemical Aspects of Silicosis" (H. K. Lewis & Co.,  
London, 1942).
- (31) Supplied by Gallenkamp & Co. Ltd., 17 Sun Street, Finsbury Sq.,  
London.
- (32) Supplied by T. B. Ford Ltd., 39, Kingsway, London.
- (33) Harrison, T. S., and Storr, H., J. S. C. I., 1944, 63, 154.
- (34) Supplied by Evans Electroselenium Ltd., Harlow, Essex.
- (35) Clark, W. M., "The Determination of Hydrogen Ions", pp. 106-7,  
(Williams and Wilkins Co., Baltimore, 2nd Ed., 1925).
- (36) Prideaux, E. B. R., and Ward, A. T., J. chem. Soc., 1924, 426.
- (37) Supplied by Colin Stewart Ltd., Winsford, Cheshire.
- (38) Lea, F. M., and Nurse, R. W., J. Soc. chem. Ind., 1939, 58, 277.
- (39) Beilby, G., "Aggregation and Flow of Solids", (Macmillan, London,  
1921).
- (40) Hamburger, L., Nature, 1932, 130, 435.
- (41) Ray, R. C., Proc. roy. Soc., 1922, 101A, 509.
- (42) idem, *ibid*, 1923, 102A, 640.

- (43) Sosman, R.B., "The Properties of Silica" (The Chemical Catalogue Co. Inc., New York, 1927), p.299.
- (44) Johnston. J., and Adams, L.H., J. Amer. chem. Soc., 1912, 34, 517.
- (45) Bowden, F.P., and Hughes, T.P., Proc. roy. Soc., 1937, 160A, 575.
- (46) Grimshaw, R.W., Heaton, E., and Roberts, A.L., Trans. Brit. ceram. Soc., 1945, 44, 69.
- (47) Cole, S.S., J. Amer. ceram. Soc., 1935, 18, 149.
- (48) Carborundum grinding powder, Grade B, manufactured by Ferguson and Timpson Ltd., York St., London.
- (49) Findlay, A., "Practical Physical Chemistry", (Longmans, Green and Co., London, 1941), p.314.
- (50) Choong, S.P., Proc. Phys. Soc., 1945, 57, 49.
- (51) Clark, W.M., "The Determination of Hydrogen Ions", p.200, (Williams and Wilkins Co., Baltimore, 2nd Ed., 1925).