THE EFFECTS OF SURFACE MODIFICATION ON THE HIGH TENSION SEPARATION OF MINERALS.

by

Edward Levin

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ABSTRACT.

The variables of high tension separation are defined in detail. The pinning behaviour of minerals is shown to be more strongly influenced by

1) the current flow between the ionising electrode and the drum,

2) the relative humidity within the separation zone,

3) the conductivity of the air within the separation zone. This factor is related to three of the more important process variables, viz., potential gradient, current flow and length of the air gap.

It is demonstrated that the pinning value of a mineral is inversely proportional to its surface conductivity.

Details are given of the strength and geometry of the ionising field under various conditions, on the basis of field plotting with the help of an analysing electrode. The pinning behaviour of minerals is related to field changes and a mechanism of the process of high tension separation is postulated

Determinations carried out under standardised high tension conditions show that the surface conductivities of quartz and kyanite depend on the quantity of adsorbed

water as well as on the moisture content of the surrounding air. The latter variable has, however, a stronger effect because it controls the intensity of the ionising field and the conductivity of the solid-air interface.

Treatments of quartz and kyanite with metal salt solutions of varying concentrations and under ranges of pH, produce a wide variety of changes in pinning behaviour. Improved surface conductivities are attributed to (1) the increased hydration of solid surfaces, (2) the capacity of adsorbed layers to take-up water and (3) the water-avidity of deposited salts. Increased pinning is ascribed to (1) the dehydration of mineral surfaces and (2) the insulating properties and/or hydrophobicity of oxidised surface layers.

The treatment of quartz with organic flotation reagents produces pinning behaviours which are correlated with the floatability of the mineral. High pinning values of treated quartz and kyanite are attributed to the water-repellency of their surfaces.

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1.0 INTRODUCTION

High tension separation is based on differences in the electrical properties of minerals, particularly their conductivities. Minerals with large differences in conductivity can be separated efficiently, i.e. an insulator is readily separated from a conductor. The process of high tension separation depends basically on two operations:

(1) charging of the mineral particles by intense ion bombardment in an ionising field, and

(2) discharging of the particles in a static field. The rate of discharge controls the separation of the particles into conducting and non-conducting fractions.

The separation of minerals by electrical methods of concentration has become important in recent years and in this respect the process of high tension separation has brought about the most significant advance. The first permanent commercial plant was built in 1908 but further development was retarded when in 1918 the froth flotation process became widely applicable, especially to sulphide ores, and replaced almost entirely electrostatic methods of separation. Under these circumstances and in view of the low capacity of the machines, apart from the inherent disadvantage that fine sized materials are detrimental to the efficient operation of the separators, electrostatic separating techniques did not find a ready field of application in mineral technology.

In 1940 titanium minerals became important and the usefulness of the process was once more realised as beach sands containing the valuable mineral were readily amenable to separation by electrostatic means. It was at this time that Carpenter[1] developed the new high tension technique, based on high electrical potentials and effective use of high tension fields.

When the need arises to separate minerals of similar electrical properties, the high tension process fails. Numerous attempts have been made to widen the applicability of the process by selectively modifying the surface conductivity of minerals. The conductivity of mineral particles is not controlled by their composition and structure alone, but depends to a large extent on the condition of their surfaces. Ideally, surface conductivity is only a fraction of bulk conductivity, but the former value increases considerably if an extremely thin film of conducting material is adsorbed, or if the structure of the surface layer is so altered as to render it conducting. In this respect the influence of water adsorption on the conductivity of insulators has been referred to often in the literature. Since the electrical properties of a mineral surface can dictate the mineral's behaviour in an electric field, an insulator can be made to behave as a conductor, and vice versa, by suitable surface treatment.

Earlier work has indicated that by various means, i.e. heating, X-ray and electron bombardment, chemical treatment, etc., surfaces may be formed with electrical properties quite different from those of the bulk mineral. In 1910 Swart[2] in a United States patent was the first to mention the effect of adsorbed matter, other than adsorbed surface moisture, on electrostatic behaviours. He had listed 200 different methods of conditioning mineral surfaces. Schniewind[3] must have been the first to realise the profound influence air humidity has on the electrostatic separation of minerals, particularly those that are hydrophilic. The influence of the water adsorbing capacity of minerals on their behaviour in high tension fields has been studied by Kakovsky[4]. He illustrated the possibility of deliberately manipulating the surface electrical properties of minerals in a fashion comparable to that used in the field of flotation. The surface conductivity of insulating minerals is greatly dependent on the presence of adsorbed water and hence, by suitable control of the hydrophilicity of mineral surfaces, the electrical properties can be modified through a wide range. Kakovsky had attempted to show that the theoretical principles of the treatment of the surface of a mineral before high tension separation and flotation are similar, thus opening the possibility of using extensive experience accumulated in flotation practice.

The Research Project

The work presented in this thesis was undertaken with the aim of

(1) exploring the scope of methods of modifying the surface conductivities of minerals and

(2) elucidating the surface phenomena and the fundamental principles involved in the processes that change the conductivity.

The investigations included methods of reducing the natural conductivities of minerals as well as others to increase conductivities. A wide range of variables was explored in each instance in order to find optimum conditions and a general pattern of behaviour was deduced from the results. Particular attention was paid to the influence of water in various forms, i.e. whether associated with, or taken up by, separate phases adsorbed on the surface of a mineral or present as "free" water molecules attached to the solid surface.

The assessment of the modification of the electrical properties produced by a particular treatment was determined on a high tension separator. In support of the primary purpose of the work, it was necessary to establish the details of the process of high tension separation more precisely and to define the characteristics and ranges of influence of several ill-defined variables pertaining to the minerals, the equipment and to the environmental conditions under which separations are performed.

2.0 MATERIALS USED IN THE PROJECT.

2.1 Choice of materials.

In view of the fact that surface properties are greatly dependent on variations and inhomogeneities in the chemical composition of minerals, it was decided to eliminate such spurious hazards as far as possible by using two stable and inert insulator minerals, quartz and kyanite, for the main portion of the work. These minerals provided the opportunity for observing changes in surface properties without undue masking by other chemical changes. At the same time, contrasts between free silica and the combined alumino-silicate crystal lattice represent differing surface conditions and dissimilar water adsorbing capacities, thereby providing differences in behaviour under the various methods of treatment.

A kyanite ore consisting almost entirely of kyanite and quartz was used for the ancillary project of the thesis. The advantages in using such a material were:

(1) The kyanite ore was readily available in the large quantities required for the preliminary investigations.

(2) Brewis[5] devised a chemical treatment whereby the quartz fraction of the ore was made conducting. He was able to show that under optimum machine conditions a good high tension separation of the two constituents

was possible. An insulator - conductor mixture was thus available for studying the influence of environmental and machine variables on the high tension behaviour of minerals of dissimilar surface conductivities.

Chromite and ilmenite were chosen for the investigation of the effects of organic reagent treatment on the electrical properties of conductors. The minerals were available in bulk and screened to the required mesh size.

2.2 Description of Materials.

2.2 (a) Main project.

1. Quartz. (SiO_2)

The mineral used was a white optical grade silver sand from Cornwall, mostly -36 + 150 mesh B.S. in size. The -52 +100 mesh fraction was removed by screening on a Russell vibrating gyratory screen. The coarse +52 mesh material was ground in a disc-type pulveriser and screened as above. All the test work was carried out on the -52 +100 mesh material.

The sized material was cleaned by agitation with hot 10% V/V sulphuric acid at a liquid-solids ratio of 3/1. After 30 minutes the acid solution was poured off and the mineral washed by decantation with distilled water until the pH of the wash solution was identical to that of the distilled water. The quartz was dried at about 120°C and kept in closed containers until required. All the materials used in this thesis were cleaned in the above manner.

The -52 +100 mesh quartz fraction has a specific gravity of 2.656, determined by means of a Beckman Air Comparison Pycnometer (Model 930). The particles consist of rounded grains with a few small indentations. The surface area averages about 250 to 350 sq.cm./g.[6,7] and the dielectric constant is 3.0 to 6.5.[8]

2. Kyanite. (Al_2SiO_5 or $Al_2O_3SiO_2$).

About 100 lbs. of large pieces of crystalline kyanite, ranging in size from 4 in. to about 10 in., were obtained from the Kenya Kyanite Co. The crystals were silvery-blue in appearance and occurred in clusters associated with quartz inclusions. Clean pieces were handpicked and any inclusions of quartz were removed by means of a small hammer. Because of the brittle nature of the mineral, comminution was carried out in an iron mortar and pestle. The broken material was screened through a 52 mesh screen, the oversize being returned to the mortar. About 10 kg. of minus 52 mesh material was produced. The -52 +100 mesh fraction was obtained by further screening and used in the test work.

The kyanite particles consist of long bladed crystals and have badly striated surfaces. The specific gravity is 3.669 and dielectric constant 4 to 7.2.[8]

3. Chromite. ($FeO.Cr_2O_3$).

A -52 +100 mesh fraction of chromite from

S. Rhodesia used by W.K.Ng[9] was available. The specific gravity is 4.17[9] and dielectric constant 11.0.[8]

4. Ilmenite. ($FeTiO_3$ or $FeO.TiO_2$).

A -52 +100 mesh fraction of ilmenite from Titania A/S (Norway) was used. The specific gravity is 4.5 to 5[10] and dielectric constant 33.7 to 81.[8]

2.2 (b) Ancillary project.

1. Kyanite ore.

A crushed and ground kyanite schist from Kenya, containing about 40% kyanite, was chosen for the ancillary project of studying the variables of the high tension separator. The material consists almost entirely of quartz and kyanite with minor proportions of mica, rutile and a general staining of iron oxides as impurities. The staining caused by the iron oxides is discontinuous and present on both kyanite and quartz. This impurity was removed by acid-leaching. The rutile occurs as small crystals, often included in the quartz.

About 100 lbs. of the schist were available, crushed to about 97% minus 52 mesh. The bulk of this was divided by coning and quartering, the portions being screened at 52 and 72 mesh on the Russell vibrating screen. All the preliminary test work was performed on the -52 +72 mesh fraction.

Test samples were obtained from the sized material by riffling and were conditioned in bulk by the following

method suggested by Brewis[5]:

After acid-cleaning with 10% sulphuric acid (as outlined above), 200g samples of the sized kyanite ore were treated with 600 mls. of 5% W/V sodium hydroxide solution for 60 minutes. The liquor was decanted and the solids were washed five times with 600 ml. of dilute sodium oleate solutions (0.002g/l). The samples were then dried at approximately 120°C for 3 hours and allowed to cool under ambient conditions for 18 to 22 hours. About 1000g to 1200g kyanite were so treated and homogeneous aliquots taken for the high tension tests.

According to Brewis the chemical treatment modifies the surface conductivities of the quartz and kyanite by the following mechanism: Both the minerals are rendered conducting by the alkaline conditioning. The subsequent sodium oleate treatment leads to the selective adsorption of oleate which renders the kyanite hydrophobic and insulating.

2. Carborundum.

Commercial carborundum abrasive of nominal 60 mesh size was obtained from Carborundum Co. Ltd. The material was screened to -52 +72 mesh and used as such. It has a specific gravity of 3.18[11].

3.0 THE HIGH TENSION SEPARATOR.

3.1 Description of the high tension separator.

The G.E.C. High Tension Laboratory Separator consists of two parts, the control console and the machine proper.

The control console houses the power pack which supplies full-wave, rectified, condensor-smoothed D.C. of up to 40 kilovolts. The voltage is measured on a kilovoltmeter of 0.2 kV sensitivity. Both negative and positive voltage can be supplied. A 0-250 uA microammeter of 2uA sensitivity in the machine measures the current flow between the electrode system and the earthed drum.

A diagram of the machine proper is shown in fig.1 below. The material under test is placed in hopper, A, and discharges through a sliding metal gate on to a 3½ in. Sherwen Laboratory electromagnetic vibrating feeder, B, along which the mineral particles travel 19½ in. to the point of delivery on to the drum. The baffle, C, screening the feeder from the electric field, is a plate of insulating material backed by an earthed brass plate.

The rotating drum, D, conveys the particles beneath the electrodes, E & F, and is earthed. It is 9 in. in diameter and is faced with hard-nickel steel. The drum is driven by a ¼HP motor through a Kopp variable gear and V-belting and can be run at speeds ranging from 45 to 250 rpm.

After charging, the mineral particles are either pinned

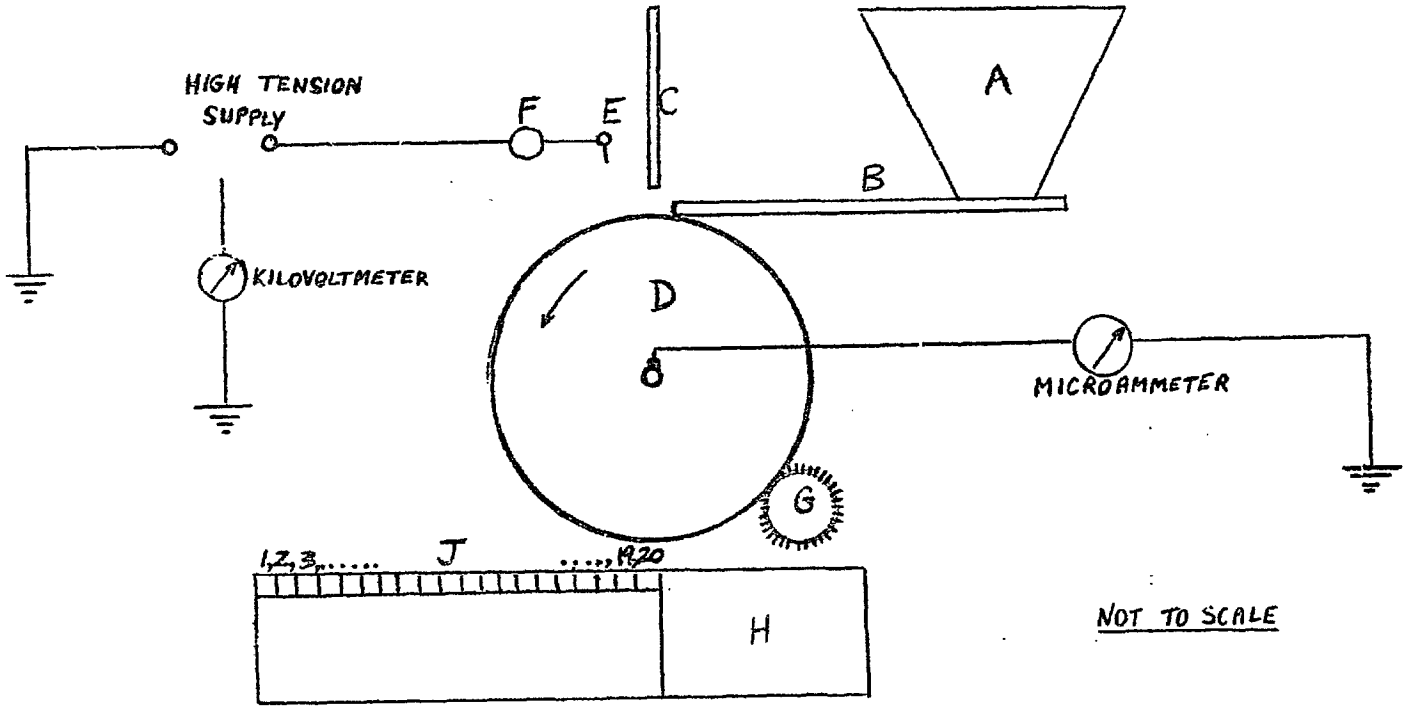


FIG. 1 THE HIGH TENSION SEPARATOR

to the drum and are brushed off by the nylon brush, G, into the receiving box, H, or the particles are thrown into a series of interlocking trays, J. There are 20 trays, each 0.6 in. apart and numbered, starting from the tray furthest from the drum. The vertical tangent to the drum corresponds to a tray position of 15.3.

The ionising electrode, E, consists of a metal rod of 0.175 in. diameter, carrying a row of needle points 0.5 in. long and 0.03 in. in diameter and spaced at intervals of 0.125 in. over a total electrode breadth of 6.25 in. The ionising electrode is supported by brackets fixed to the static electrode, F, which is a metal cylinder 0.75 in. in diameter. The centres of the two electrodes are fixed at 2 inches apart. In the field plotting study outlined in Section 5 of the thesis, it was found necessary in some cases to alter the length of this gap. The static electrode is connected by means of high tension cable to the power supply in the control console.

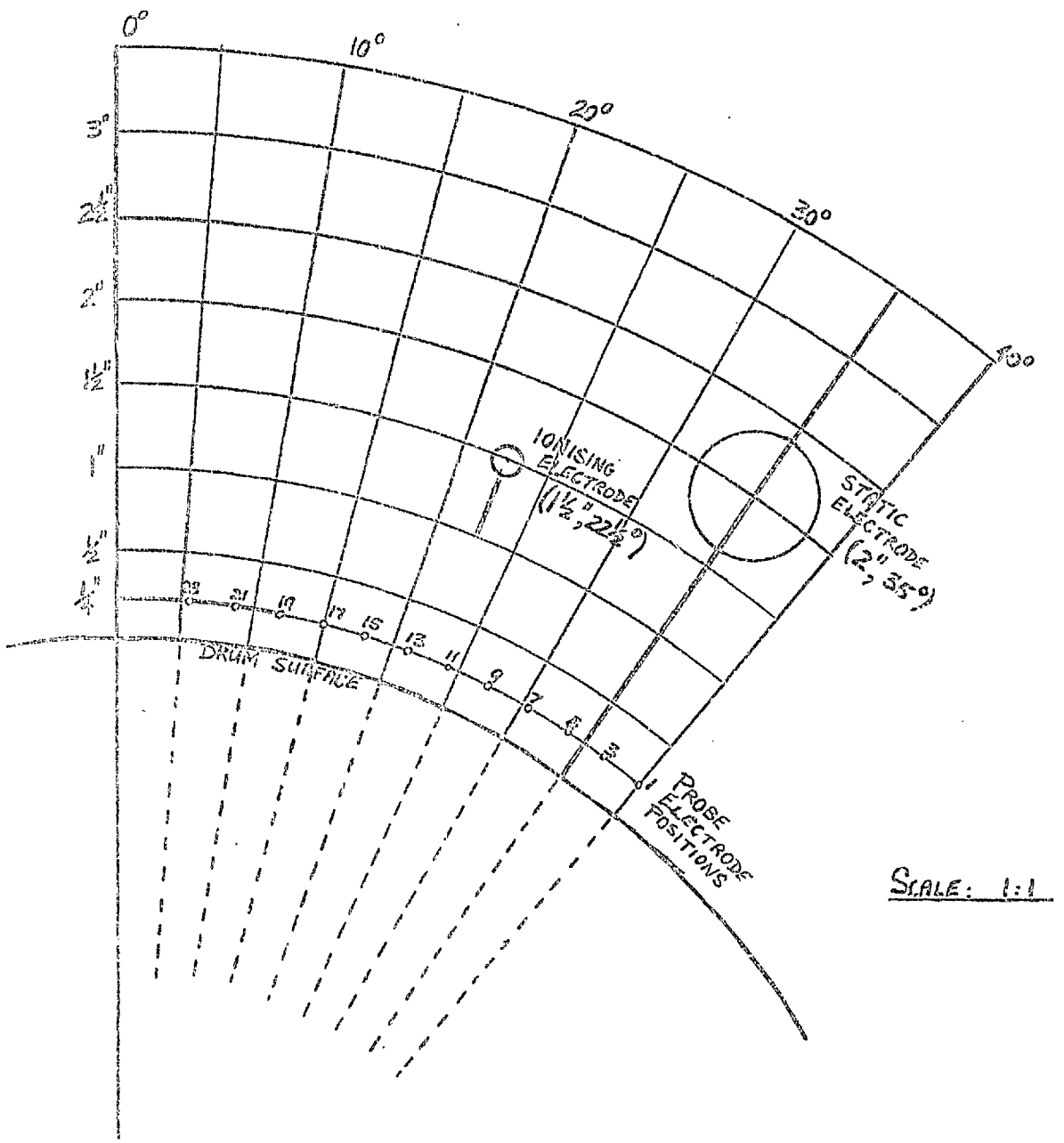
The ionising and static electrodes are set above the drum and are parallel to it and each other. The electrodes are cantilevered from a mounting consisting of a series of concentric and eccentric cylinders of insulating material. The cylinders may be rotated independently and allow the electrodes to be placed at any required position above the drum surface. The only limit imposed is that the two electrodes are always 2 inches linearly apart.

A system of reference was introduced whereby the angular location of the electrodes relative to the vertical centreline of the drum, and the distances of the electrodes above the drum surface can be measured. For example, if the static electrode is placed at the position shown on fig.2, its centre is at a radial distance of 2 in. above the drum and at an angular location of 35° to the vertical plane through the drum axis. Thus, its position is designated (2", 35°). A similar nomenclature is used to fix the location of the ionising electrode, which in fig.2 has a (1½", 22½°) position. Electrode positions are referred to by this notation throughout the thesis. The actual location of the electrodes was determined by projecting their image on to a transparent chart fixed on a perspex sheet alongside the drum. The chart (fig.2) consists of a series of concentric and radial lines of reference having their origin at the axis of the drum. Particular care was taken to minimise errors due to parallax.

The radial distance between the needle points of the ionising electrode and the drum sruface was found to be a factor of some importance in this thesis. The distance is termed the "ioniser gap" and is expressed in mms.

In the field plotting investigations, a similar nomenclature to that outlined above was used to locate the positions of a probe electrode. A position, ¼ in. above the drum surface and at an angular location of 40° (fig.2),

FIG. 2 THE ELECTRODE SYSTEM OF THE HIGH TENSION SEPARATOR



was chosen as a point of reference. Probe electrode positions were spaced ⅛ in. apart, radially and along arcs parallel to the surface of the drum. Successive positions above A1 are denoted B1, C1,etc.. while successive positions to the left of A1 and along the same arc, are designated A1,A2,A3,... etc., and similarly for positions along arcs B,C, etc.

3.2 A brief outline of the mechanism of the process of high tension separation.

In this brief account of the mechanism of high tension separation, a positive electrode polarity is assumed. When a voltage of sufficient intensity is applied to the ionising electrode, breakdown of air occurs and positive gaseous ions flow to the earthed drum. Mineral particles entering the ionising field receive a positive charge as a result of the ion bombardment. When the particles are subsequently under the influence of the static field, the charge on insulators does not leak away readily due to the non-conducting properties of the material. As a result, the particles remain pinned to the oppositely-charged drum. On the other hand, the ions adhering to the conducting particles discharge rapidly to earth. Simultaneously, by a process of induction, a charge of sign opposite to that of the static electrode is developed on the particles. The negative charge increases in magnitude, reaching a value of sufficient

strength to cause the particles to be repelled from the drum surface.

The above mechanism of the process of high tension separation is described in greater detail under Section 6 of the thesis.

3.3 The determination of the pinning behaviour of minerals.

The high tension supply was switched on about 30 minutes prior to the use of the separator. This procedure was necessitated by the observation that the voltage-current relationship for any particular electrode geometry changed with time, reaching a constant value after about 20 minutes. While the high tension supply was approaching stability, the machine variables were adjusted to the required values. About 2 minutes before the introduction of a mineral sample to the separator, the vibrational feeder and the motor driving the drum were started. Samples of 200g weight were placed in the feed hopper and the time from the appearance of the first particles in the separation chamber to the conclusion of the test was noted. Feed rates were thus determined. In subsequent work when reproducibility had been improved, the weights of samples were reduced to 50g.

Before the introduction of a constant humidity system, the relative humidity of the air within the separator was measured before each test on a mechanically-driven wet and dry bulb hygrometer.

On completion of each test, the machine was stopped and the fractions in the receiving box and trays were removed for weighing, and also for analysis in the case of experimentation involving quartz-kyanite mixtures. Tray 17 was arbitrarily chosen as the transition point between pinned and thrown material. The contents of trays 1 to 17 represented the thrown fraction, while trays 18 to 20 and the receiving box held the pinned fraction. In this thesis the amount of material pinned is termed the pinning value and is expressed as a percentage of the total weight of solids tested. It represents the pinning behaviour of the material and is indicative of the electrical properties of the substance.

3.4 Description of the relative humidity system.

Relative humidity was not controlled in the preliminary study of the machine variables, but was measured at the commencement of each test. Subsequently, it became obvious that the moisture content of the air is a factor which considerably influences the high tension behaviour of minerals. Thus, it was essential that some form of relative humidity control within the separator be introduced.

Various humidifying systems were designed and tested. The system that gave the most satisfactory performance is described below (fig.3). It was used throughout the remainder of the test work.

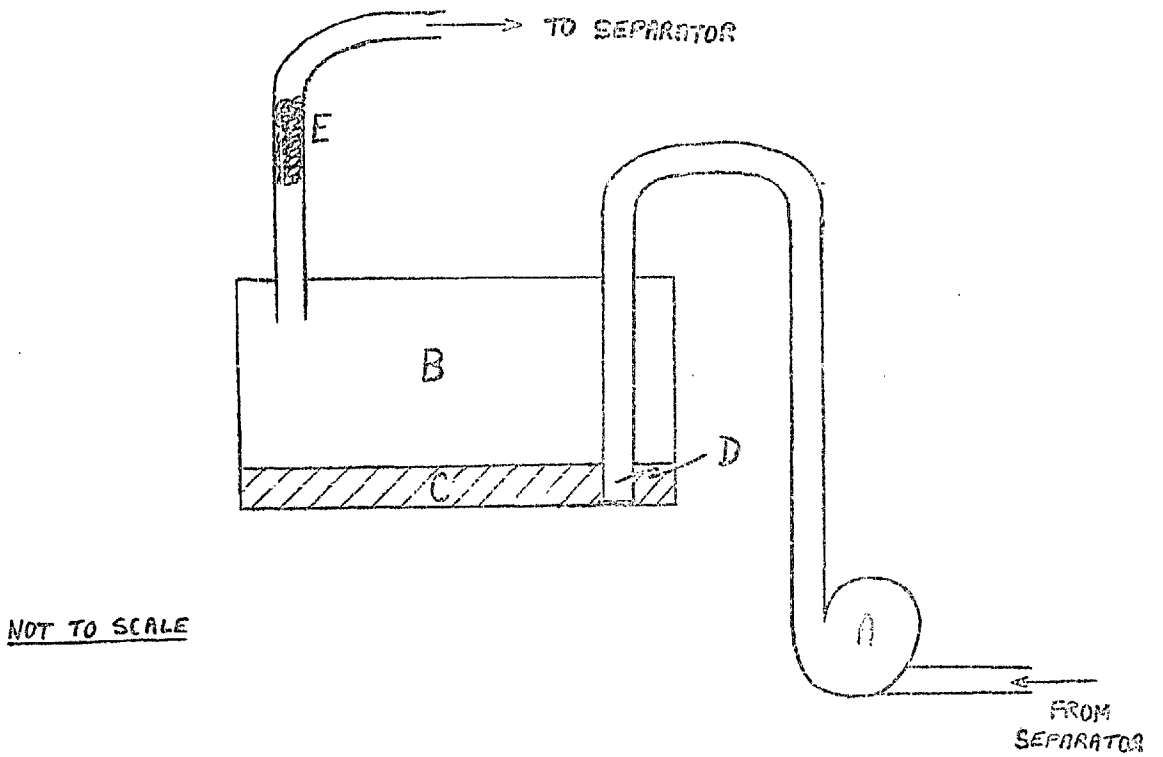


FIG. 3 THE CONSTANT RELATIVE HUMIDITY SYSTEM

Air is delivered by means of an oil-free blower, A, of 6 in. rotor diameter into a bath, B, of 14½ x 10½ x 9½ in. size. The bath contains a saturated salt solution, C, 3 cm. in depth. Various saturated salt solutions impart different constant moisture contents to the air with which they are in equilibrium. A list of the salt solutions used in this thesis, together with their corresponding relative humidities, is given in table 1 below.

The air feed is given a large surface area by passage through a bubbler, D, consisting of a closed tube perforated with many small holes. The humidified air leaves the bath at E, which is a 12 in. long tube and is loosely packed with cotton wool to trap any spray carried mechanically with the air stream.

All connecting tubing is 1½ in. in diameter. The flow rate of the outlet air was maintained at about 20 litres per minute.

The high tension separator was made airtight and the outlet of the humidifying bath was connected to a plastic cover over the feed hopper. The fan withdraws the air through an opening in the bottom of the separator directly below the drum. In this way moist air of constant humidity can be circulated through the separator.

After operating for a few minutes, the circuit was broken at E, and the relative humidity of the outlet air

was tested by means of the wet and dry bulb hygrometer. In addition the relative humidity within the separation zone of the machine was checked. In most cases the appropriate moisture content of the air was attained in 2 to 3 minutes.

TABLE 1.

SATURATED SALT SOLUTION	RELATIVE HUMIDITY PER CENT
40% w/v NaOH	20
$CaCl_2$	34
K_2CO_3	44
NaBr	58
$NaNO_2$	66
KCl	84

Under extreme conditions, for instance when the ambient air humidity was about 30% and relative humidity of 84% was required within the separator, it was found necessary to circulate the air for 5 minutes before the required high moisture content was obtained.

4.0 A PRELIMINARY STUDY OF THE FACTORS INFLUENCING THE HIGH TENSION SEPARATION OF MINERALS.

4.1 Introduction.

This part of the thesis is devoted to establishing the significant variables of high tension separation. From information thus obtained, together with data presented by the field plotting investigation (Section 5), a mechanism of the process of high tension separation is proposed.

The variables involved in this study may be classified as follows:

(a) Variables of the material.

(b) Variables of the separator.

(c) Environmental variables.

In what follows the effects of these variables are described and it is shown that it is possible to ignore certain factors because of their relative insignificance.

4.1 (a) Variables of the material.

The properties of a mineral that influence its behaviour in a high tension field are:

(i) size (ii) size range (iii) specific gravity
(iv) temperature (v) shape (vi) electrical conductivity.

It is generally accepted that minerals of small particle size and wide size range lead to poor separation efficiencies. The minimum size particle that is amenable

to high tension separation using roll-type separators is about 200 mesh. The effect of the specific gravity of minerals on their electrostatic behaviour has not been widely studied. Items 1 to 3 inclusive affect the trajectory of particles through the separator. Consequently, the greater the range in any of these properties, the lower is the efficiency of separation.

The temperature of minerals can affect their electrical properties by:-

(1) directly influencing their conductivities and

(2) controlling the adsorption of water, which can have a marked influence on the surface conductivity of hydrophilic insulators.

Ference et al[12] have illustrated that the surface density of charge on a substance depends on the shape of the material. The charge density is highest at the points of greatest curvature. In addition Mora[1] showed that the charge on a prolate mineral was about 13 times greater than that on a spherical mineral of equal insulating properties. In this work, it was found that the elongated kyanite particles which have almost the same dielectric constant as spherical quartz, report as 95% pinning against the 68% for quartz, under identical high tension conditions. The difference in pinning values cannot be attributed solely to the shape factor, as the quartz particles are more hydrophilic and thus have a higher surface conductivity than the kyanite.

The five variables listed above were kept relatively constant as far as possible and were disregarded in this study.

Electrical conductivity is of considerable importance as a variable in high tension separation and forms the very basis on which one mineral is separable from another. Modification of the surface conductivities of minerals was widely studied and forms the major subject of this thesis. The methods and principles involved in the modification of the electrical properties of materials are dealt with in Sections 7, 8 and 9.

4.1 (b) Variables of the separator.

The variables involved in the operation of the high tension separator include:
(i) feed rate (ii) particle-drum contact resistance (iii) electrode geometry (iv) polarity (v) drum speed (vi) voltage (vii) ioniser gap. (viii) current.

(i) Feed rate. Balint[13] studied the effects of feed rate on the pinning behaviour of quartz and found that at values less than 90g/min., feed rate is a variable of little importance. In the preliminary work a feed rate fluctuating between 20 and 30g/min. was used.

(ii) Particle-drum contact resistance. The particle-drum contact resistance is a variable of some importance in high

tension separations as it determines the ease with which charges can transfer between the particle and the drum. The rate of transfer controls the pinning behaviour of the particles. Hudson[14] found that the electrostatic behaviours of zircon and rutile can be altered on a plate-type separator using plate surfaces of varying composition and resistivity. Fraas[15] claimed that the selectivity of electrostatic separations may be improved by coating the rotating drum with a high resistance solid film or with a semi-conducting layer. In addition, it has been reported[16] that the indiscriminate oxidation of the brass drum of a roll-type separator led to erratic mineral behaviours. The above references illustrate the important role that the resistivity of the drum surface plays.

In the present work a drum surface of hard-nickel steel was used throughout the work. It was qualitatively observed that the surface resistivity of the drum altered with time and use under conditions of ionic charging. A series of reproducibility tests showed that on any particular day, a small standard deviation resulted from a number of pinning values of an identical material. When representative samples of the same material were tested on another occasion, reproducibility was again good, but the mean value was generally different from that found earlier. The mean value fluctuated from day to day and since a

standard procedure was employed throughout, the variation was attributed to the variable resistance of the drum surface.

The drum surface of hard-nickel steel used in this work can readily form an oxide layer of high resistance.[16] The oxide formation is time-dependent and is accelerated by prolonged exposure to ionic charging.

When this project was commenced, the high tension separator was over two years old and presumably had a thick oxide layer on the surface of the drum. The first standard sample passed through the separator showed a pinning value of 73%. Subsequent standard samples tested on the same occasion, showed a constant decline in the pinning value until a constant level was reached at 68%. It is suggested that the pinned material lodging in the brush abraded some of the loosely-held oxide layer of the drum surface. To overcome this difficulty the drum was polished with fine emery paper before the commencement of each series of tests. The gradual initial decrease in pinning was eliminated.

The practice of cleaning the drum surface with emery cloth was abandoned subsequently when it was observed that the mean pinning value of a standard material continued to decrease and approached 55%. This was attributed to a gradual removal of a firmly attached oxide layer. When the cleaning was stopped, the standard pinning value began

to increase. The problem of an initial decrease in the pinning value occurred whenever the separator was not in use for 2 or 3 days. The difficulty was eliminated by passing 300 to 400g. of the standard material through the machine and taking the pinning value of the last 50g only.

(iii) Electrode geometry. The influence of electrode geometry on the high tension behaviour of minerals has been observed[5,13,17] but has not been empirically investigated. In this thesis changes in the ionising field intensities caused by variations in the electrode geometry were correlated with the pinning behaviour of minerals. The work is described under Section 5 dealing with the field plotting studies.

(iv) Polarity. Ralston[8] quotes Johnson who observed that insulators and semi-conductors sometimes respond more definitely to either the negative or positive charge on the active electrode. This was attributed in part to the ability of electrons to flow more easily in one direction across an interface than in the reverse direction. Brewis[5] observed the same phenomenon. In the present work a positive electrode polarity was used throughout. However, a study was made of the effect of negative polarity on the ionisation process (Section 5.3).

(v) Drum speed. Drum speed can radically influence the pinning and throwing behaviours of materials as

illustrated in Section 6, describing the mechanism of the process of high tension separation.

(vi), (vii), (viii). Current, voltage and ioniser gap. A thorough study was made of these three variables and it was possible to relate the pinning behaviours of insulators and conductors to a single factor, air conductivity (Section 4.4).

4.1 (c) Environmental variables.

In this category are included the variables relative humidity and air temperature.

(i) Relative humidity. The moisture content of the air between the electrodes and the drum surface has a considerable influence on the electrical properties of minerals, particularly hydrophilic insulators. At high air humidities the pinning of hydrophobic insulators can be greatly reduced. The variable, relative humidity, was widely studied in this thesis and its effects are discussed under the sections describing

(a) the influence of current, voltage and ioniser gap on the pinning of insulators and conductors (Section 4.3).

(b) the field plotting experiments (Section 5.5).

(c) the modification of the electrical properties of clean quartz by means of water adsorption (Section 7).

(ii) Temperature. The temperature of the air within the separation zone can radically influence the high tension behaviour of minerals by altering the relative humidity. Temperature was not controlled but remained reasonably constant at 20° ± 2.0°C throughout the test series.

In this section of the thesis, investigations were confined to a study of the effects of current, voltage, ioniser gap and relative humidity on the high tension separation of insulator and conductor particles.

4.2 Experimental procedure.

200g samples of chemically-treated kyanite ore were passed through the high tension separator under conditions specified in table 2 below. The recorded relative humidities were those prevailing at the start of each test. At this stage of the work air humidity was not controlled. The required changes in the ioniser gap, current and voltage values were obtained by adjustment to the ionising electrode position and variation in the high tension power supply. Throughout this series the static electrode was kept at (2", 35°). In all tests the feed rate fluctuated between 20 and 30g/min. and the drum speed was kept constant at 65 rpm.

After the completion of each test, the materials reporting in the thrown and pinned trays were weighed.

TABLE 2.

Current μA	Voltage kV	Ioniser Gap mms.	Relative Humidity %	Quartz Pinned %	Kyanite Pinned %
5	10.0	20.6	63	17.7	58.0
5	16.8	49.2	44	63.5	90.0
5	16.8	49.2	64	8.8	57.8
5	17.0	50.8	67	25.8	72.8
5	17.0	50.8	28	48.0	50.3
5	25.0	66.7	63	15.3	79.5
5	25.0	68.3	55	28.5	84.0
5	26.8	71.4	64	2.0	63.0
5	30.0	76.2	42	48.8	86.8
5	30.0	76.2	56	33.8	80.2
5	26.8	71.4	67	1.2	58.0
5	25.0	68.3	24	88.5	92.8
5	25.9	68.3	61	4.2	66.3
10	10.0	20.6	48	40.1	79.8
10	17.0	46.0	53	44.7	85.8
10	25.0	61.9	51	37.8	85.8
50	10.0	14.3	50	59.7	88.8
50	14.0	30.2	36	86.5	96.3
50	14.5	30.2	37	82.8	95.4
50	17.0	30.2	50	67.8	92.3
50	25.0	39.7	52	49.5	86.2

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Table 2 contd:

Current A	Voltage kV	Ioniser Gap mms.	Relative Humidity %	Quartz Pinned %	Kyanite Pinned %
50	25.0	41.3	67	41.8	81.0
50	25.0	46.0	40	79.0	93.8
50	25.0	46.0	57	60.4	89.1
50	30.0	52.4	40	77.0	92.5
50	30.0	52.4	54	50.0	87.6
50	40.0	63.5	43	73.8	91.8
50	14.0	30.2	42	84.9	95.9
50	25.0	39.7	25	96.1	99.0
50	14.5	30.2	37	84.2	95.8
100	30.0	46.0	45	88.0	96.0
150	10.0	12.7	50	76.5	94.8
150	17.0	23.8	52	78.0	91.3
150	25.0	36.5	55	64.3	92.8

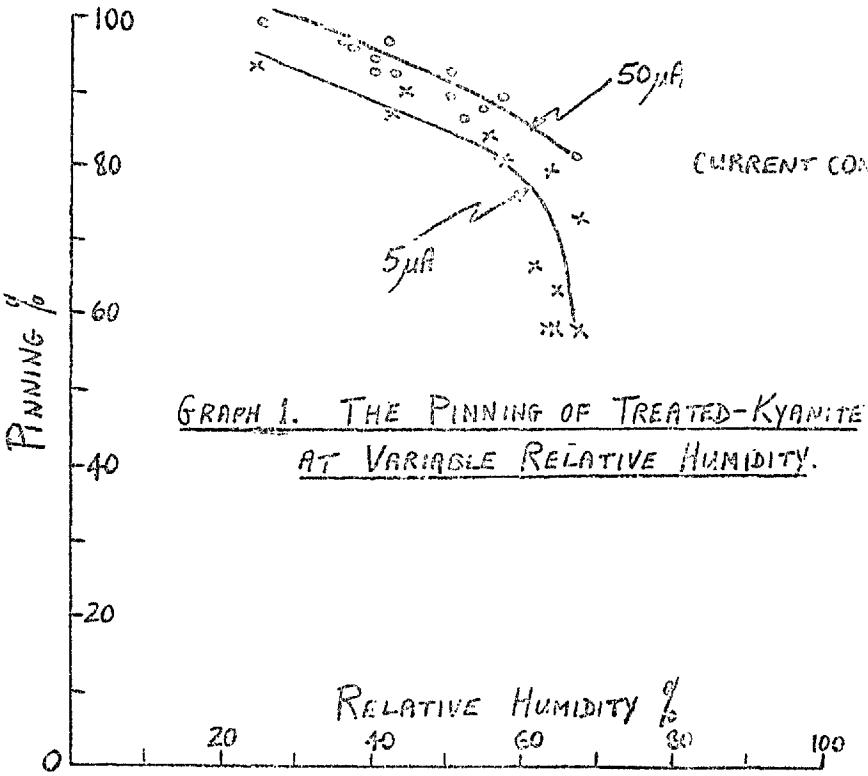
Representative samples of each fraction were examined microscopically and percentages of quartz and kyanite were determined by particle counting. The percentages of each mineral pinned were calculated separately and tabulated in table 2.

4.3 Results and discussion.

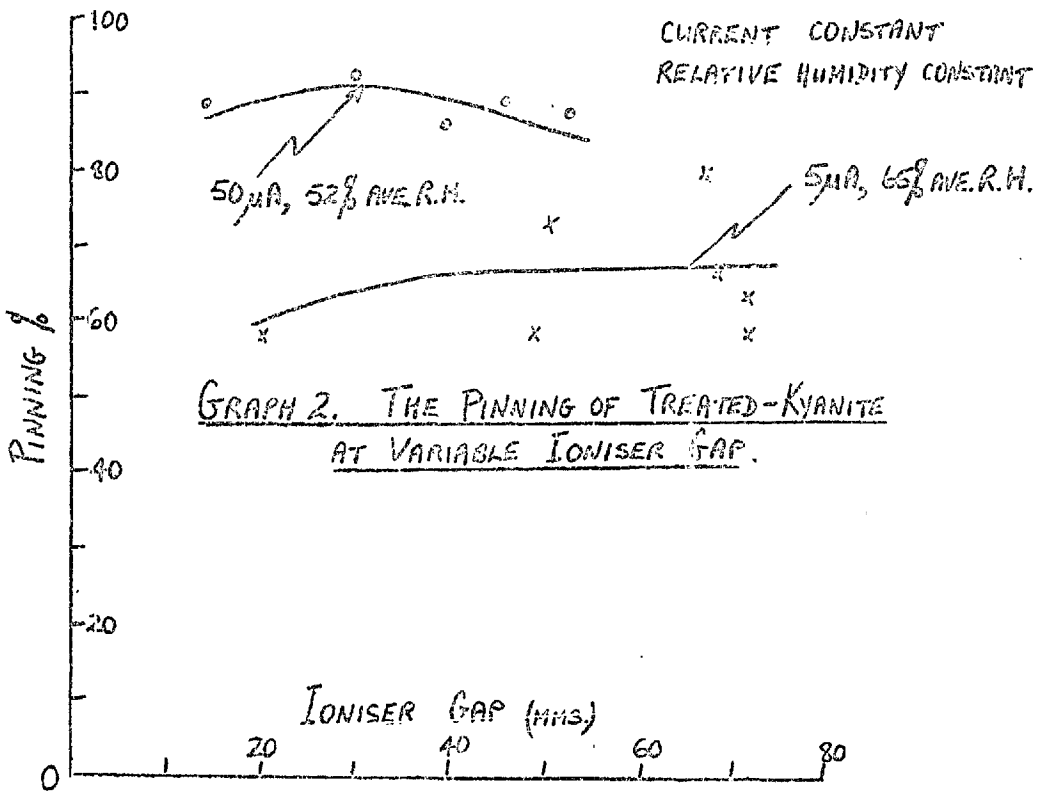
In the discussion that follows the conditioned quartz and kyanite fractions are often referred to as "conductors" and "insulators" respectively.

The results tabulated above were used in the construction of graphs 1 to 6, which show the relative effects the variables current, ~~voltage~~, ioniser gap and relative humidity have on the pinning behaviours of insulators and conductors. There is an appreciable scatter of points in some of the graphs, although on any particular occasion reproducibility of identical tests was good. A thorough investigation revealed that reproducibility could be improved and the deviation of results was attributed to the following factors:

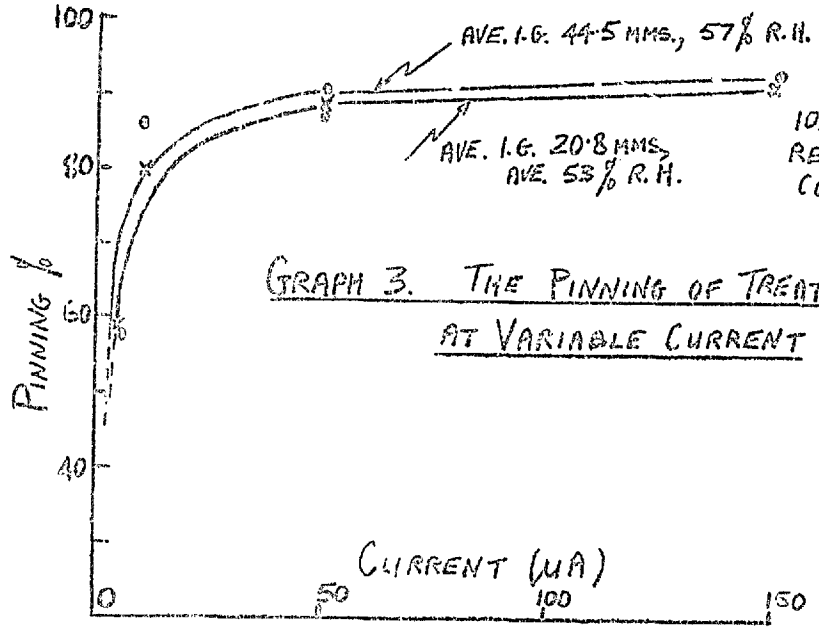
(1) The recorded relative humidities did not necessarily represent the true humidity prevailing throughout a test. The subsequent introduction of a constant relative humidity system ensured that a constant and accurate air humidity prevailed at all times.



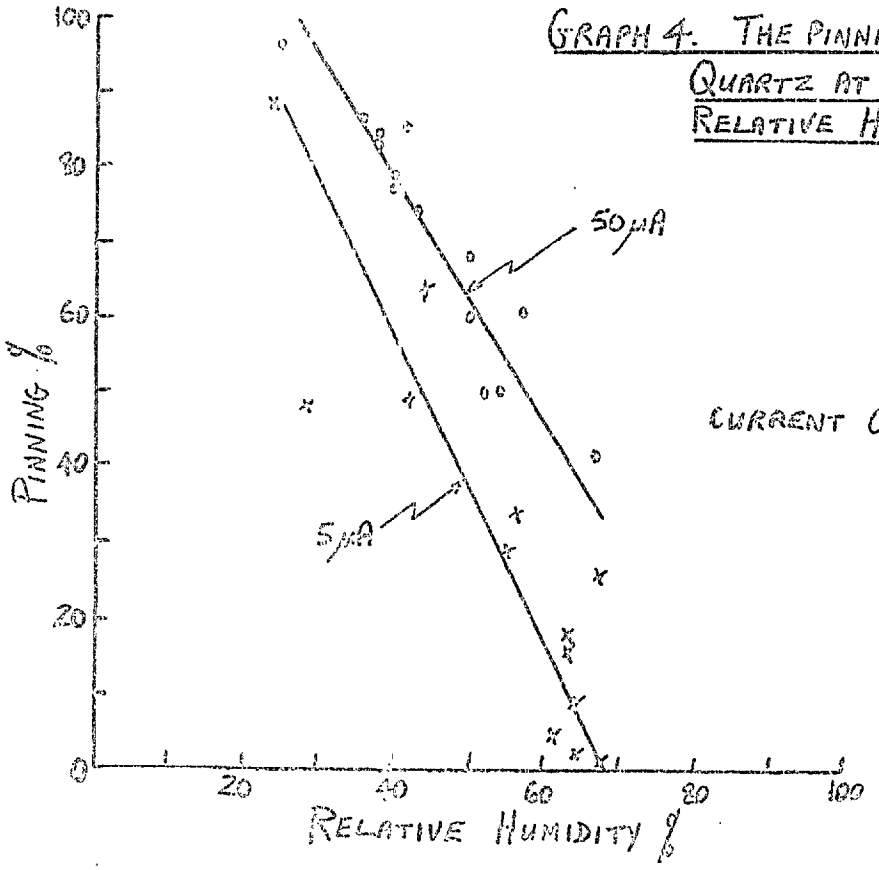
GRAPH 1. THE PINNING OF TREATED-KYANITE AT VARIABLE RELATIVE HUMIDITY.



GRAPH 2. THE PINNING OF TREATED-KYANITE AT VARIABLE IONISER GAP.

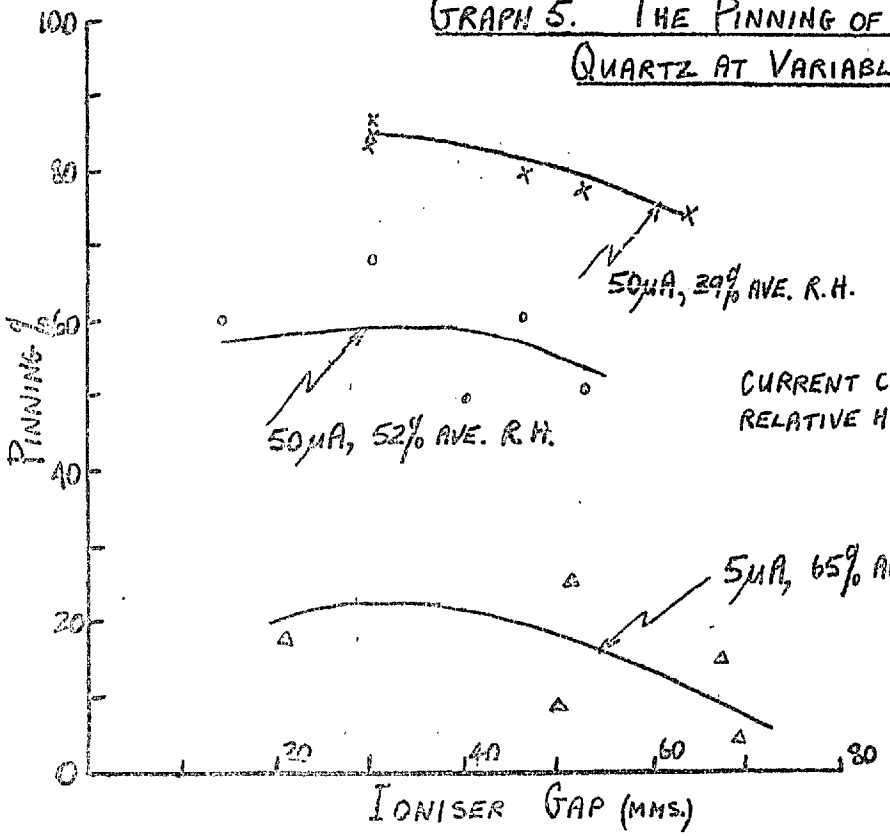


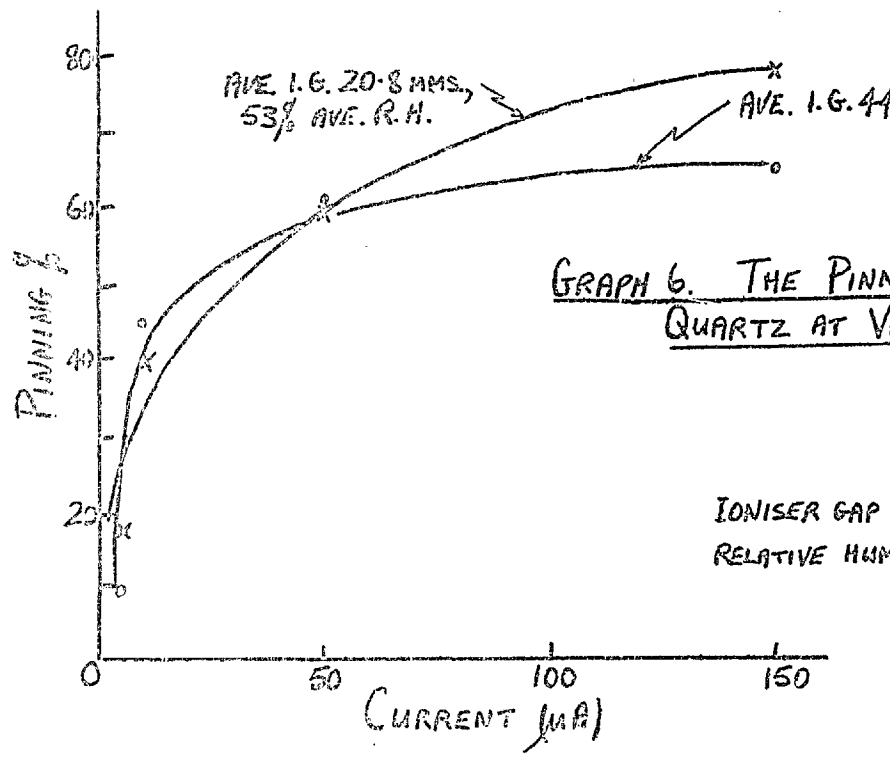
GRAPH 3. THE PINNING OF TREATED-KYANITE AT VARIABLE CURRENT



GRAPH 4. THE PINNING OF TREATED-QUARTZ AT VARIABLE RELATIVE HUMIDITY.

GRAPH 5. THE PINNING OF TREATED QUARTZ AT VARIABLE IONISER GAP





GRAPH 6. THE PINNING OF TREATED QUARTZ AT VARIABLE CURRENT.

(2) The amount of water adsorbed by the hydrophilic quartz was not controlled. The magnitude of adsorbed water strongly influences the surface conductivity of some materials (Section 7).

(3) The method of particle counting used for determining the proportions of quartz and kyanite can lead to inaccuracies. Single mineral systems were used in later work, thereby eliminating discrepancies associated with assaying procedures.

(4) It has been illustrated earlier (page 32.) that the oxidation of the drum surface increases with time and usage under ionic charging conditions. Oxidation leads to an increase in the particle-drum contact resistance, a variable almost impossible to control. The difficulty was overcome by referring all further test results to a machine standard. For this purpose a standard material was passed through the machine before and after each test run, using standard conditions and measuring any departure of the standard material from its normal behaviour. Calculated correction factors were applied to the test results.

4.3 (a) <u>The effect of current</u>.

Comparison of graphs 3 and 6 demonstrates that the pinning of both insulator and conductor particles increases with current until a critical value is reached, above which pinning remains constant. Others[5,13,17] have observed the same phenomenon. For both minerals, the critical current is in the vicinity of 50 uA under the conditions employed in this work. The maximum pinning value is higher in the case of the insulator material.

The phenomenon of maximum pinning at a critical current is in agreement with Mora's[1] idea that a particle under the influence of an ionising field acquires a maximum charge. After a particle has been coated with a certain number of ions, others can no longer be attracted and are in fact repelled.

4.3 (b) The effect of voltage.

At a constant ioniser gap, the flow of current is related to the potential difference between the electrode and the drum (graph 7). Pinning and current should thus show similar relationships to the voltage employed. However, no correlation between voltage and the pinning behaviours of insulators or conductors was observed, as shown by the data in table 2. Any apparent relationship between voltage and pinning is an indirect one inasmuch as the potential difference serves the purpose of maintaining the required current flow over a given length of air gap.

Although voltage per se is of secondary status in the ionising field, it can play an important role in the static field, as suggested by Mora and proved experimentally in this thesis. This topic is discussed in detail in Section 6 dealing with the mechanism of high tension separation.

4.3 (c) The effect of the ioniser gap.

Graphs 2 and 5 show that the gap between the

ionising electrode and the drum has distinctive effects on the high tension behaviour of materials. The detailed exploration of the ionising field, as reported on pages 73 to 75 , showed that the effect of the gap was conditioned by the geometry of the field. Increasing the ioniser gap at constant currents leads to a reduction in the intensity of the ionising field and an extension in its effective length of influence. The two opposing changes result in the relationship of pinning vrs ioniser gap (graphs 2 and 5) displaying maxima.

4.3 (d) The effect of relative humidity.

A profound influence of relative humidity on the high tension behaviour of minerals was observed and is illustrated in graphs 1 and 4. Graph 4 demonstrates that hydrophilic insulator minerals show great sensitivity to changes in relative humidity. At high water vapour contents of the air they become in effect good conductors (Section 7).

At low currents (5uA) the pinning of the hydrophobic mineral decreases strongly at relative humidities in excess of about 60%. This effect is attributed to a marked reduction in field intensity which reduces the magnitude of the ionic charge acquired by particles.(Section 5.5).

4.4 The pinning behaviour of minerals as a function of air conductivity.

At a particular value of the applied voltage, the current that will flow between the ionising electrode and the drum depends on the length of the ioniser gap. Hence, air resistance is a function of the applied voltage and the length of the air gap.

The ionising electrode was set at various distances above the drum surface, and the flow of current corresponding to different applied potentials was noted (graph 7). Results from this study are utilised below.

The resistance or conductivity of air can be related to the variables current, voltage and ioniser gap, all of which can influence the pinning behaviour of minerals. The resistance, R, of a specimen of a substance is given by

$$R = \frac{u\ell}{A} \qquad (1)$$

where u is a constant dependent on the electrical properties of the substance, ℓ is the length and A the cross-sectional area.

If it is assumed that A is constant under the conditions studied, one may write

$$u_A = \frac{R}{\ell} \qquad (2)$$

where u_A incorporates a constant factor to account for A. Resistance is a function of the potential and current flow,

$$\text{i.e.} \quad R = f\left(\frac{E}{i}\right) \qquad (3)$$

where E = potential gradient, i = current and f = a function.

From (2) and (3) $u_A = f\left(\frac{E}{i}\right)\frac{1}{\ell}$ (4)

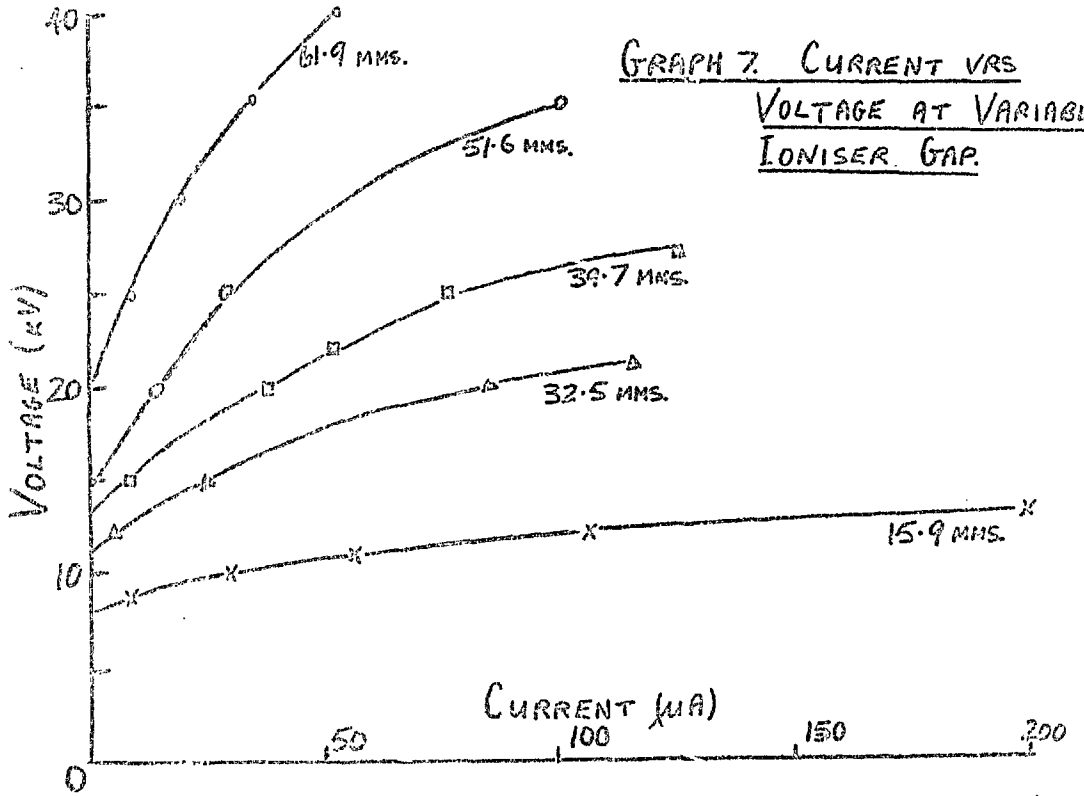
Since conductivity, σ, is the reciprocal of u,

$$\sigma = \frac{\ell}{f\left(E/i\right)} \qquad (5)$$

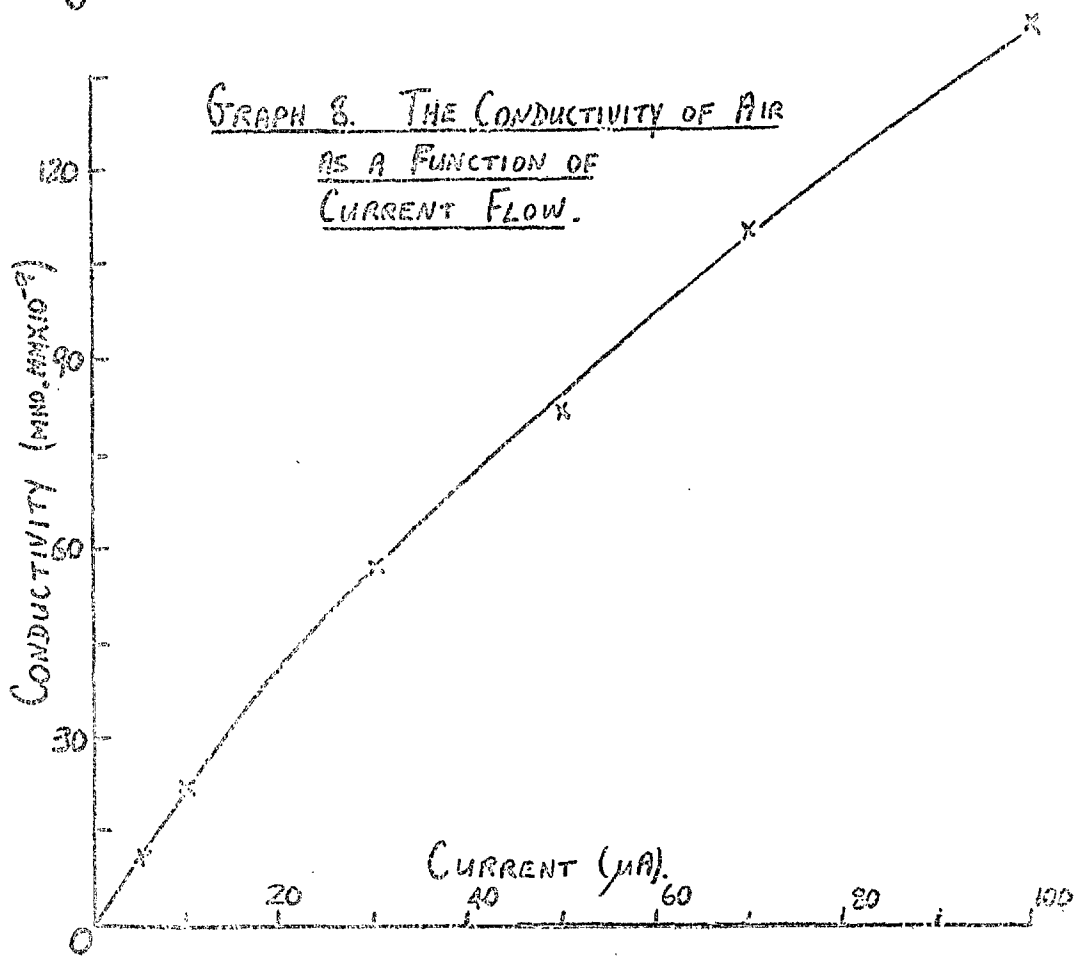
It was not necessary to determine the mathematical expression of f $(\frac{E}{i})$ because a relationship between σ, ℓ, E and i could be determined graphically from the curves of voltage versus current at varying ioniser gaps (graph 7). Some of the relevant values are included in table 3, while graphs 8 and 9 show how air conductivity changes with current and ioniser gap respectively.

The similarity between these two graphs and graphs 2,3,5 and 6 showing the pinning behaviour of an insulator and a conductor as a function of the ioniser gap and current, is very striking. Values taken from the six graphs establish the relationship between air conductivity and the pinning of minerals (graph 10).

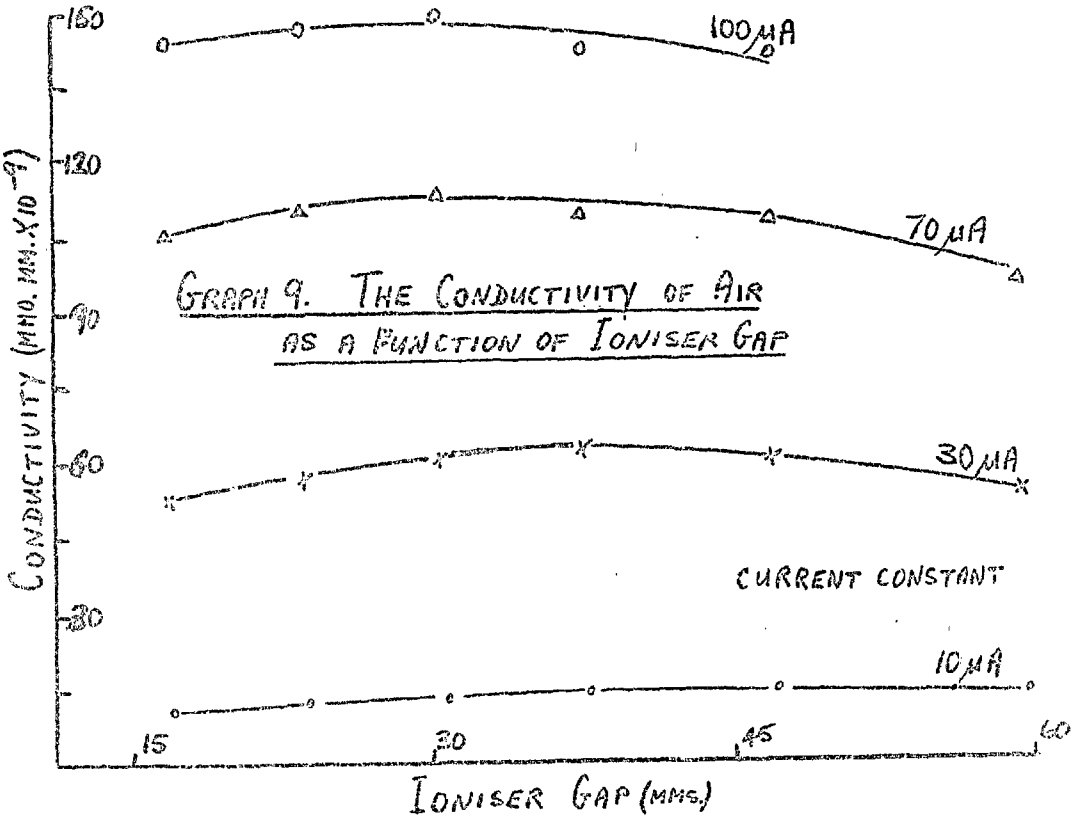
This information obviates the former tedious process of empirical determination of the correct permutation of current, voltage and ioniser gap for the optimum high tension separation of an insulator from a conductor mineral at a constant relative humidity. By choosing, say, four



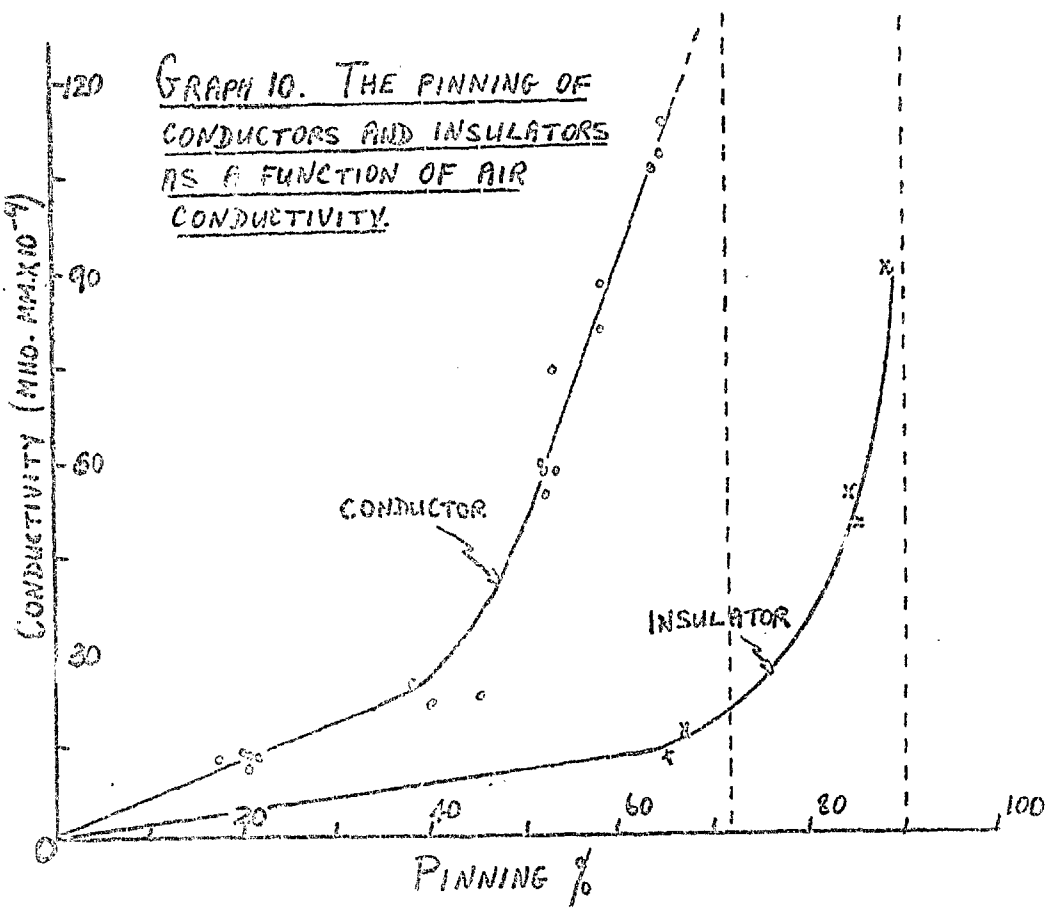
GRAPH 7. CURRENT VRS VOLTAGE AT VARIABLE IONISER GAP.



GRAPH 8. THE CONDUCTIVITY OF AIR AS A FUNCTION OF CURRENT FLOW.



GRAPH 9. THE CONDUCTIVITY OF AIR AS A FUNCTION OF IONISER GAP



GRAPH 10. THE PINNING OF CONDUCTORS AND INSULATORS AS A FUNCTION OF AIR CONDUCTIVITY.

TABLE 3.

Ioniser Gap 1 mms.	Current i(uA)	Voltage E(kV)	Conductivity = $\frac{1}{u_A}$
61.9	5	22.4	13.8
61.9	30	33.0	56.4
61.9	50	39.3	78.6
51.6	5	17.5	14.9
51.6	30	25.1	61.9
51.6	50	28.8	89.9
51.6	100	34.7	148.6
39.7	5	14.4	14.0
39.7	30	18.6	64.0
39.7	50	21.7	91.3
39.7	100	26.5	149.7
32.5	5	12.8	12.7
32.5	30	15.4	63.5
32.5	50	17.3	94.0
32.5	100	20.7	157.2
26.2	5	10.8	12.1
26.2	30	13.2	59.5
26.2	50	14.4	91.0
26.2	100	16.8	155.9
19.8	5	9.3	10.8
19.8	30	10.8	55.2
19.8	50	11.8	84.1
19.8	100	13.0	152.6

values of air conductivity (irrespective of the relative values of i, ℓ or E) it should be possible by interpolation to find the value of σ resulting in the optimum separation of the minerals under test. Although the air humidity can have a marked influence on the effective electrical properties of minerals, it does not alter measurably the conductivity of air. This phenomenon is discussed later under Section 5.5.

4.5 Correlation between surface conductivity and the Pinning behaviour of minerals.

4.5 (a) Introduction

It is generally accepted[1,4,18] that the pinning behaviour of minerals tested under constant high tension conditions is dependent on their electrical conductivities. The relationship was established qualitatively in this work by determining the pinning of a few minerals under the standard conditions outlined below, and relating these values to the dielectric constants of the materials.

TABLE 4.

MINERAL	% PINNING	DIELECTRIC CONSTANT[8]
QUARTZ	68	3.0 - 6.53
KYANITE	95	4.0 - 7.2
CHROMITE	12	11.0
ILMENITE	5	33.7 - 81
CARBORUNDUM	1	

The kyanite mineral has a higher pinning value than that expected from its dielectric constant. This is attributed to its elongated shape factor as discussed earlier.

In the preliminary work relating to the modification of the surface electrical properties of quartz, it was demonstrated that the pinning of quartz could be altered through wide limits by chemical treatment. The change in

pinning behaviour was attributed to alterations in the surface conductivity of the mineral. A quantitative correlation was therefore sought between the behaviour of quartz in a high tension separator and its fundamental physical property, surface conductivity.

4.5 (b) Measurement of surface conductivity.

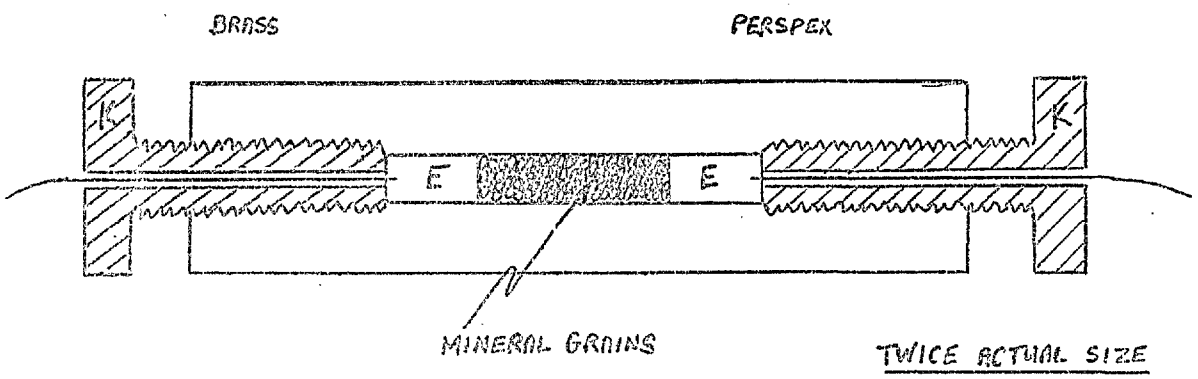
Surface conductivity was measured by a plug-resistance method suggested by Cooke[19].

(i) Apparatus and electrical circuit.

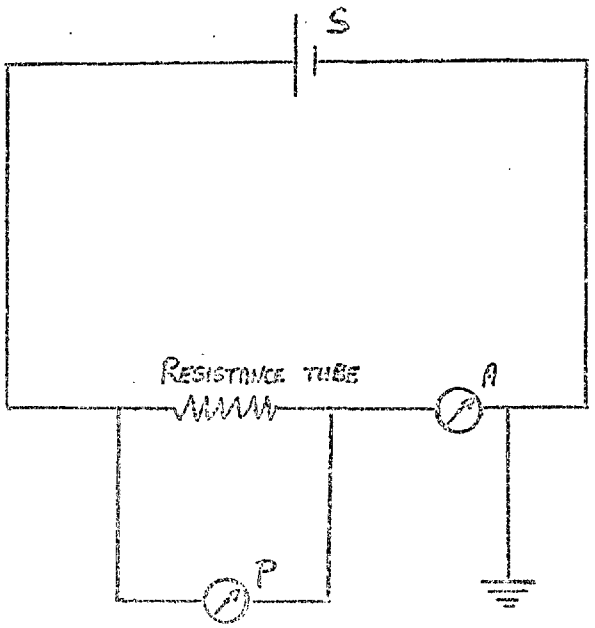
A resistance tube of the type used by Cooke was constructed with certain modifications (fig.4). The apparatus consists of a ½ in. perspex rod drilled with a hole 9/64 in. in diameter. O.B.A. threads were cut at each end to hold brass plungers, K. The brass electrodes, E, are ¼in. long, 9/64 in. in diameter and connected by electric cable passing through the centres of the plungers, to a voltage supply, S, via an "ammeter", A, in series and a voltmeter, P, in parallel. On tightening the plungers, the electrodes do not rotate about their axes and hence, attrition of the material in the proximity of the electrode surfaces is prevented.

A 1.5 volt dry-cell was used in order to minimise leakage losses. A is a valve-type electrometer capable of measuring currents down to 10^{-12} amp. with a sensitivity

FIG. 4 RESISTANCE TUBE AND CIRCUIT



TWICE ACTUAL SIZE



of 0.05 x 10^{-12}amp. at the lowest range. Reproducibility is approximately 3%. P is a Pye portable potentiometer of 0.0005 volt sensitivity and excellent reproducibility. Measurements were carried out in a glove box containing air at a constant 44% relative humidity to standardise static effects.

Initially, the brass electrodes were thoroughly cleaned before each series of measurements. Reproducibility of results was found to be poor from day to day. Later it was observed that if the electrodes were not cleaned but allowed to form a tarnish finish, reproducibility was greatly improved. Similar difficulties were experienced elsewhere[16] where the use of a brass drum in a high tension separator led to erratic mineral behaviours.

(ii) Experimental procedure.

Quartz samples of -52 +100 mesh size were chemically-treated by the various means described throughout the thesis. After drying and cooling overnight in a desiccator containing silica gel, the samples were placed in the glove box. After 60 minutes an approximate 0.2g aliquot was placed in the resistance tube. Attempts were made to standardise as far as possible the packing of the mineral grains by employing a standard procedure for filling the tube. The material, occupying about 1 cm. length between the electrodes, was compressed by applying moderate

pressure to both plungers. The magnitude of the applied pressure used in the test work was of no significance in influencing the overall resistance of the plug of material. Cooke made the same observation.

The circuit was completed and the voltage and current flow across the resistance tube were recorded. The resistance of the material was calculated. The effective length of the plug of material was measured on a travelling microscope and the weight of the sample was also noted. The procedure was repeated four to six times for different aliquot s of the same sample and an average taken of the results.

4.5 (c) Determination of the pinning behaviour of chemically-treated quartz samples.

In determining the pinning behaviour of the chemically-treated quartz samples, it was essential that machine and environmental variables be standardised as far as possible. The choice of the standard high tension conditions (outlined below) was in part arbitrary and in part swayed by the results of the preliminary investigation described in Section 4.3.

VARIABLE	VALUE
Current	30 μA
Voltage	17.3 kV
Ionising electrode position	(2", 19°)
Ioniser gap	36.5 mms.
Static electrode position	(2", 35°)
Relative humidity of separation	44%
Relative humidity at which minerals are humidified	44%
Humidifying time	60 mins.
Feed rate	10-15g./min.
Drum speed	55 rpm.
Temperature	20.0° ± 2.0°C

The samples were humidified for 60 minutes in air at 44% relative humidity and their pinning values determined under the above standard conditions. In all subsequent test work described in this thesis, the identical standard conditions will apply.

4.5 (d) Relation between surface conductivity and pinning.

Cooke has suggested that surface conductivity, S, may be related to the diameter of the tube, d, length of material between electrodes, ℓ, average diameter of material, D, and overall resistance of the tube, R, by the formula

$$S = \frac{2\,D\ell}{\pi d^2 R} \qquad (6)$$

D and d are constants, so that

$$S = \frac{K\ell}{R} \qquad (7)$$

The relation between the weight and lengths of the plugs of material was determined. The weight, W, of the samples is directly proportional to ℓ (graph 11).

$$\text{Hence } S = \frac{K^1 W}{R} \qquad (8)$$

$$\text{i.e. } \frac{R}{W} \text{ is proportional to } \frac{1}{S}$$

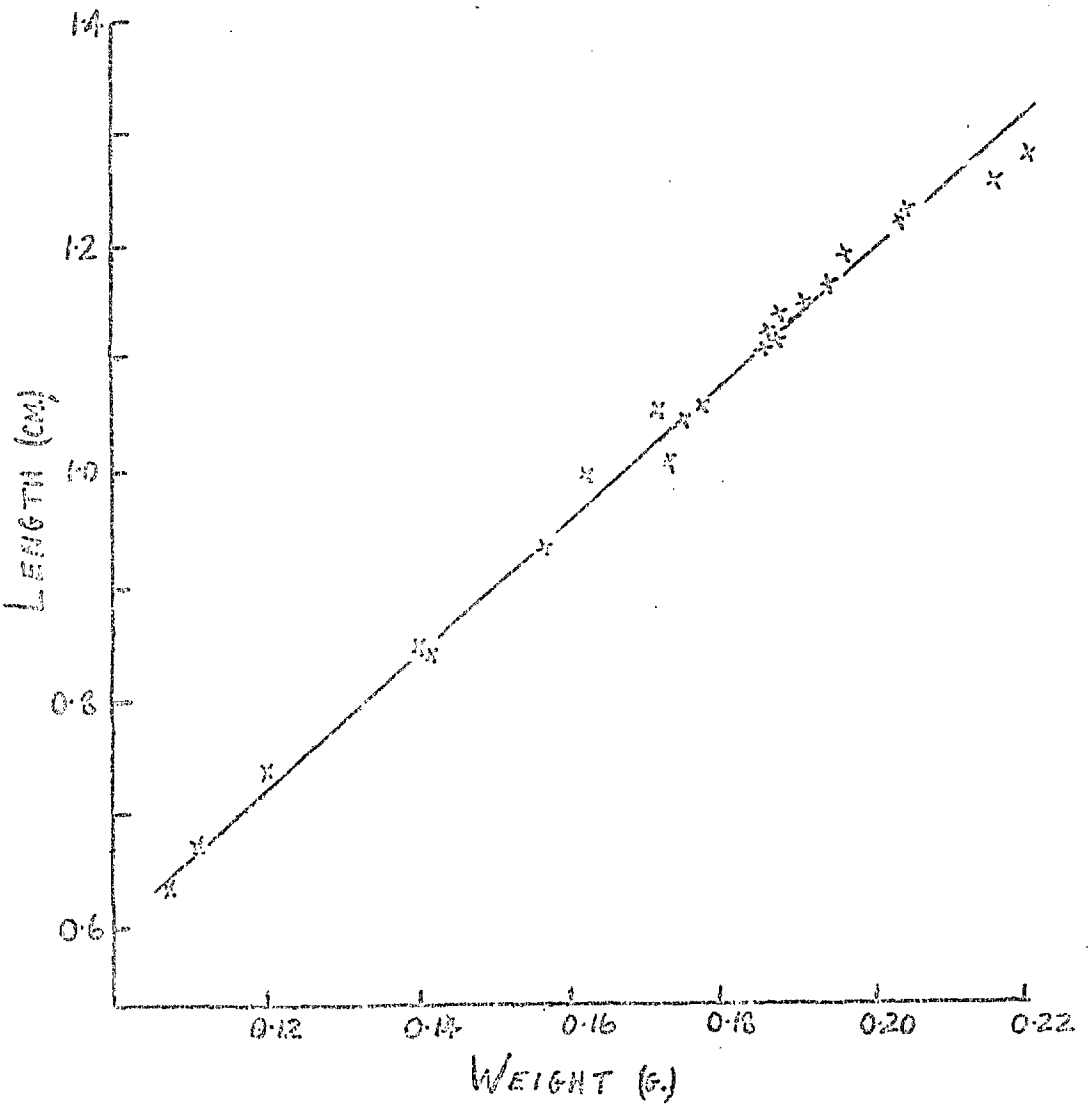
The pinning behaviours of the treated samples were plotted against R/W. A linear relationship was found to exist as illustrated in graph 12, thereby confirming the postulation that the pinning behaviour of minerals can be correlated with their surface conductivities.

4.5(e) <u>The correlation between pinning behaviour and contact charging of minerals</u>.

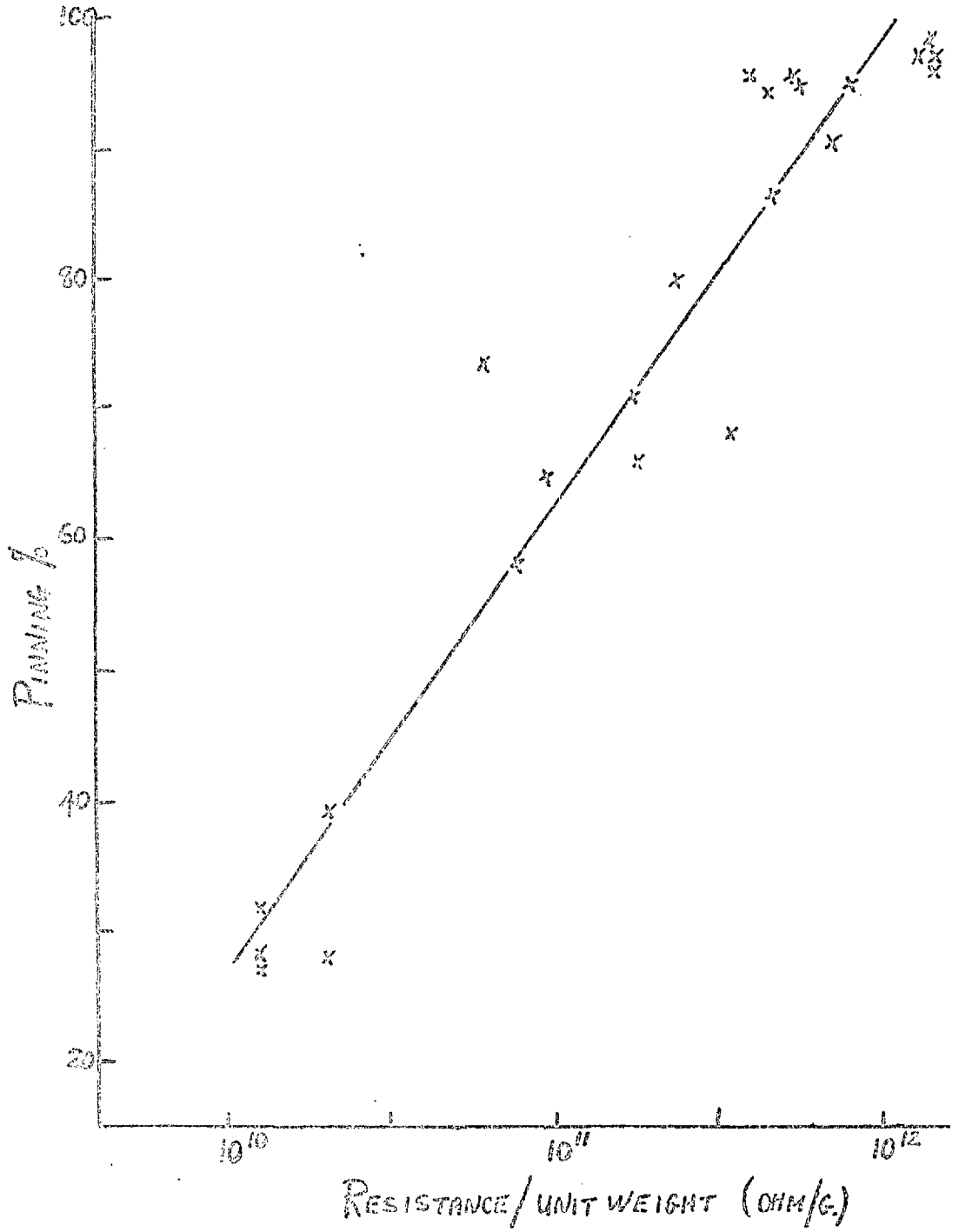
There is a qualitative correlation between the pinning values of materials and the magnitude and sign of the frictional charges acquired by similar substances. Cooke has reviewed the literature pertaining to the contact charging of non-metal/metal systems. Together with the results of his own work and the survey, he listed the following observations.

(i) insulators (particularly quartz) acquire relatively strong negative charges from contact with metals.

GRAPH II. THE RELATIONSHIP BETWEEN THE LENGTH AND WEIGHT OF QUARTZ PLUGS.



GRAPH 12. THE RELATIONSHIP BETWEEN PINNING AND RESISTANCE / UNIT WEIGHT.



(ii) dry insulators acquire higher charges than "moist" insulators.

(iii) high air humidities lead to small negative charges on insulators.

(iv) dry ionic compounds (e.g. NaCl crystals) acquire weak negative or weak positive charges.

(v) "moist" ionic compounds and conductors acquire strong positive charges.

In the present work the pinning behaviours were determined on materials similar to those discussed by Cooke, with the following results.

(a) dry insulators (quartz, kyanite and amine-treated quartz) have very high pinning values.

(b) moist insulators acquire moderately high pinning values.

(c) high air humidities result in a strong reduction in the pinning of insulators.

(d) dry NaCl-treated quartz yields small pinning values.

(e) conductors and "moist" NaCl-treated quartz produce very low pinning values.

Cooke measured surface conductivity using the plug-resistance method described above and found that for surfaces of the same material, the maximum contact charge is inversely proportional to surface conductivity.

Using the same method of resistance measurement, it has been shown (page 57) that the pinning of chemically-treated quartz is proportional to the reciprocal of surface conductivity. This observation, together with the correlation illustrated above, leads to the suggestion that the processes of charge transfer in contact charging and charge leakage in high tension separation are closely related. A widely accepted opinion is that contact charging can be ascribed to the equilibrium redistribution of a mobile charged species on the surfaces of the non-metal and the metal. It has been suggested[34] that H^+ ions may be the dominant charge carrier. Other conceivable carriers are electrons and hydroxyl ions.

5.0 THE FIELD PLOTTING INVESTIGATION

5.1 Introduction

Inconsistencies of mineral behaviour were encountered in the course of a systematic experimentation involving a study of the influence of electrode geometry on the pinning behaviour of minerals. One suspected cause was uncontrolled field changes due to variables other than those known to influence the strength and geometry of the ionising fields i.e. current, voltage and distance of the electrodes from the earthed drum.

More detailed knowledge of the reaction of the fields to changes in variables in the system was therefore sought and two sets of investigations were carried out. One was concerned with the preliminary study of the ionisation of air and was performed with the aid of an "ionisation box". The other was concerned with plotting the actual fields beneath the electrode system of the high tension separator with the help of an analysing electrode under varying conditions and relating field changes to the pinning behaviour of minerals.

5.2 Ionisation of air.

A gas in its normal state consists of uncharged molecules and is almost a perfect insulator as it has no charged particles to carry a current. However, when an

electric field is established between two electrodes in the gas, it can become a conductor. The transition from an insulating to an almost completely conducting state is called the electrical breakdown. Before a large current can develop in a previously insulating gas, the current must build up by some ionisation mechanism from a very small value. The fundamental process of ionisation is complex and any attempt at an explanation is beyond the scope of this thesis.

Once ionisation has commenced the components of the air become ionised into gaseous cations and anions. In response to the polarity of the ionising electrode, there will be a flow of one species of gaseous ions away from the point of ionisation to the earthed drum of opposite polarity. This passage of ions constitutes current flow.

Since the ionisation process involves the passage of current, a method was available for its study. Some idea of the variation in current flow with length of air gap and potential gradient could have been obtained from the study of air conductivity (Section 4.4). However, information concerning conditions existing below the breakdown of air was lacking due to the restricted sensitivity of the microammeter of the high tension separator. An "ammeter" capable of reading currents ranging in value from 10^{-12} to 8×10^{-5} amp. was therefore used with an "ionisation box"

APPROXIMATELY ACTUAL SIZE

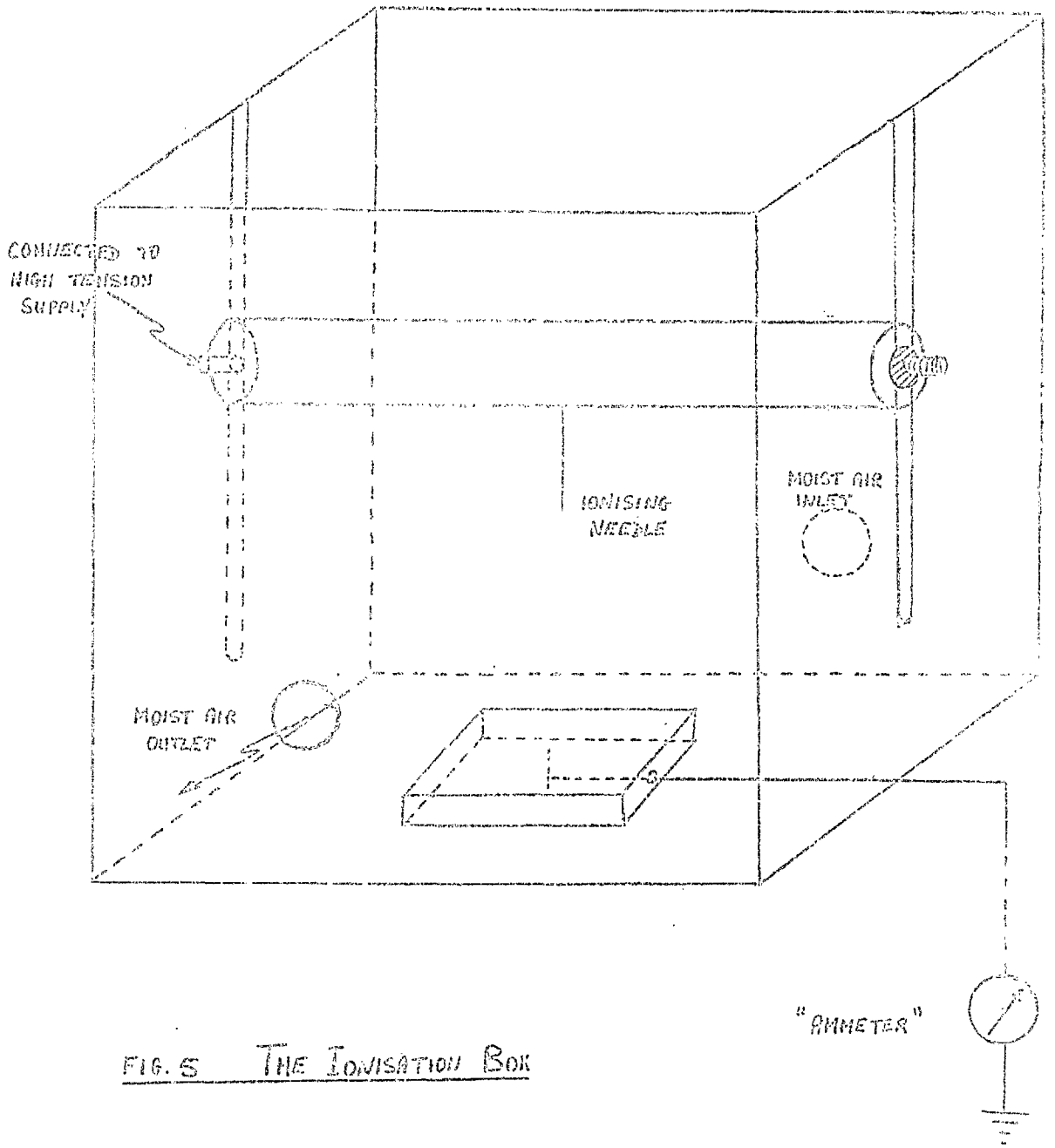


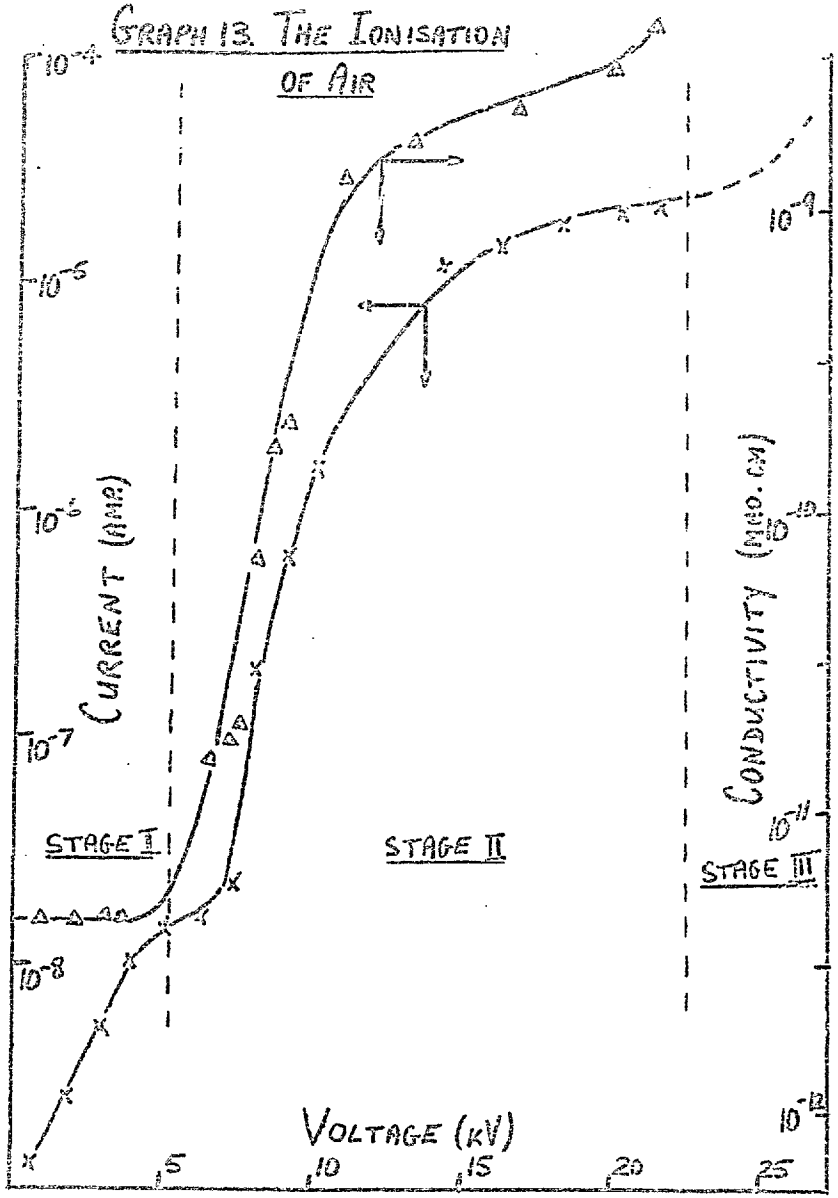
FIG. 5 THE IONISATION BOX

as shown in fig.5. The apparatus consists of a cubical perspex box,10.1 cm. side,with openings to allow the circulation of air of the required moisture content. A brass rod of ½ in. diameter with a sharp pointed needle 1.7 cm. long mounted in the centre, is held in position by means of nuts screwed on each end. The needle constitutes the point of ionisation. The vertical height of the ioniser can be adjusted. One end of the rod is connected to a high tension supply with a maximum output of 40kV. Directly beneath the ioniser is another needle of identical dimensions mounted in perspex such that 0.74 mm. of the point protrudes. The other end of the needle is electrically connected to earth via the "ammeter".

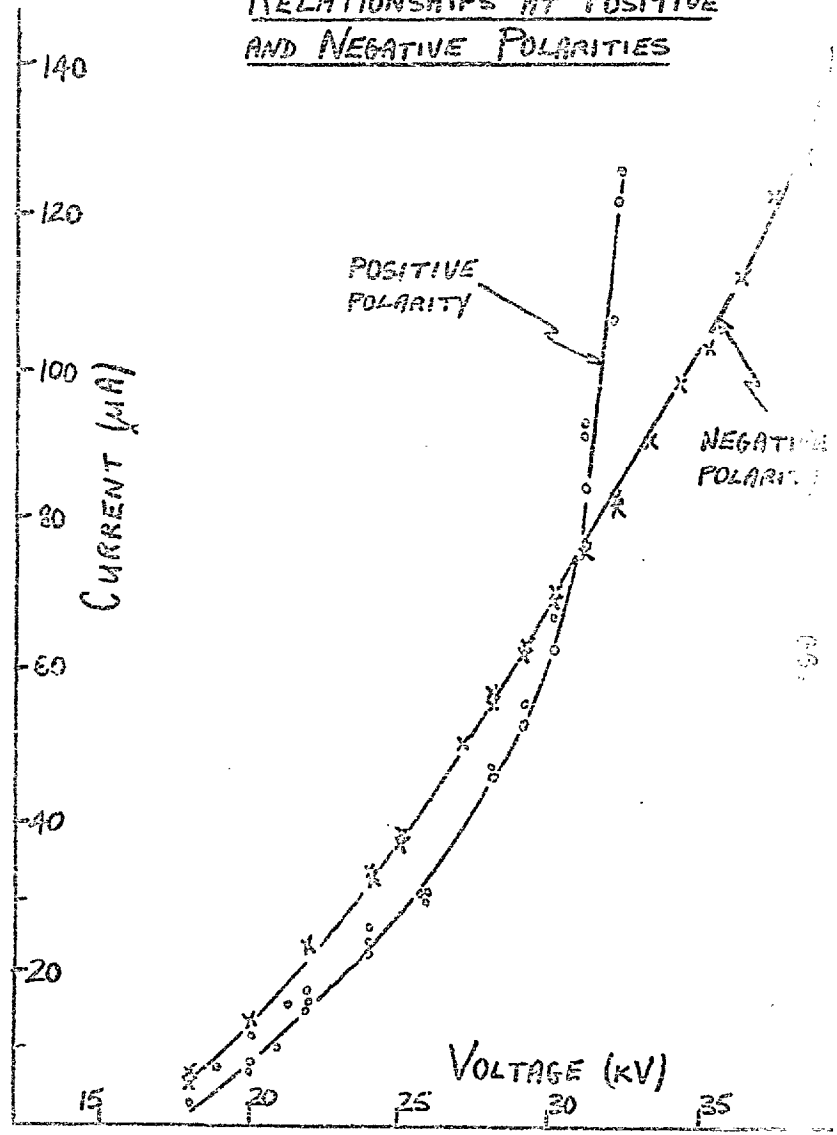
The length of the air gap between the two needle points was measured with a travelling microscope. With a distance of 33.50 mm. and at a constant relative humidity of 66%, a relationship between current and voltage was established as shown in graph 13. This graph displays a second plot using conductivity as ordinate, derived from equation (5).

The ionisation process represented by changes in current and conductivity with rising voltage can best be described by subdividing the curves of graph 13 into three stages. Over stage 1, the air behaves as an excellent insulator obeying the ohmic relationship, R = E/i. The

GRAPH 13. THE IONISATION OF AIR



GRAPH 14. VOLTAGE – CURRENT RELATIONSHIPS AT POSITIVE AND NEGATIVE POLARITIES



absolute resistance under these conditions corresponds to 5×10^{11} ohm per 3.35cm. gap, i.e. approximately 1.5×10^{11} ohm/cm. With further increase in voltage (Stage II), the transition point where air begins to display conducting properties is reached. Air conductivity increases rapidly at this point, which is called the breakdown potential and corresponds to about 6 kV. After the initial rapid increase the relationship between conductivity and voltage is parabolic, tending to reach a constant conductivity value at about 20 kV. When the voltage is increased still further (Stage III), intense electrification at the ioniser point causes sparking and a large current flows between the electrodes. Under these conditions, the conductivity of air approaches that of a metallic conductor.

5.3 Effect of electrode polarity on the ionisation process

The above discussion relates to the use of a positive polarity of the ionising electrode so that the predominant charge carriers are gaseous cations. When a negative polarity is employed, electrons and gaseous anions contribute to the flow of current. This is indirectly illustrated by graph 14 which shows that the current-voltage relationship approaches linearity at negative polarity. The linearity over the restricted range can be ascribed to the electron flow promoting an ohmic relationship between the values of applied potential and current flow.

In this study the ionisation box was not used, the values having been obtained with the electrode system of the high tension separator. Throughout this thesis a positive electrode polarity was employed for all the work.

5.4 The analysing electrode and the procedure for field plotting.

The apparatus constructed for the field plotting investigation consists of a perspex stand (sketch in fig.6), which can be fixed in a stationary position beneath the electrode system of the high tension separator. Holes spaced at accurate distances of $\frac{1}{8}$ in. were drilled in the two side plates so that a thin brass rod $\frac{1}{16}$ in. diameter and 6¼in. long (corresponding to the length of the ionising and static electrodes) could be placed at any position parallel to the longitudinal axes of the two electrodes. The brass rod which forms the analysing or probe electrode is connected to earth via a microammeter of 0 to 100 uA range and 0.2 uA sensitivity.

The apparatus was fixed beneath the separator electrodes after they had been adjusted to the desired positions. The probe electrode was then placed in the appropriate holes corresponding to position A1. (The nomenclature relating to probe electrode positions has been outlined in Section 3.1 describing the high tension separator). A potential gradient was applied between the

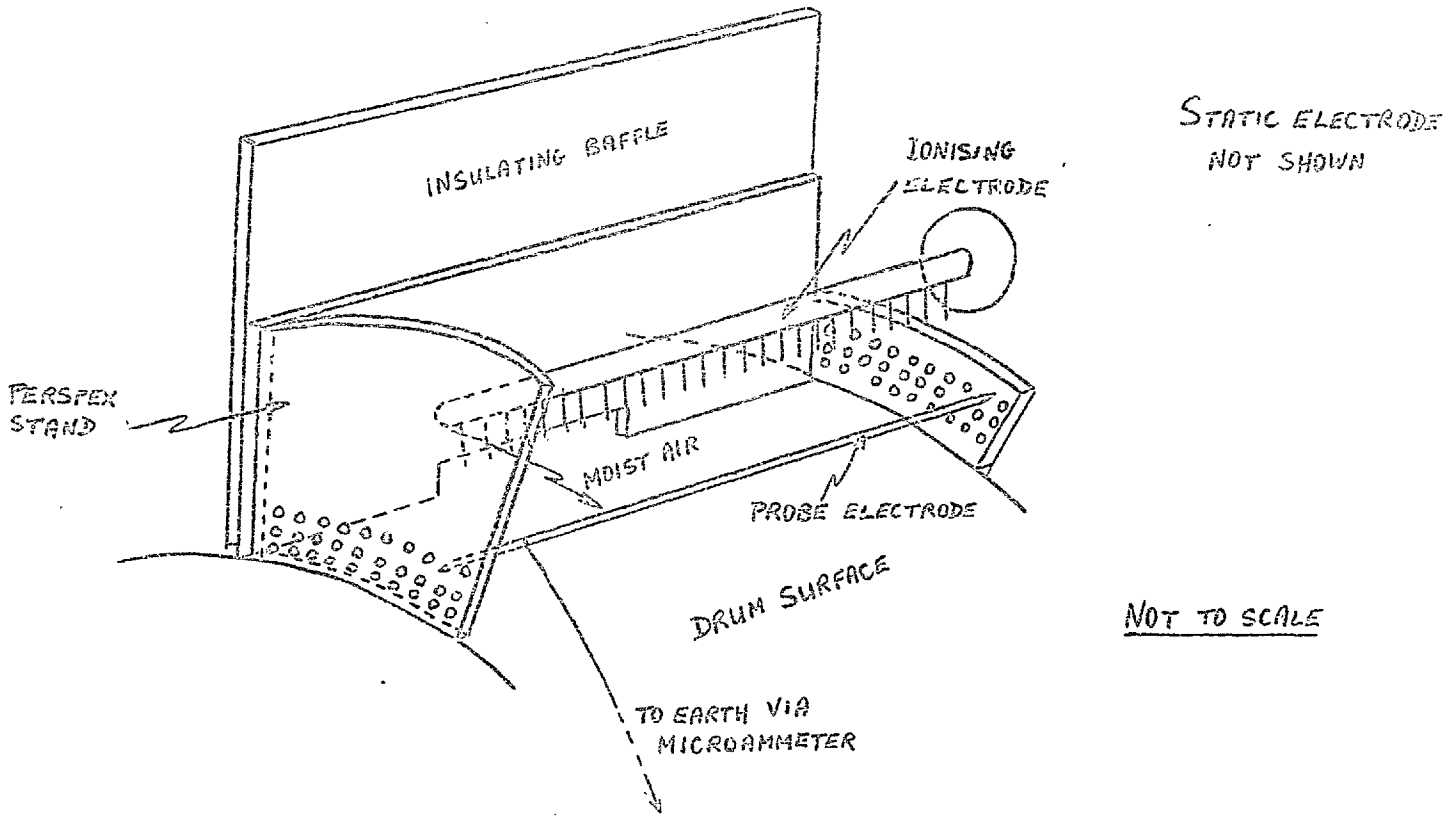


FIG. 6 FIELD PLOTTING APPARATUS

electrode system and the drum, and the separator currents and the probe electrode currents were noted at several values of the applied potential. The probe electrode was then moved to alternate positions A3,A5,A7, ... etc. and the procedure repeated. From the graph of probe electrode current vrs separator current for each probe electrode position (an example is shown in graph 15), the current distribution prevailing beneath the electrode system at constant separator current was constructed.

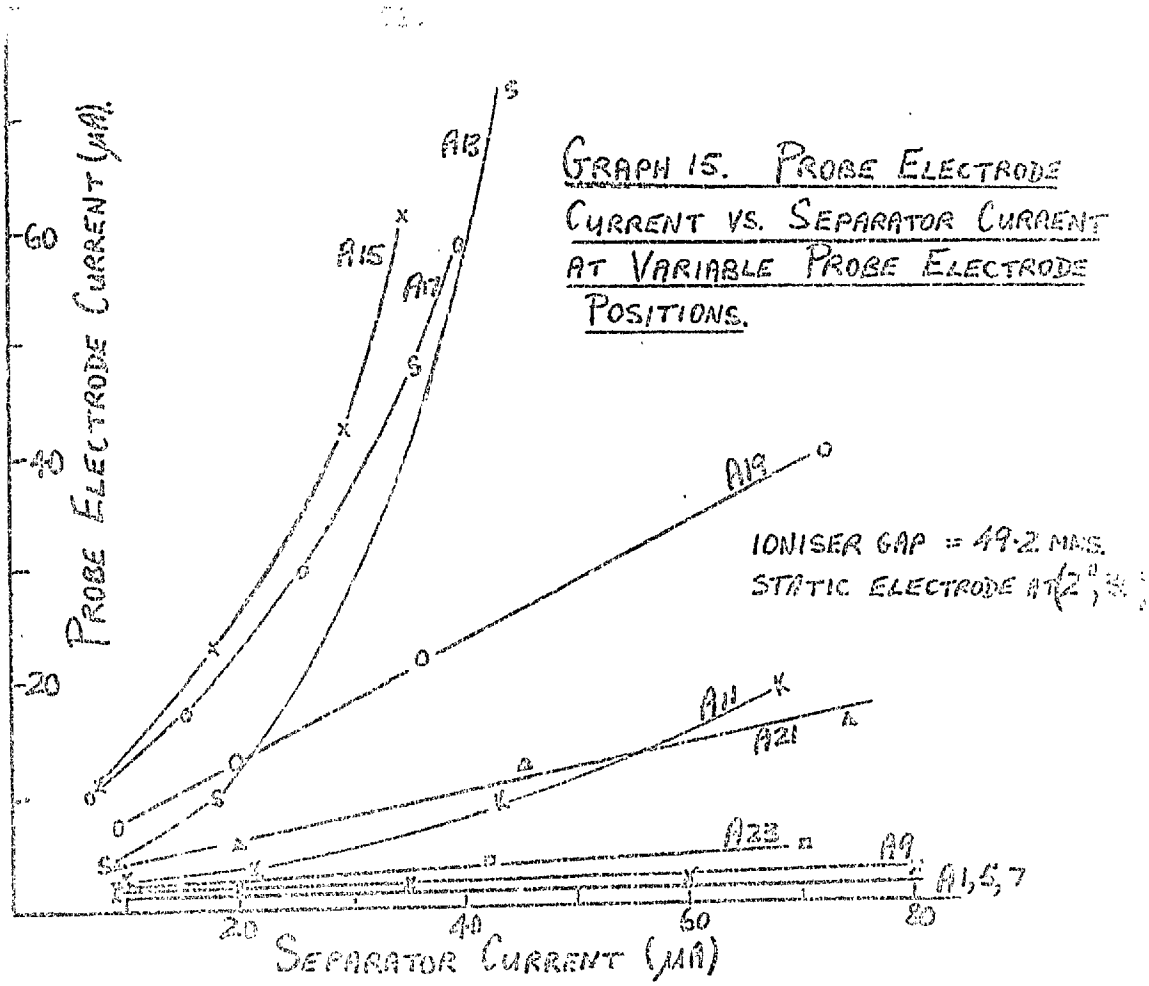
It is suggested that the magnitude of the current distribution is related to the intensity of the ionising field. By using the probe electrode at varying heights above the drum surface, it is possible to plot lines of equal current, from which the equi-current pattern on the drum surface can be estimated by extrapolation.

The effects of each separator variable on the current distribution within the ionising field are discussed below.

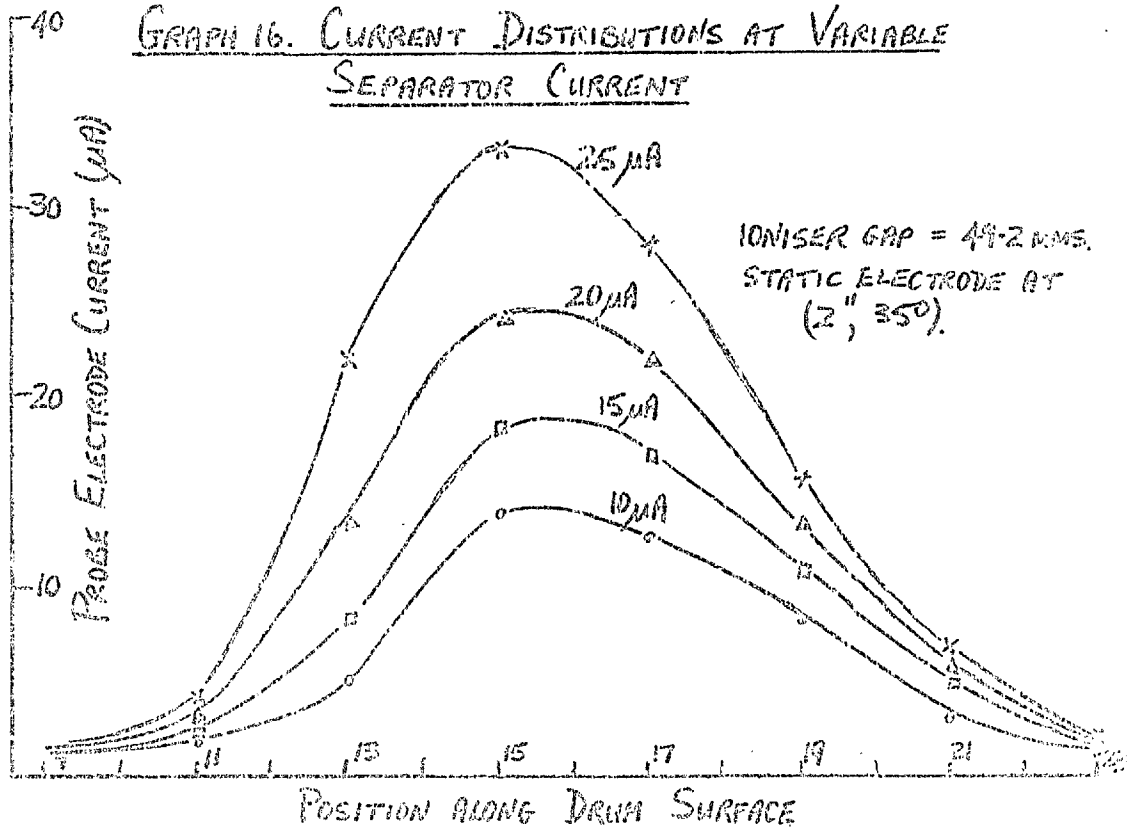
5.5 Results and discussion.

5.5 (a) The effect of current.

In this study the static electrode was kept at a stationary position (2", 35°) and a constant ioniser gap of 49.2 mms. was employed. The ionising electrode position was (2½", 19°) and the probe electrode height above the drum surfaces was ¼in. The conditions used for each subsequent series of tests will be stated on the relevant graphs.



GRAPH 15. PROBE ELECTRODE CURRENT VS. SEPARATOR CURRENT AT VARIABLE PROBE ELECTRODE POSITIONS.



GRAPH 16. CURRENT DISTRIBUTIONS AT VARIABLE SEPARATOR CURRENT

The current distributions in graph 16 show that raising the separator current has the effect of increasing the maximum probe electrode current (I_p max.) in analogy with the increased pinning of particles. The peaks of the curves are directly beneath the ionising electrode. The curves tend to be asymmetrical due to the presence of the static electrode and will be discussed later (Section 5.5).

The pinning behaviours of insulating and conducting particles at constant relative humidity and ioniser gap can be quantitatively correlated with the I_p max. values found under identical conditions. The correlation is illustrated in table 5, which shows that the pinning of conductors is directly proportional to I_p max. values up to about 20 uA separation current. Thereafter, pinning values increase at a much lower rate. This is ascribed to the mineral surfaces becoming saturated with ionic charges, so that pinning tends to a maximum. The insulating mineral shows similar behaviour.

TABLE 5.

SEPARATOR CURRENT (uA)	I_p MAX (uA)	PINNING OF INSULATORS P_I	PINNING OF CONDUCTORS P_c	$\frac{P_I}{I_p \text{ MAX}}$	$\frac{P_c}{I_p \text{ MAX}}$
5	9.8	60	22	6.1	2.2
10	14.4	77	38	5.4	2.6
15	18.8	82	44	4.4	2.3
20	24.4	84	47	3.4	1.9
25	33.2	86	50	2.6	1.5
40	72.8	89	56	1.2	0.8

5.5 (b) The effect of the gap between the ionising electrode and the surface of the drum.

The ioniser gap was varied between 23.8 and 65.1 mm. while maintaining a constant separator current of 20 uA. The other conditions are stipulated on graph 17, which shows that decreasing ioniser gaps lead to increasing I_p max. values.

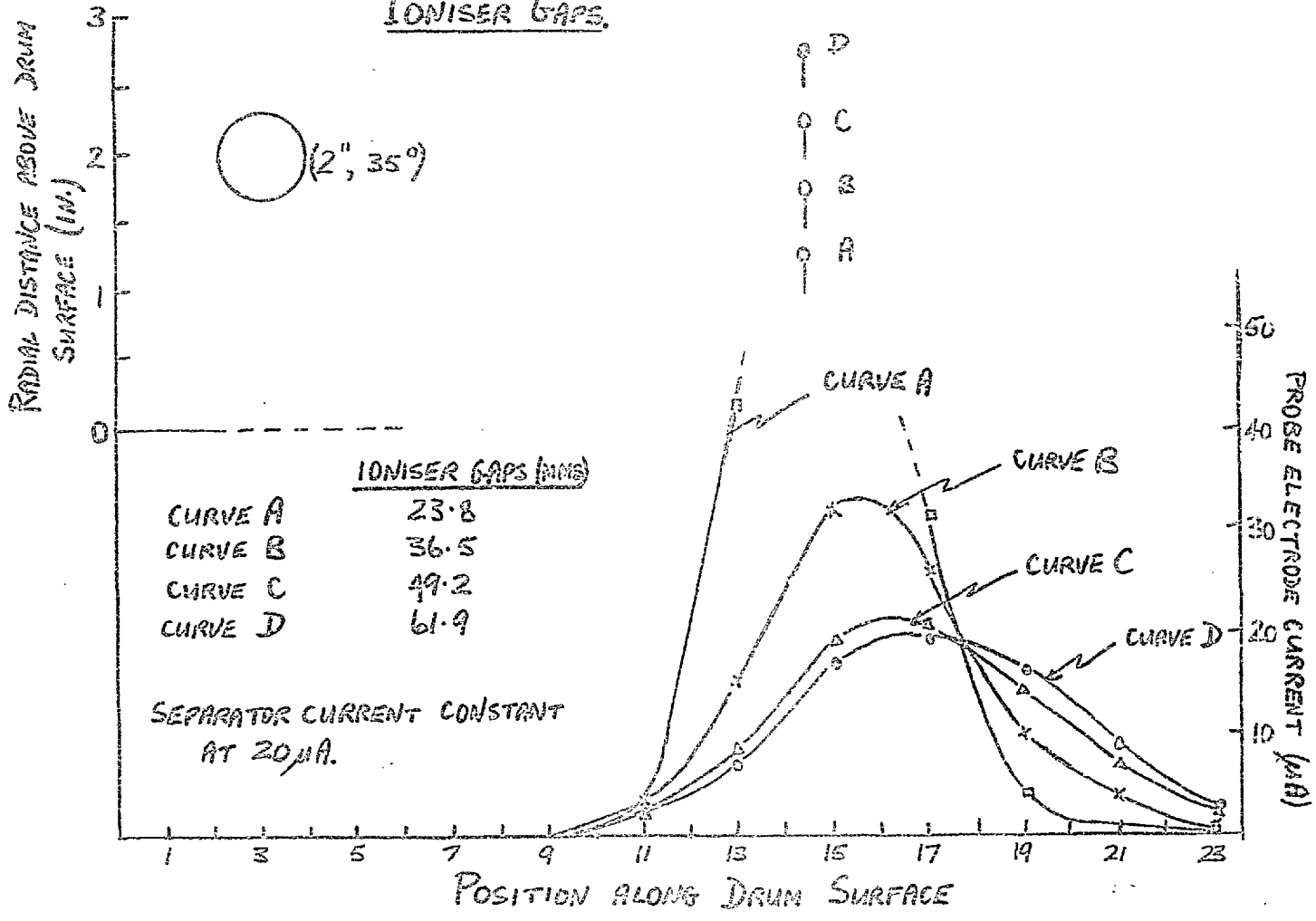
The large I_p max. values associated with small ioniser gaps could be expected to lead to high pinning values. This was not the case because the reduction in the ioniser gap leads to a corresponding reduction in the path length along which a particle is subjected to ionic charging. Table 6 shows the relation between I_p max., length of influence of ionising fields, ioniser gap and pinning of insulators and conductors.

TABLE 6.

IONISER GAP (mms.)	LENGTH OF INFLUENCE OF IONISING FIELD (mms.)	I_p MAX uA	% PINNING OF INSULATORS	% PINNING OF CONDUCTORS
23.8	12.1	$\geq$60	62	22
36.5	14.1	31.2	65	22
49.2	15.2	20.8	65	18
61.9	15.7	19.4	63	10

It is difficult to compare lengths of current distributions directly on the abscissa, i.e. at zero probe electrode current. An arbitrary value of 5uA was taken as the

Graph 17 Current Distributions at Variable Ioniser Gaps.



plane of reference along which lengths were measured. The pinning values reported in table 6 are those obtained on quartz and kyanite at a current of 5 uA and corresponding ioniser gaps.

The results show that although I_p max. values increase markedly with diminishing ioniser gaps, the pinning of minerals remains relatively constant due to the decreasing length of influence of the ionising fields. It is therefore postulated that on entering the ionising field, a particle will acquire a charge, the magnitude of which depends on the intensity and length of influence of the field.

The peaks of the family of curves are displaced from the position vertically below the ionising electrode when the latter is level with, or closer to the drum surface than, the static electrode (Graph 17). This phenomenon is discussed under Section 5.5 (e).

5.5 (c) The effect of the orientation of the ionising comb

This investigation was prompted by a reference in the literature[8] which indicated that in a high tension separator of the roll-type, the ionising comb had to be pointed directly at the insulating baffle otherwise the pinning of material would have been too severe. So far the comb of the ionising electrode had been used pointing radially downwards and a study of the effects of comb

orientation on current distributions was undertaken. A rotation of 60° about the axis of the ionising electrode, displaces the peak of the current distributions 3/8 in. without any other appreciable change.

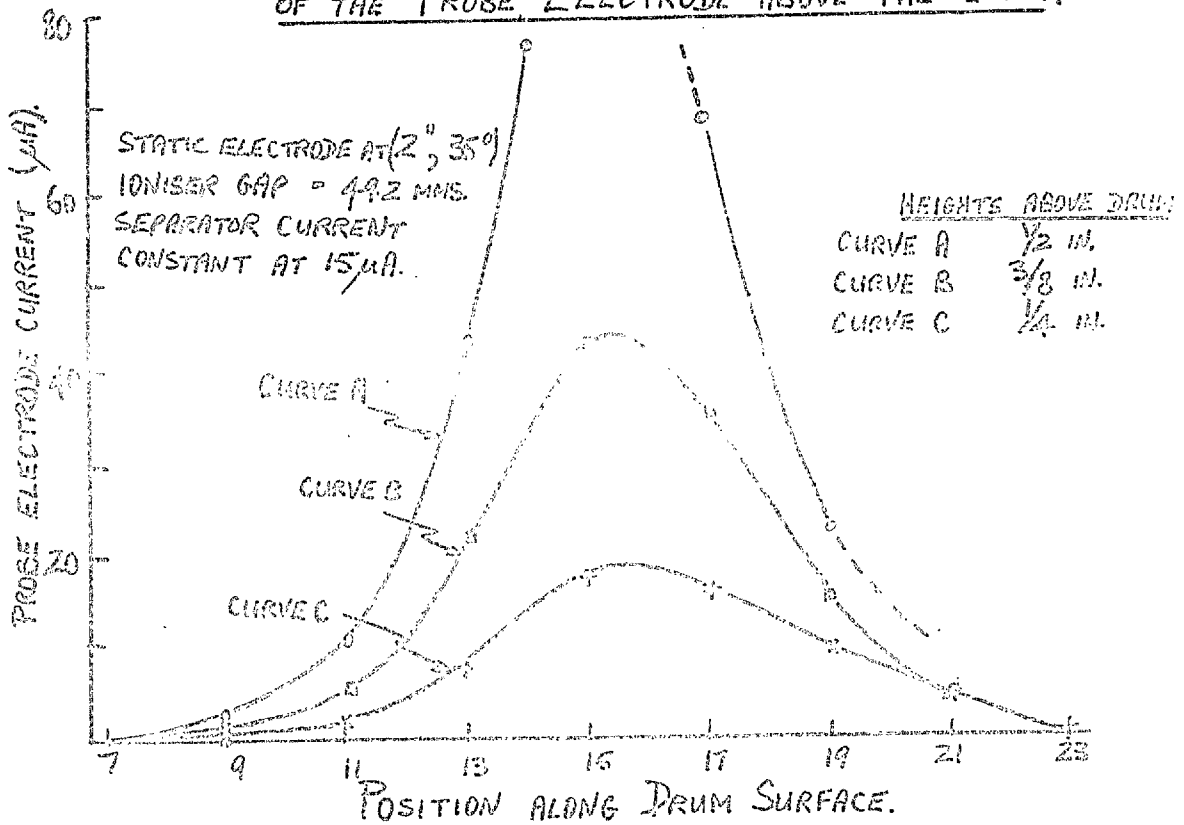
The radial orientation of the comb electrode was resumed for all field plotting studies.

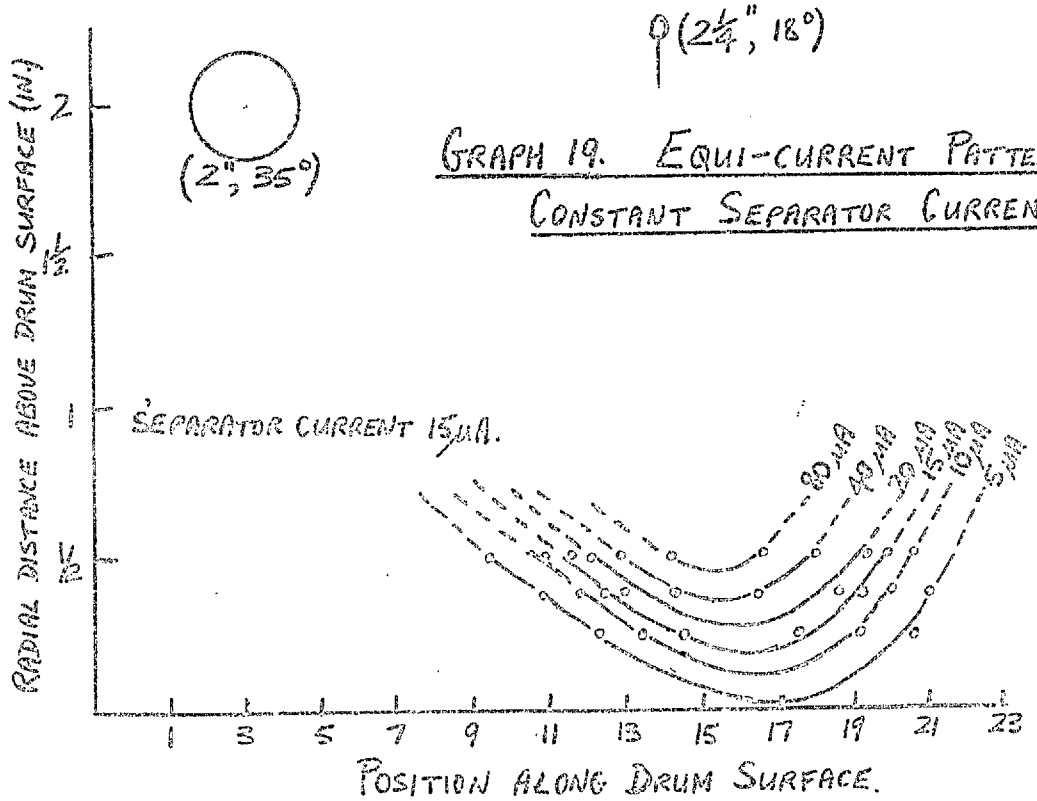
5.5 (d) The effect of the distance between the probe electrode and the drum surface.

All field plotting studies were carried out with the probe electrode at a fixed distance of ¼in. above the surface of the drum. It was impracticable to study effects at any lesser distance, due mainly to difficulties in manipulating the probe. Although the current distributions at heights of ¼in. give qualitative indications of conditions existing at the drum surface, more precise information was sought. This was accomplished semi-quantitatively by determining current distributions at various heights above the drum surface as shown in graph 18. From this graph lines of equi-current were constructed (graph 19) and the field existing on the surface of the drum was defined by extrapolation of gradients.

The intensities of the fields on the drum surface are much lower than those existing ¼in. above the drum. The other characteristics of geometry and intensity under the various conditions studied remain unchanged.

GRAPH 18. CURRENT DISTRIBUTIONS AT VARIABLE HEIGHTS OF THE PROBE ELECTRODE ABOVE THE DRUM.





GRAPH 19. EQUI-CURRENT PATTERN AT CONSTANT SEPARATOR CURRENT

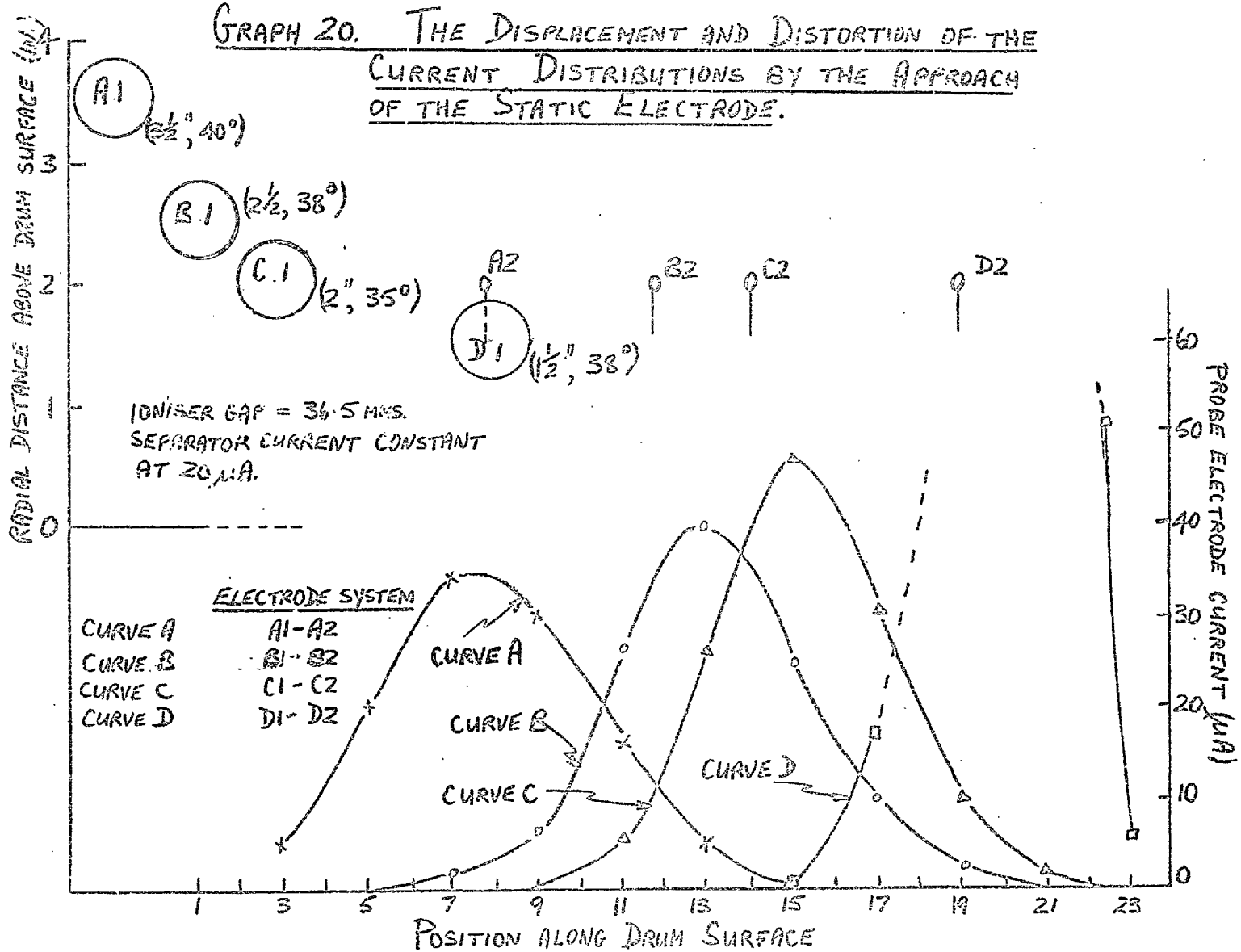
5.5 (e) The effect of the position of the static electrode

During the field plotting study it became apparent that the static electrode can influence the geometry and the intensity of the ionising field. Investigations showed that at a constant ioniser gap, movement of the static electrode towards the drum surface has the effect of displacing the current distribution pattern in the direction of the movement, and of increasing the I_p max. value (graph 20). If the static electrode is placed on the opposite side of the ionising electrode, the displacements are of a similar magnitude but in the opposite direction.

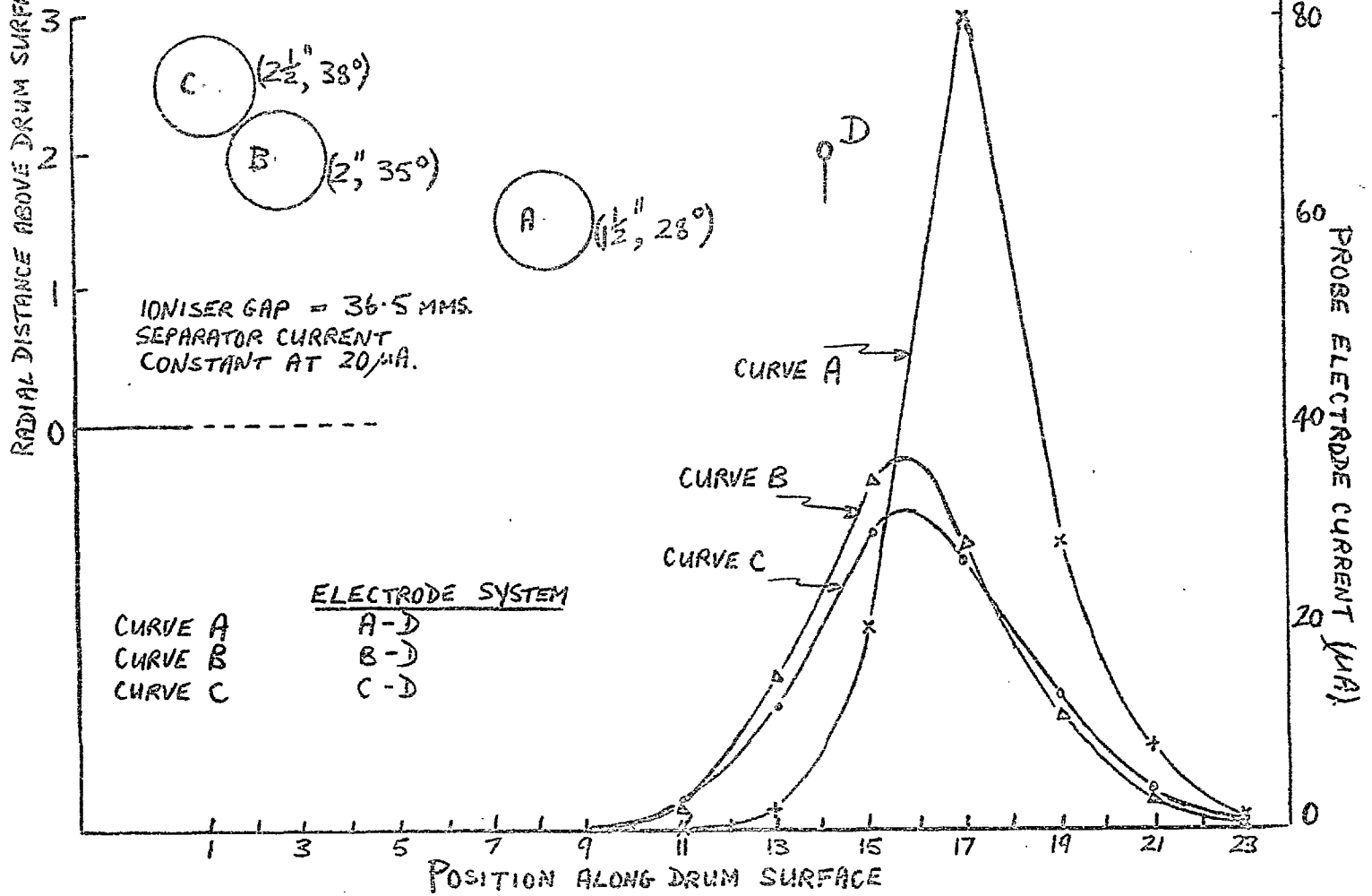
The linear distance between the static and ionising electrodes is fixed at 2 in. Hence any displacement of the static electrode results in a corresponding displacement of the ionising electrode. By adjusting the gap between the two, it was possible to maintain a constant ionising electrode position and ioniser gap with varying positions of the static electrode. The effects are similar to those found earlier (graph 21).

In attempts to elucidate this phenomenon, the static electrode was kept stationary while the ioniser was moved in an arc maintaining a constant ioniser gap. In this case (graph 22) there was no increase in maximum current values, but in electrode systems B & C the peaks of the current distributions were displaced to the right of the

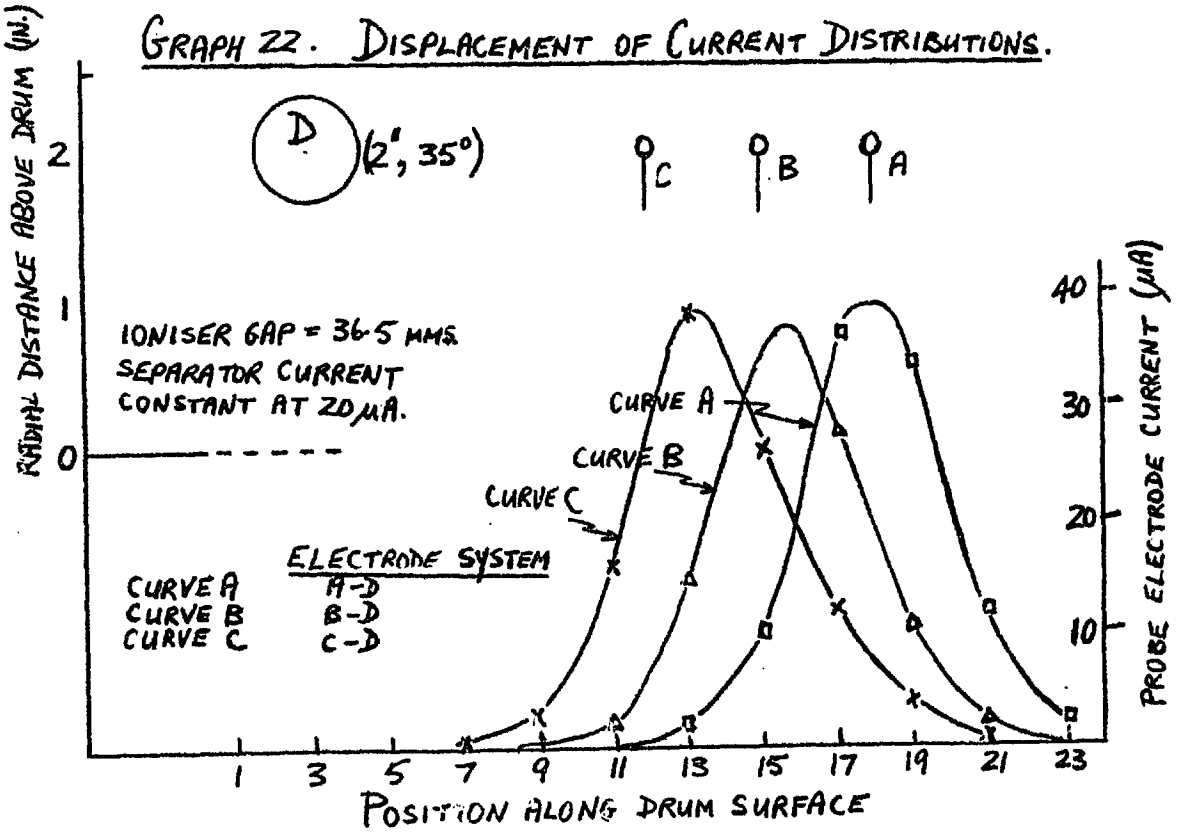
GRAPH 20. THE DISPLACEMENT AND DISTORTION OF THE CURRENT DISTRIBUTIONS BY THE APPROACH OF THE STATIC ELECTRODE.



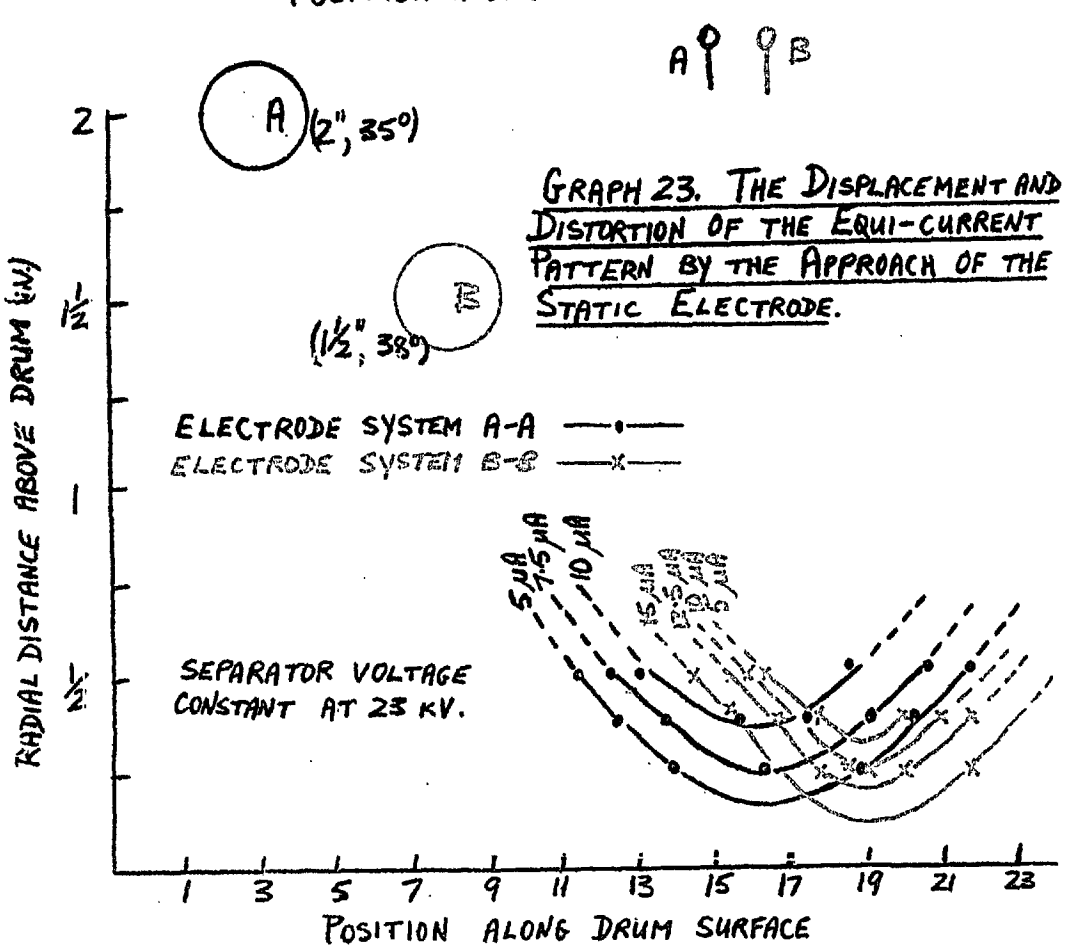
GRAPH 21. THE DISPLACEMENT AND DISTORTION OF THE CURRENT DISTRIBUTIONS BY THE APPROACH OF THE STATIC ELECTRODE. (IONISING ELECTRODE STATIONARY).



GRAPH 22. DISPLACEMENT OF CURRENT DISTRIBUTIONS.



GRAPH 23. THE DISPLACEMENT AND DISTORTION OF THE EQUI-CURRENT PATTERN BY THE APPROACH OF THE STATIC ELECTRODE.



ionising electrode position. This indicates that the static electrode displaces the ionising field only when closer than about 5 cm. to the ionising electrode. (The distance of 5 cm. is approximate and may be different for other ioniser gaps.) Furthermore, within the 5 cm. limit a reduction in the radial height of the static electrode above the drum increases the intensity of the ionising field.

It is suggested that the mechanism whereby the static electrode distorts the ionising field is as follows: The intensity of the static field resulting from the separation of the positively-charged static electrode and the negatively-charged drum varies inversely as the square of their distances apart[12]. Hence, as the static electrode approaches the drum surface, the intensity of its field increases, and when in close proximity to the ionising field causes a repulsion of the lines of force radiating from the ionising electrode. The crowding of the lines of force distorts the field and results in an increased field intensity. This effect is illustrated schematically in graph 23 which shows how the equi-current pattern beneath the ionising electrode is displaced and distorted by the approach of the static electrode.

The displacement of the ionising field towards the insulating baffle in a fashion comparable to that used in graph 20 resulted in increased pinning values of quartz[13],

thereby confirming the postulation that the pinning behaviour of minerals is related to the intensity of the ionising fields.

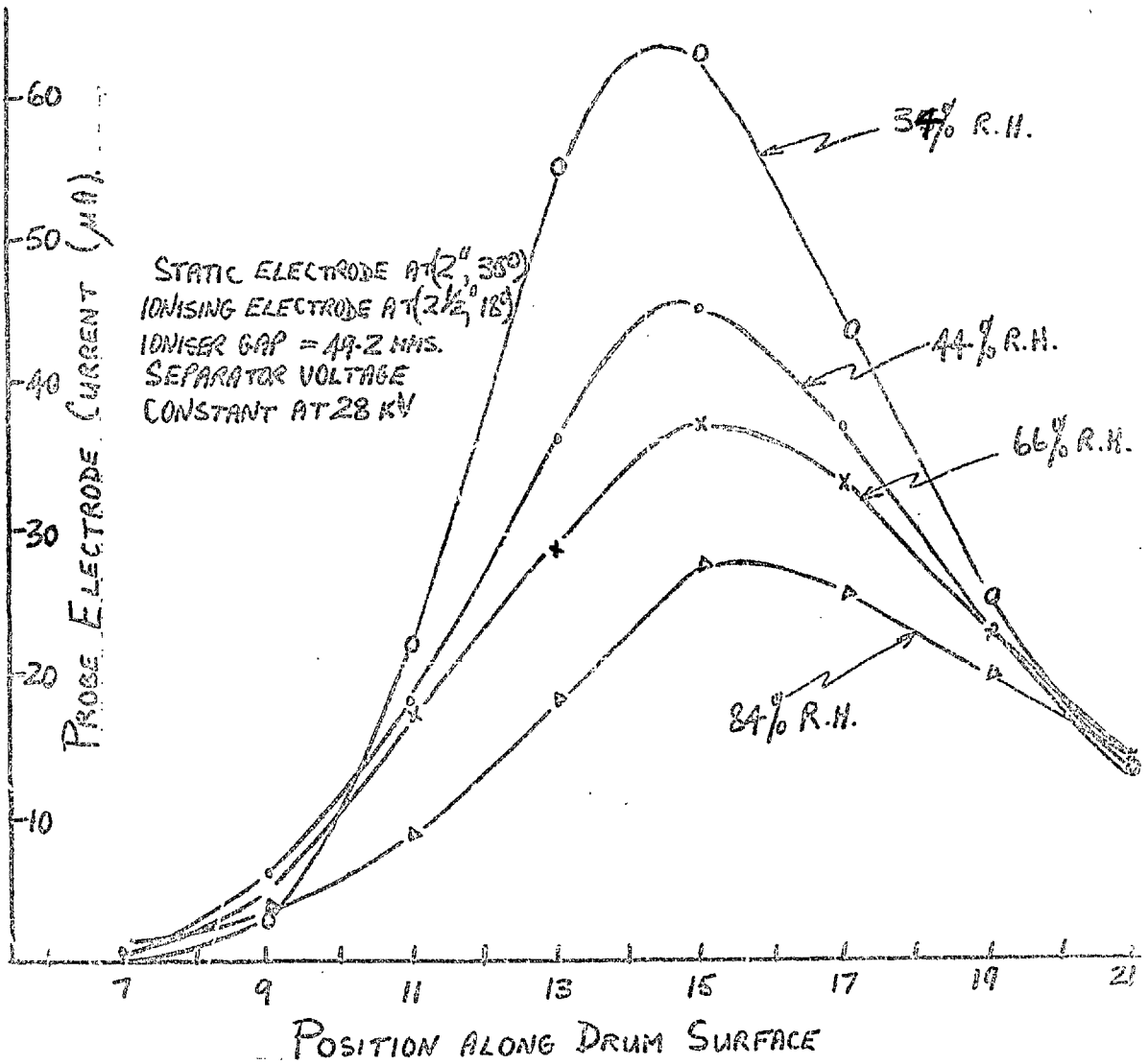
5.5 (f) The effect of relative humidity.

The field plotting investigations were carried out under natural conditions fluctuating between 40 and 50% relative humidity. It was necessary, therefore, to determine whether the relationship between the machine current and probe electrode current was affected to any significant extent by changes in relative humidity. The probe electrode was used at a height of 3/8 in. above the surface of the drum and experimentation was performed at a constant separator voltage of 28 kV and an ioniser gap of 49.2 mms.

The results are plotted in graph 24, which shows the dependence of field intensity on the humidity of the surrounding atmosphere, i.e. at low moisture contents of the air, the maximum probe electrode current is large. It was stated in Section 4.4 that the current-voltage relationship at constant ioniser gap is apparently independent of relative humidity. It is suggested that the relationship does in fact alter with variation in humidity, but the kilovoltmeter and microammeter of the separator are not sensitive enough to detect the change.

The mechanism whereby water vapour pressure influences

GRAPH 24. CURRENT DISTRIBUTIONS AT VARYING RELATIVE HUMIDITY.



the current distributions beneath the ionising electrode of the separator is as follows:

The electrode system and the drum surface may be compared with a parallel-plate condensor consisting of air as the dielectric material between the plates.

According to the laws of electrotechnics[12], the dielectric constant, K, is the ratio of the field when no dielectric is present, to that when a dielectric is present, i.e.

$$\frac{K_1}{K_o} = \frac{F_o}{F_1} \quad \text{and} \quad \frac{K_2}{K_o} = \frac{F_o}{F_2} \qquad (9)$$

where K_o, K_1, K_2 are respectively the dielectric constants of vacuum, dry air and moist air, resulting in field intensities of F_o, F_1 and F_2. From equation (9)

$$\frac{K_2}{K_1} = \frac{F_1}{F_2} \qquad (10)$$

On increasing the moisture content of the air, the dielectric constant of the material between the plates of the condensor will rise in value[8] i.e. $K_2 > K_1$, and according to equation (10), the intensity of the field will be lowered, accounting for the low magnitude of current distributions at high humidities.

The lowering of I_p max. values with increasing relative humidities accounts for the tendency of hydrophobic particles to decrease in pinning with rising water vapour

contents of the air (Section 7).

5.6 The distribution of current in the ionising field at constant electrode potential.

All data on the various factors influencing current distributions in the ionising fields presented so far were obtained at constant separator currents. It was noted, however, that the voltage necessary to maintain a constant separator current increased as the probe electrode approached the area of maximum field intensity beneath the ionising electrode. A few of the tests were therefore repeated under identical conditions, except that the separator voltage was kept at constant values in place of the separator current. The current distributions and equi-current patterns were found to be identical to those obtained previously, but of a lower order of magnitude.

It is deduced that on approaching the area of maximum intensity the probe drew an increasing current, and a larger voltage was necessary to maintain the separator current at a constant value. The increased voltage supplied additional current to the probe electrode, thereby increasing the apparent intensity of the ionising field. The gaseous ions striking the probe electrode represent a diverted current which cannot be registered on the microammeter of the separator. Some relationship must exist therefore between the total current available, the

probe electrode current and the separator current at constant voltage.

5.7 The relationship between the total, separator and probe currents.

I_T = The total current available, i.e. the separator current when no probe is present.

I_s = The separator current at any probe position.

I_p = The probe electrode current.

The total current, I_T, i.e. the current flow between the electrode system and the drum, is constant for a specific potential gradient and length of air gap. If some device, e.g. the probe electrode, at an infinitessimal distance above the drum surface intercepts a portion of the ions constituting the current flow before they reach the drum surface, then I_T should always be equal to $I_s + I_p$. This, however, is not the case, because the probe electrode is at a finite distance above the drum, so that the existing potential is operative over a shorter length of air gap. This produces an increased potential gradient and a proportionately higher probe electrode current. Some correction factor must be applied to the measured I_p values to derive the smaller current abstracted from the separator flow.

The correction factor should be governed by the

inverse square law and the validity of the application of this law to the present system merits examination.

According to the inverse square law,

$$\frac{I_1}{I_2} = K \left(\frac{L_2}{L_1}\right)^2 \qquad (11)$$

where I_1, I_2 are the currents flowing at a constant potential gradient across air gaps of L_1, L_2 lengths respectively. K is a constant and should equal unity for air.

Under ionising conditions the resistance of air varies considerably with potential gradient, length of air gap, temperature and pressure. Only the first two of these factors were used as variables in this investigation and the others were kept constant.

The study was performed with the ionisation box (described in the section of the thesis dealing with the ionisation process) because of the greater accuracy with which air gaps could be measured. Applied voltages (varying between 12 and 21 kV) and the resulting currents were recorded at electrode separations varying between 33.5 and 50.0 mms. The readings are tabulated in table 7.

The average value of K was found to be 1.033 ± 0.005, so that within the limits of experimental error, K may be regarded as unity.

$$\text{Hence} \quad \frac{I_1}{I_2} = \left(\frac{L_2}{L_1}\right)^2 \qquad (12)$$

and the inverse square law holds for the system studied.

TABLE 7.

READING NUMBER	VOLTAGE kV	CURRENT uA	LENGTH OF AIR GAP (mms.)	COMBINATION OF READINGS	RATIO OF CURRENTS	$\left(\text{INVERSE RATIO OF AIR GAPS}\right)^2$	K
1	12.0	7.4	33.5	1 - 2	1.233	1.036	1.190
2	12.0	6.0	34.1	2 - 3	1.034	1.110	0.932
3	12.0	5.8	35.8	3 - 4	1.381	1.409	0.981
4	12.0	4.2	42.5	4 - 5	1.500	1.383	1.085
5	12.0	2.8	50.0	1 - 3	1.276	1.143	1.116
6	18.0	25.6	33.5	2 - 5	2.143	2.149	0.997
7	18.0	23.8	34.1	6 - 7	1.076	1.036	1.039
8	18.0	22.6	35.8	7 - 8	1.053	1.110	0.949
9	18.0	14.2	42.5	8 - 9	1.592	1.409	1.130
10	18.0	10.6	50.0	9 - 10	1.340	1.383	0.969
11	21.0	40.0	33.5	6 - 8	1.133	1.143	0.991
12	21.0	37.0	34.1	7 - 10	2.245	2.149	1.045
13	21.0	35.4	35.8	11 - 12	1.081	1.036	1.043
14	21.0	25.4	42.5	12 - 13	1.045	1.110	0.941
15	21.0	16.2	50.0	13 - 14	1.394	1.409	0.989
				14 - 15	1.568	1.383	1.134
				11 - 14	1.130	1.143	0.989
				12 - 15	2.284	2.149	1.063
						AVE:	1.033

By application of the inverse square law, the correction factor may be postulated as $\frac{a^2}{b^2}$, where a = the distance between the probe electrode and the ionising electrode, and b = the distance between the drum surface and the ionising electrode along the shortest line passing through the probe electrode. Therefore:

$$I_T = I_s + \frac{a^2}{b^2} I_p \qquad (13)$$

The validity of equation (13) was confirmed by the results from the field plotting determinations at constant voltages. Twenty seven specimen results are given in table 8, showing that the equation holds under all conditions studied (except at potentials which cause spark discharges). The data relate to field plots with the static electrode in position (2" , 35°) and an ioniser gap of 49.2 mms. When the probe electrode is used at distances of ¼ and ⅜ in. above the drum surface, the mean values of $\frac{a^2}{b^2}$ are 0.78 and 0.67 respectively.

5.8 The distortion of the ionising field due to the presence of the probe electrode.

The probe electrode possesses finite dimensions and can thus be assumed to concentrate lines of force by virtue of having a higher dielectric constant than the surrounding air. The concentration of the lines of force represents a distortion of the existing field, resulting

TABLE 8.

PROBE ELECTRODE POSITION	VOLTAGE kV	I_s	I_p	$\left(\frac{a^2}{b^2}\right)I_p$	$I_s+\left(\frac{a^2}{b^2}\right)I_p$	I_T
A7	20	11	-	-	11.0	11
A9		11	-	-	11.0	
A11		11	0.6	0.5	11.5	
A13		9	3.6	2.8	11.8	
A15		6	6.6	5.1	11.1	
A17		5	7.2	5.6	10.6	
A19		6	5.2	4.1	10.1	
A21		8	2.4	1.9	9.9	
A23		10	0.4	0.3	10.3	
					10.8 ± 0.4	11
A7	23	22	-	-	22.0	22
A9		22	0.4	0.3	22.3	
A11		20	2.6	2.0	22.0	
A13		16	9.0	7.0	23.0	
A15		12	12.8	10.0	22.0	
A17		11	12.6	9.8	20.8	
A19		15	9.4	7.3	22.3	
A21		18	4.6	3.6	21.6	
A23		20	1.2	0.9	20.9	
					21.9 ± 0.5	22
B7	20	11	-	-	11.0	11
B9		12	0.4	0.3	12.3	
B11		11	2.4	1.6	12.6	
B13		8	6.4	4.3	12.3	
B15		4	9.4	6.3	10.3	
B17		3	10.2	6.8	9.8	
B19		6	7.6	5.1	11.1	
B21		8	3.6	2.4	10.4	
B23		10	1.4	0.9	10.9	
					11.2 ± 1.0	11

in a higher current density and increased values of the current distribution.

This distortion may be adduced by theoretical considerations. According to the derivation of equation (13), the corrected probe electrode currents should represent the actual field prevailing on the drum surface at each point of measurement. The probe electrode currents were measured at ¼ in. intervals and since the probe electrode is 1/16 in. in diameter, the sum of the corrected probe electrode values should equal ¼ I_T. Hence, the total values of I_p derived from the ratio $\frac{a^2}{b^2}$ should be equal to one quarter of the total current available.

This, however, is not the case because the results indicated that at probe heights of ¼ and 3/4 in. the sum of the $\left(\frac{a^2}{b^2}\right) I_p$ values are respectively 7.4 and 10.2 times greater than ¼ I_T.

By applying the corrections to the probe electrode currents (at constant voltage) for the height of probe above the drum and for the distortion produced by the probe, it is possible to obtain a reasonably accurate assessment of the magnitude of the fields existing on the drum surface.

6.0 THE MECHANISM OF THE PROCESS OF HIGH TENSION SEPARATION.

6.1 Introduction.

There has been much controversy concerning the theory of the process of high tension separation using roll-type machines. Wentworth[8] argued that a negatively-charged electrode "attracts" a positive charge from earth to a point on the drum surface beneath the electrode. The convective discharge of ions from the negative electrode is neutralised by meeting this positive charge. Solid particles on the drum intercept the discharge of ions and become negatively charged, unless they are good conductors, in which case they conduct negative charges to the drum as fast as they arrive. If ion bombardment is not too severe, conductors acquire a positive charge from the drum and are thus repelled from it.

Schnitzler[20] postulated that a particle charged by ionising means acquires a maximum charge which can subsequently leak away at an exponential rate, analogous to the discharge of a condensor through a resistance. All particles are assumed to receive a charge of the same sign as the ionising electrode, which then discharges to earth at a rate dependent upon the capacity of the particle and the resistance of the particle-drum contact, ultimately becoming zero. A particle left the drum surface when the

centrifugal force exceeded the electrostatic pinning force.

Grey and Whelan[27] elaborated on Schnitzler's theory and showed that when the particle-drum contact resistance is low the particles may in fact leave the ionising zone with a net charge of opposite sign to the ionising electrode. The ionic charging inhibited the growth of the induced charge on the particle.

In 1958 Mora[1] postulated a theory of high tension separation which is basically in agreement with the results of the experimental work outlined in this thesis.

In describing the process of high tension separation it is not intended to present a rigorous mathematical model of the process, but to show a mechanism based on theoretical considerations and substantiated by experimental evidence.

High tension separation is somewhat similar to the process of froth flotation in comprising several subsidiary step . Mineral particles experience the following events in the high tension separator.

(1) feeding to the rotating drum.

(2) charging in the ionising field.

(3) discharging in the static field.

(4) inductive charging in the static field.

(5) mechanical separation into pinned or thrown fractions.

There is reason to believe that steps (3) and (4) take place concurrently in the static field and will thus be discussed under the same heading.

6.2 Feeding to the rotating drum.

In the G.E.C. High Tension Separator used for this work, the material is placed in a hopper and is delivered to the drum by means of a vibrating feeder with a chute 19½ in. long. This entails an inherent risk of frictional charging of insulator materials, particularly at low humidities. The charges developed on conductors are generally low in magnitude due to an increased conductivity promoting charge leakage.

The theoretical maximum surface density of charge possible on particles subjected to contact electrification is about $\pm$ 8e.s.u/cm.^{2}, the limit being set by the breakdown of the air[19]. Harper[22] has shown that the frictional charge acquired by quartz is held on an area of 10^{-6} cm.^{2}. It thus appears that contact charging under ideal conditions can lead to the development of a charge on an extremely small area only. On the other hand, ionic bombardment results in the charging of an area in excess of half the total surface of the solid. In addition, pinning is largely dependent on the charges acquired on mineral surfaces and has been shown (graphs 3 and 6) to increase with current to a constant value at 50 uA.

The potential necessary to maintain this current across the air gap used is 25 kV, i.e. well above the breakdown potential of air. This shows that the overall charge acquired by particles in the ionising field is greatly in excess of any charges developed by frictional means. Contact charging of mineral grains on the vibrating feeder therefore cannot have much influence on the process of high tension separation.

6.3 Charging in the ionising field.

In the following discussion of the charging process in the ionising field a positive polarity of the electrode system is considered. With appropriate changes of sign the considerations apply equally to a negative polarity of the electrodes.

On entering the ionising field, the mineral particles immediately come under intense ionic bombardment by gaseous cations emitted by the ionising electrode. The ions adhere to the mineral surface by electrostatic forces of attraction. Mora has suggested that the gaseous cations adhere to any bound negative charges produced on the particle surface by polarisation in the ionising field.

Mora demonstrated in theory that there is a maximum charge (Qm) which a particle can acquire under ionic bombardment, given by the formula

$$Qm = 4\pi\epsilon_o \, a^2 \, kE_i \qquad (14)$$

where ϵ_o = permittivity of free space

a = radius of electrical equivalent ellipsoid.

k = function of ellipticity $\frac{c}{a}$ and dielectric constant of the particle.

E_i = ionising field strength (volt/unit length)

The concept of a maximum charge on a particle implies that after deposition of a certain number of ions on its surface, further charges can no longer be attracted to the particle and are in fact repelled. This is in agreement with results described earlier in this thesis (Section 4.3) where it was shown that the pinning of conductors and insulators increases strongly with current to a maximum at about 50 uA.

If the particles were isolated and not in contact with the drum, conducting minerals would acquire a greater charge than insulating particles. The difference in charging density is attributed to the fact that conductors have large dielectric constants and tend to concentrate lines of force. However, the particles are in contact with the drum during the charging and there is a simultaneous transfer of electrons from the drum across the particle-drum interface[12]. The electrons neutralise the gaseous cations on the particle surface, i.e. discharge of ions takes place. The rate of ionic discharge depends on the conductivity of the particles, i.e. in the case of

a perfect insulator there is no discharge.

It appears that when a particle is under the influence of the ionising field, there is at all times a movement of ions towards the mineral surface and a simultaneous leakage of some ions from the particle to the drum. At equilibrium a steady-state charge exists, which for conductors can be very considerably less than Qm. Mora has calculated that the time required to achieve a steady-state charge on a particle is virtually nil for any kind of particle so that, within limits, the speed with which a particle is carried through the ionising field is of little significance.

6.4 Discharging and inductive charging in the static field.

On leaving the influence of the ionic field, particles have a net charge of the polarity of the electrode system and of a magnitude dependent on the insulating properties of the particles. The behaviours of insulators and conductors must be considered separately.

6.4 (a) Insulators.

The charge on an insulator cannot leak away readily due to its low conductivity and hence the particles retain their positive charges. In practice there are no perfect insulators, so that some discharge occurs

at a slow rate, but the leakage losses are likely to be very small.

According to Coulomb's law of forces,

$$F = \frac{1}{k} \frac{q_1 q_2}{r^2} \qquad (15)$$

where F = force of attraction and r = distance between particles of charges q_1 and q_2. The force of attraction between the drum and the insulator in close proximity, i.e. negligible r, can be very considerable. Thus insulator particles are strongly pinned to the drum surface.

Insulating materials are not amenable to charging by induction means. However, surface charges can be induced by the process of polarisation.[12] The magnitude of the charges involved are small and can be neglected.

6.4 (b) Conductors.

The leakage of charge continues when conducting particles leave the influence of the ionising field, the rate of this discharge increasing considerably in the static field. Simultaneously, a charge of sign equal to that of the drum is developed by a process of induction on the side of the particle nearest the static electrode. The induced charge increases in magnitude with time and redistributes itself about the surface. Eventually, the particles have a net negative charge, which increases

further in magnitude, until according to the equation

$$F = qE \qquad (16)$$

where F = electrical force

q = charge

E = electric field,

an electrical force is developed of sufficient energy to cause the particles to be repelled from the drum surface.

6.5 The mechanism of the process of induction charging.

The mechanism of the process of charging particles by induction in the static field of the high tension separation is as follows:- On entering the static field a conductor will have positive ions uniformly distributed over the face of the mineral (fig. 7a). The cations spread over the mineral surface and discharge to the earthed drum (fig. 7b). The gaseous ions are mobile[6] so that the process of charge leakage probably involves a simultaneous transfer of electrons and cations in opposite directions across the particle-drum interface. The path taken by the charged species depends on whether bulk or surface conductivity contributes to the conducting properties of the mineral. When an insulating particle has a large surface conductivity, for example, quartz containing adsorbed layers of water, the flow of electrons and gaseous ions is almost entirely along the surface of the particle. In

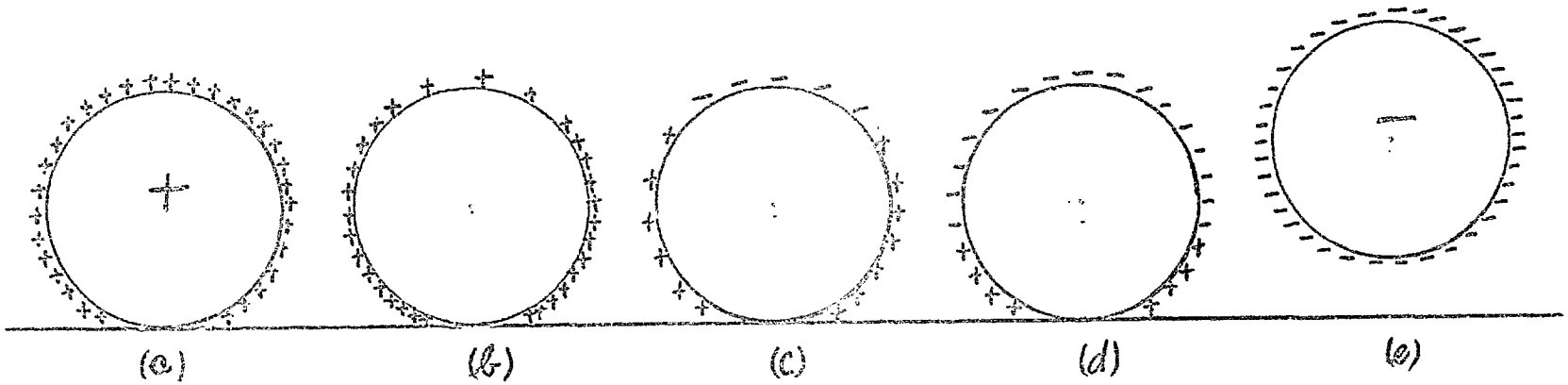


FIG. 7 THE MECHANISM OF THE PROCESS OF INDUCTION CHARGING

this case a high moisture content of the air aids the process of discharging by increasing the conductivity of the solid-air interface.(6)

During the charge leakage, free electrons present in the particle and excess electrons donated by the drum are attracted to the end of the particle nearest the static electrode (fig. 7c). The electrons redistribute about the surface while the positive charges continue to leak away to earth (fig. 7d). Eventually the particle has a net negative charge which increases in magnitude until according to equation (16), an electrical force is developed of sufficient strength to cause the particle to be repelled from the negatively-charged drum surface (fig. 7e). In this thesis it has been shown experimentally (page 115) that the intensity of the induced charge depends on the magnitude of the initially acquired ionic charge, i.e. the longer the time for leakage to be completed, the greater is the value of the induced charge.

According to Mora the net charge, Q_N, developed on particles by the process of induction in the static field of a high tension separator, depends on the applied potential (E), the time spent in the field (t), the capacitance of the particle (C_p) and its equivalent total resistance (R_p) according to the equation

$$Q_N = C_p E\left(1 - e^{\frac{-t}{R_p C_p}}\right) \qquad (17)$$

The capacitance and total equivalent resistance of a particular mineral are unaffected by changes in field strength. Experimentation was therefore confined to a study of the influence of voltage and time on the magnitude of the induced charge.

6.5 (a) <u>The effect of voltage on the magnitude of the induced charge</u>.

Hudson[14] studied the behaviour of mineral particles on a plate-type electrostatic separator. He demonstrated that the charge acquired by the particles can be related to the change in the median of the distribution of thrown material by the equation,

$$\log y = V(KV - E) \qquad (18)$$

where y = displacement of the median

V = charged electrode voltage

E = average frictional charge acquired by the particles passing over the feed plate surface

K = constant related to the conductivity of the mineral.

KV is numerically equal to the average induced charge acquired by the particles.

Similarly, Plaksin et al[62] and Balint[11] related the magnitude of charges on the surfaces of mineral particles to the equation of the path taken by the solids when falling between charged electrodes.

In the present work it has been shown that voltage does not have a great influence on the pinning behaviour of insulators and conductors (Section 4.3). In studying the effect of voltage on the magnitude of the induced charge, variations in pinning behaviour are therefore an insensitive measure of the changes produced. In this investigation the landing distribution of the thrown material was noted and the variation in the mean landing position was chosen as the criterion for determining the influence of voltage and time on the value of Q_N.

The minerals employed in this study were the chemically-treated quartz and the carborundum described in Section 2.2. A constant drum speed of 55 r.p.m. was used. The quartz samples were passed through the separator at 10 uA current and 51% relative humidity. The weight distribution of the material thrown into the trays 1 - 17 was determined and the mean landing position calculated for each voltage studied (table 9).

TABLE 9

VOLTAGE (kV)	MEAN LANDING POSITION TRAY NUMBER	PINNING VALUE %
10.0	8.8	40.1
17.0	6.3	44.7
25.0	6.1	37.8

The mean landing position was displaced from the vertical tangent to the drum with increasing voltage. The percent weight of material thrown remained relatively constant.

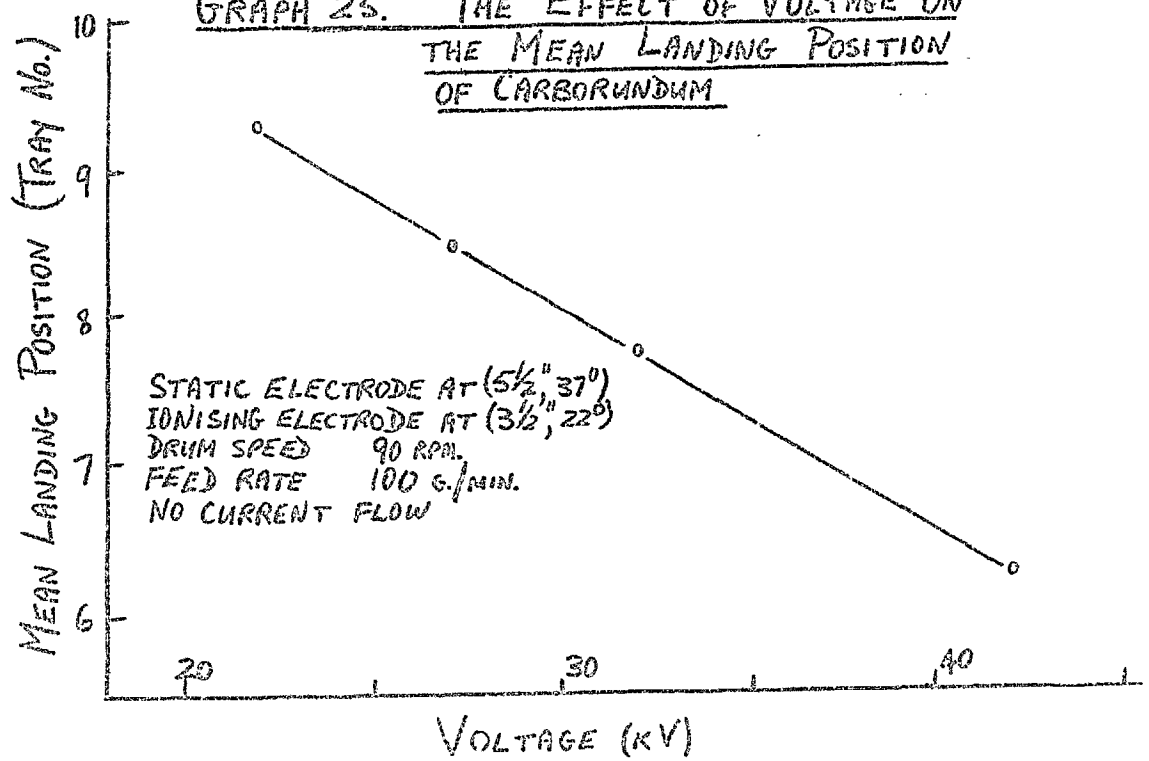
The further a particle is thrown from the drum surface, the greater is the electrical force which had produced the throwing. Thus, from equation (16) relating the electrical force to the intensity of the electric field and the charge on the surface of the particle, it appears that Q_N can be related to the mean landing position. The mathematical relationship is presented below.

The gap between the ionising electrode and the drum surface varied in the above study and hence ionic charging was an uncontrolled variable. In order to eliminate this variable, the ionising electrode was set in a fixed position and 100 g. carborundum samples were passed through the separator under purely static conditions i.e. no current flow between the electrodes and the drum. This was achieved by rotating the ionising comb radially away from the drum. The conditions used in this investigation are stipulated on graph 25.

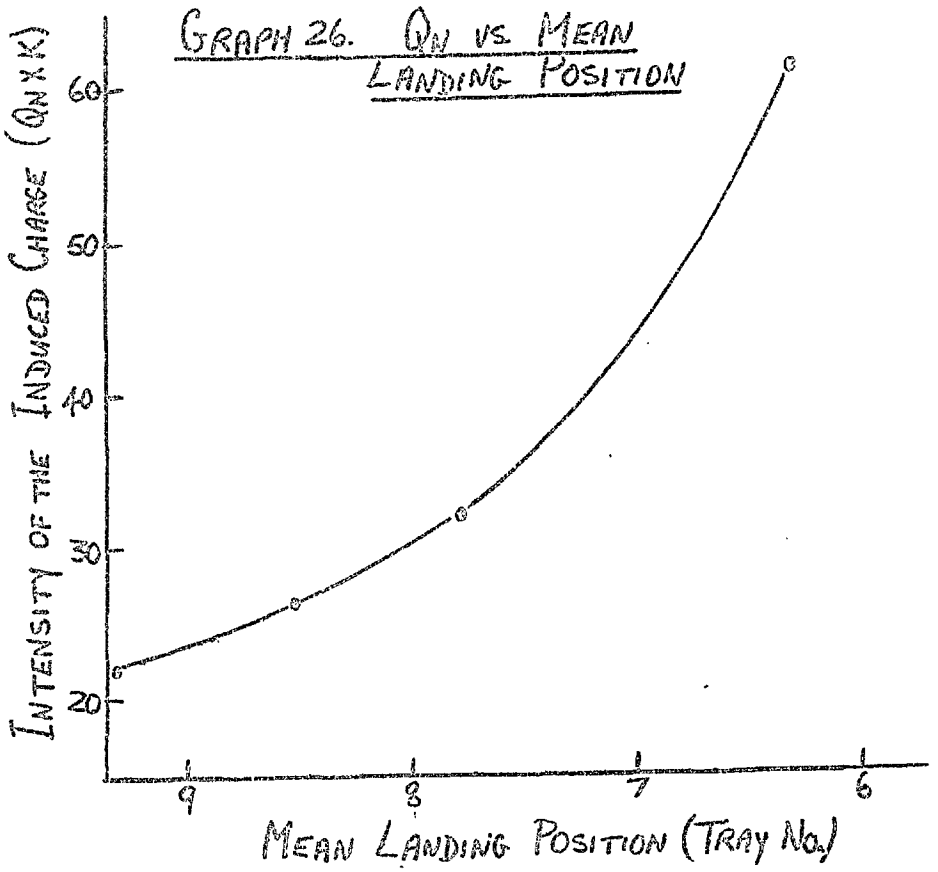
The weight distributions at varying voltages were noted and the calculated mean landing position, L, plotted against the voltage, E, (graph 25). The linear plot shows that L is directly related to E, by the equation

$$L = -aE + b \qquad (19)$$

GRAPH 25. THE EFFECT OF VOLTAGE ON THE MEAN LANDING POSITION OF CARBORUNDUM



GRAPH 26. Q_N VS. MEAN LANDING POSITION



where a and b are constants equal to 0.15 and 12.6 respectively for the system studied. Pinning values increased from nil at 22 kV to 1.5% at 42 kV and this is attributed to a small degree of ionisation at high voltages promoting ionic charging.

The relationship between mean landing position and the magnitude of the induced charge can be derived from equations (17) and (19).

From (17) $$Q_N = C_p E(1 - e^{\frac{-t}{R_p C_p}})$$

C_p, R_p and t are constants for a given material and drum speed. Therefore,

$$Q_N = EK, \qquad (20)$$

where $$K = C_p(1 - e^{\frac{-t}{R_p C_p}})$$

Substituting (20) in (19),

$$L = -a\frac{Q_N}{K} + b$$

$$Q_N = \frac{K}{a}(b - L)$$

$$Q_N = \frac{C_p}{a}(1 - e^{\frac{-t}{R_p C_p}})(b - L) \qquad (21)$$

The graphical representation of equation (21) shows that rising Q_N values cause particles to be thrown greater distances from the vertical tangent to the drum (graph 26). The mean landing position approaches a limiting value,

suggesting that the particles acquire a maximum induced charge similar to that postulated for charging by ion bombardment (Section 6.3).

6.5 (b) The effect of time on the magnitude of the induced charge.

The influence of time on the charging of particles by induction was investigated with the aid of alterations to the drum speed. The throwing behaviour of 100 g. samples of carborundum was determined at speeds of rotation of the drum varying between 45 and 200 r.p.m. The other separator variables used in the tests are specified on graph 27. The mean landing positions of the thrown material ~~was~~ were investigated under the following conditions:-

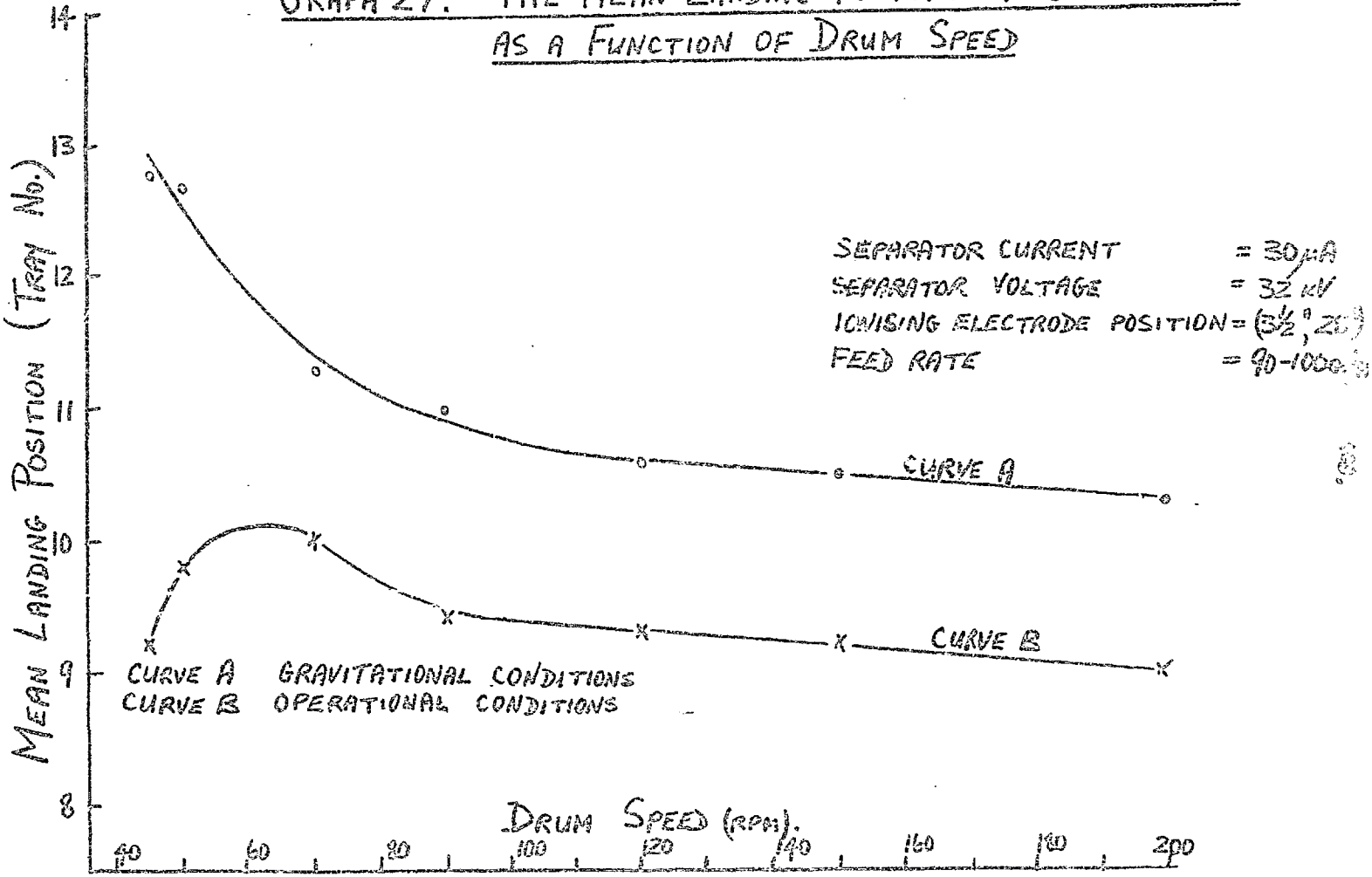
(i) gravitational trajectory conditions i.e. no applied voltage.

(ii) normal operational conditions i.e. an applied voltage and flow of current.

(i) Gravitational trajectory conditions.

A particle will be projected from a rotating drum from a position on the circumference which is constant for a given speed of rotation and diameter of the drum. In this discussion let B designate the take-off position. The distance between B and the boundary of the ionising field influences the process of induction charging and therefore has important effects on the pinning behaviour of minerals. Attempts to locate B quantitatively proved

GRAPH 27. THE MEAN LANDING POSITION OF CARBORUNDUM AS A FUNCTION OF DRUM SPEED



unsuccessful.

The approximate locus of B was found by determining the mean landing position of carborundum as a function of speed under gravitational trajectory conditions (graph 27, curve, a). The landing position is displaced from the vertical tangent to the drum with rising speed, reaching a constant value at about 110 r.p.m. From this behaviour it is deduced that B moves back along the circumference with increasing speed of rotation of the drum. Above a critical speed the particles slip on the drum surface and B tends to remain stationary. Gray and Whelan[21] confirmed the possibility that particles slide relative to the drum surface at high speeds of rotation.

The suggested displacement of B with increasing drum speed is depicted in fig. 8.

(ii) Operational conditions.

The mechanism whereby the mean landing position of particles is displaced by variation in drum speed under normal operational conditions (graph 27, curve b) is as follows: At the lowest speed studied (45 r.p.m.), a particle spends a relatively long time in the gap between the boundary of the ionising field and B. A large charge is induced on the particle causing it to be thrown a long distance. A rise in drum speed narrows the length of influence along which a particle discharges and decreases the time spent by the particle in the static field. As a

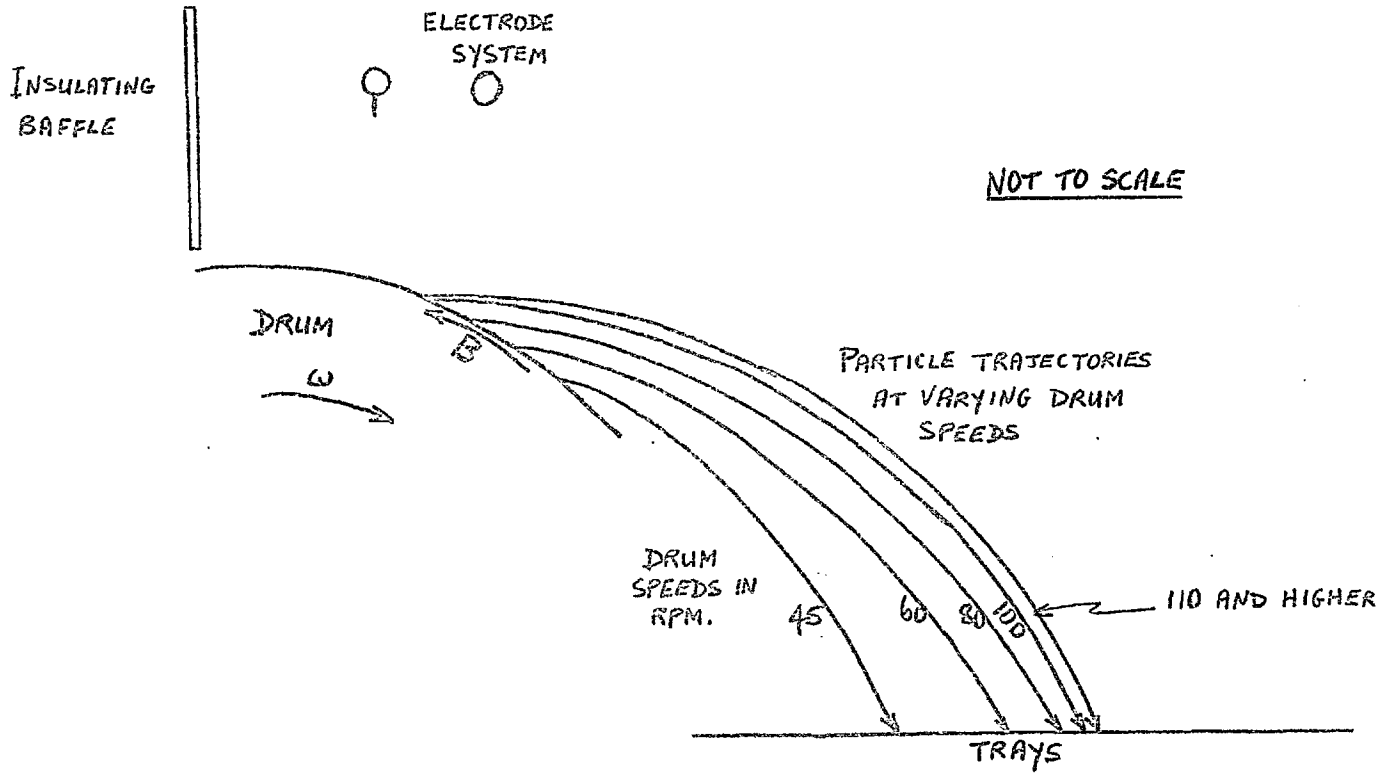


FIG. 8 THE DISPLACEMENT OF THE TAKE-OFF POSITION WITH INCREASING DRUM SPEED.

result the induced charge diminishes in value and the mean landing position approaches the drum. A critical speed is reached where the centrifugal force exceeds the electrical force of pinning and the distance of throwing again increases in magnitude. The critical speed was found to be 65 r.p.m. for the system studied. Above this speed the mean landing positions of carborundum exceed those found under natural trajectory conditions by a constant 0.78 inches (graph 27, curves a and b). It is suggested that at drum speeds greater than 65 r.p.m., the magnitude of the charge induced on the carborundum particles remains constant, thereby resulting in a constant electrostatic lift over and above the lift due to the centrifugal force.

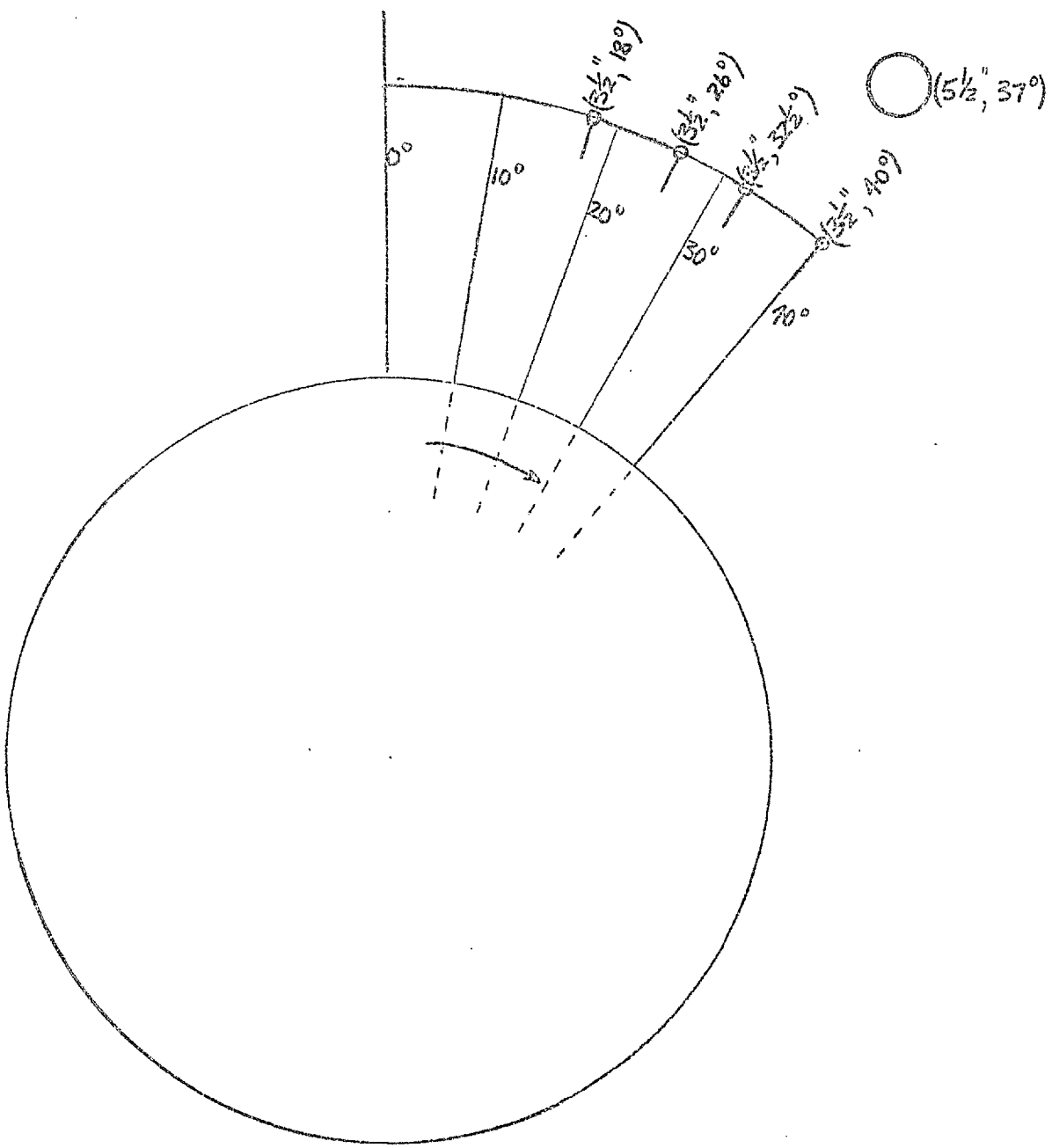
6.5(c) The effect of the displacement of the ionising field on the magnitude of the induced charge.

Widening the boundaries between the ionising and static fields provides a second means of altering the time a particle spends in the static field. By suitable adjustment to the electrode system, the static electrode was kept stationary at position (5½", 37°) and the ionising electrode was displaced in an arc maintaining a constant ioniser gap (fig. 9).

The mean landing position of carborundum was noted under static and operational conditions with variable location of the ionising electrode (Table 10). Two

FIG. 9 THE ELECTRODE GEOMETRY FOR THE STUDY OF THE EFFECT OF THE DISPLACEMENT OF THE IONISING FIELD ON THE MAGNITUDE OF Q_N.

SCALE: HALF ACTUAL SIZE.



positions of B were studied by using drum speeds of 60 and 90 r.p.m.

TABLE 10

TEST CONDITIONS	IONISING ELECTRODE POSITION	MEAN LANDING POSITION TRAY NUMBER	
		DRUM SPEED 60 rpm	DRUM SPEED 90 rpm
STATIC	3½", 40°	8.8	8.3
	3½", 32½°	9.0	7.4
	3½", 26°	8.4	8.1
	3½", 18°	8.4	8.1
OPERATIONAL	3½", 40°	11.5	11.4
	3½", 32½°	9.9	9.0
	3½", 26°	6.3	5.4
	3½", 18°	4.2	4.1

The results of table 10 show that under static conditions the mean landing position is approximately constant for a particular drum speed, implying that throwing of conductors is independent of the geometry of the electrode system.

When the particles are subjected to ionic charging, short lengths between the boundaries of the ionising and static fields result in insufficient time for the full development of an induced charge. Hence the particles are weakly thrown as indicated by the landing positions of 11.5 and 11.4 for drum speeds of 60 and 90 r.p.m. respectively.

As the boundaries are extended, throwing improves due to the development of higher Q_N values. At gaps larger than that corresponding to position (3½",30°) of the ionising electrode, throwing exceeds that found under static conditions, i.e. a particle which has been subjected to ionic charging will acquire a greater final charge than a particle which has not undergone the initial ionic bombardment. This fact leads to the assumption that charge leakage and charging by induction are interdependent and occur similtaneously, as discussed earlier in the thesis (Section 6.4).

6.6 Mechanical separation of minerals.

The rotating drum serves the dual purpose of

(1) transporting material through the ionising and static fields. The speed with which a particle is carried through these fields is an important factor in determining the high tension behaviour of the particle.

(2) aiding in the final dispatch of the particles into pinned or thrown fractions. The speed of rotation of the drum can markedly influence the pinning and throwing behaviours of minerals.

The centrifugal force, W, acting on a particle of mass, m, at the circumference of a rotating drum, radius, r, and angular velocity w, is given by

$$W = mrw^2 \qquad (22)$$

If W exceeds P, the electrical force of pinning, the behaviour of insulators can be profoundly altered. Balint[13] has shown that the centrifugal force can influence the pinning of particles at high speeds. He investigated the effect of drum speed on the pinning behaviour of clean quartz of -52 + 60 mesh size. The separator variables used were favourable for extreme pinning values, i.e. ½ in. ioniser gap and 250 uA current. Under these conditions, pinning remained relatively constant at 82 - 88% when the speed was varied between 55 and 80 r.p.m. Thereafter, pinning fell rapidly, reaching 31% at 150 r.p.m. Similar results were found for other size fractions of quartz. The results suggest that for a -52 + 60 mesh quartz sample, the centrifugal force exceeds the maximum electrical force of pinning at drum speeds exceeding 80 r.p.m. For finer sized fractions and materials of greater insulating properties, the speed at which $W > P$ is greater than 80 r.p.m.

Since the centrifugal force is always complementary to F, the electrical force developed by conductors (equation 16) the angular velocity of the drum does not adversely affect the total weight of conductors thrown. However, the landing position of conducting materials can be displaced by changes in the drum speed which influence the centrifugal force and the magnitude of the charges induced on the particles.

7.0 THE EFFECT OF ADSORBED WATER ON THE SURFACE CONDUCTIVITY OF INSULATING MINERALS.

7.1 Introduction.

In 1939 Fahrenwald[23] ~~first~~ noted that variations in the humidity of the air and in the moisture content of a mixture of mineral particles could cause uncontrollable mineral behaviours in an electrostatic separator. For example, quartz is a good insulator when heated; however, when exposed to moist air at room temperature, it behaves as a conductor and may be separated from zircon[24]. Johnson and Fahrenwald[8] emphasised the necessity for controlled water vapour contents in order to bring about certain separations. Kakovsky et al[4] showed that the similar electrical properties of some minerals are affected differently by changes in humidity, so that an optimum relative humidity may arise for their separation. Simkovich[25] quoted seven references which illustrate that the resistance of a solid insulator decreases markedly with increasing humidity of the surrounding atmosphere. Schniewind[3] found a similar effect in the electrostatic separation of coal from ash.

In studying the contact charging of materials, various investigators[19,26] have demonstrated that insulators usually acquire negative charges at low humidities. When the moisture content of the air is

increased, the magnitude of the contact charge decreases sharply, more particularly so if the solids are hydrophilic. This phenomenon is ascribed to an increased surface conductivity promoting the leakage of charge. The conductivity of hydrophobic insulators depends little on air humidity change[4,24].

This section of the thesis is devoted primarily to a study of the effects of adsorbed water and relative humidity on the surface conductivity of a hydrophilic insulator, viz. quartz. In addition, insulators of smaller water-avidity were employed to investigate further the influence of the two variables. The minerals used were kyanite and a hydrophobic quartz sample, prepared by treating clean quartz with a solution of hexadecylamine. Details of the chemical treatment are presented on page 126.

7.2 The structure of quartz.

Quartz belongs to the hexagonal crystal system and is formed from singly linked atoms of silicon and oxygen. Each silicon atom is bonded to four oxygen atoms to form a SiO_4 tetrahedron (fig.10), each oxygen atom being common to two such tetrahedra.

In order to cleave a quartz crystal, a number of Si - O bonds must be broken. The net result is the creation of an ionic surface, terminating in either

FIG. 10 SILICA TETRAHEDRA.

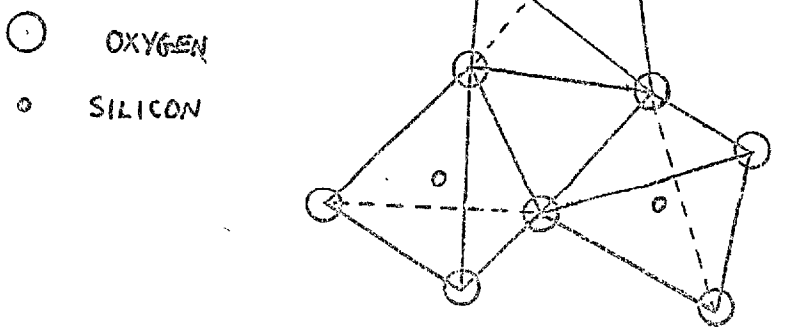
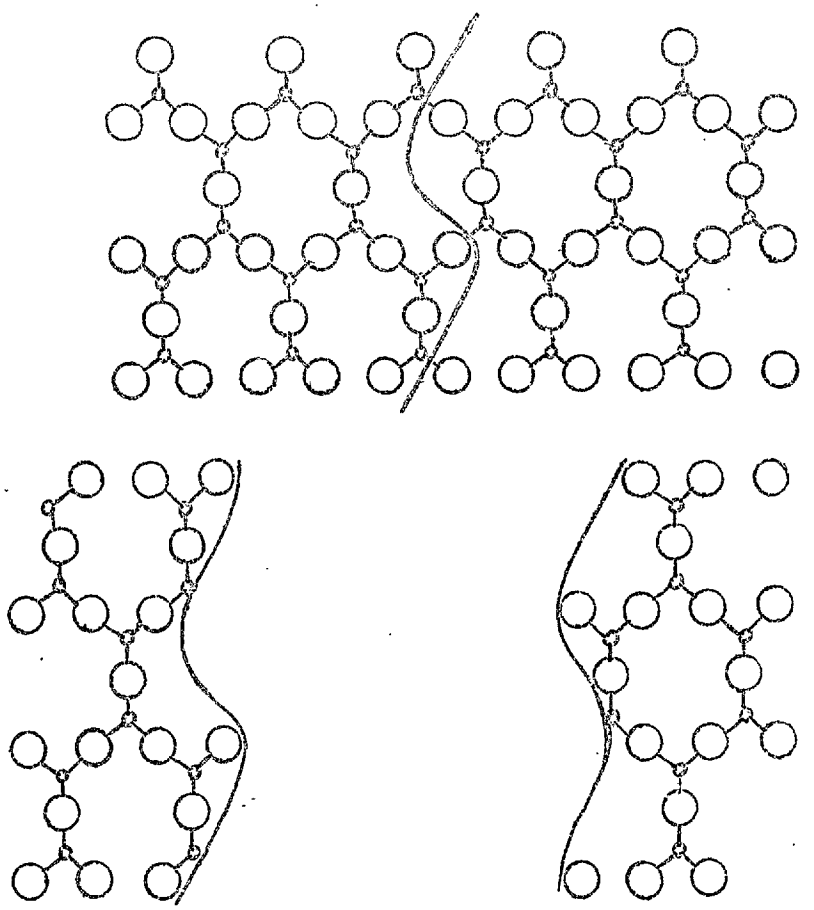


FIG. 11 CLEAVAGE OF THE QUARTZ LATTICE



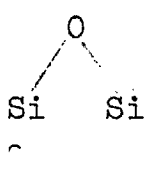
oxygen atoms with an excess of electrons and a negative charge, or silicon atoms with a deficiency of electrons and positively-charged. The cleaved surface is illustrated schematically in fig.11[27], which shows a two-dimensional model of the three-dimensional lattice of quartz. The silicon is shown as being co-ordinated to three oxygen atoms instead of four.

There is reason to believe that an amorphous layer exists on the surface of crushed quartz. The existence of such a layer has been confirmed by electron diffraction means[28] and by studies of quartz dissolution[29,30,31]. Measurements of the magnitude and rate of the solubility of quartz powders (with large surface areas) in water have shown that an initial period of rapid dissolution is followed by much slower rates. Celland and Ritchie[32] attributed the initial rapid dissolution of quartz to the presence of a disturbed surface layer. The general consensus of opinion[10] is that this layer is from 0.3 to 0.5 μ thick. Holt and King[33] studied the solubility of the surfaces of crushed silica by a radiotrace technique. They showed that silica surfaces adsorb silicic acid and that the adsorbed layer is identical in behaviour with the high solubility layers studied by other workers. The layer can be removed by reaction with alkali and reformed from silicic acid solutions. Holt and King divided published data on the solubility of quartz into two groups.

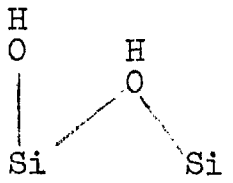
The first, the "high solubility layer" is attributed to the dissolution of the adsorbed silicic acid, the second portion represents the attack of water on the true undistorted quartz or silica lattice.

The existence of a more or less complete surface layer of amorphous silica on quartz must be taken into account in any study of the behaviour of this mineral consequent upon surface properties, such as electrical conductivity and water adsorption. It is implied that the behaviour of quartz particles is conditioned by the properties of the amorphous surface layer and a consideration of the known properties of silica gel is pertinent to this investigation.

The surface of quartz and silica is ordinarily covered by siloxane groups and hydrated siloxane, or silanol groups, known as "bound water"[29,34,35].



Siloxane

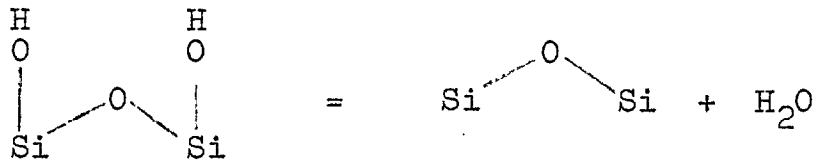


Silanol

The "bound water" is in the form of hydroxyl groups bound to silicon atoms[29,36,37,38]. The silanol groups were initially bound together in complexes containing more than two groups each. In fact, it has been observed by infra-red adsorption spectroscopy that unheated silica

contains both single and geminal surface hydroxyls[39].

The stabilities of silanol groups vary[35]. On heating silica to above 300°C, favourably situated pairs react to evolve water and form surface siloxane groups by the following mechanism.



At temperatures approaching 940°C, silanol groups still exist even under good vacuum conditions. These seem to be anchored in position and do not migrate on the surface.

A mixed topography of silanol and silaxane groups is therefore postulated as the surface on which adsorption of water and resultant changes in conductivity are to be considered.

7.3 The Adsorption of water on the surface of quartz.

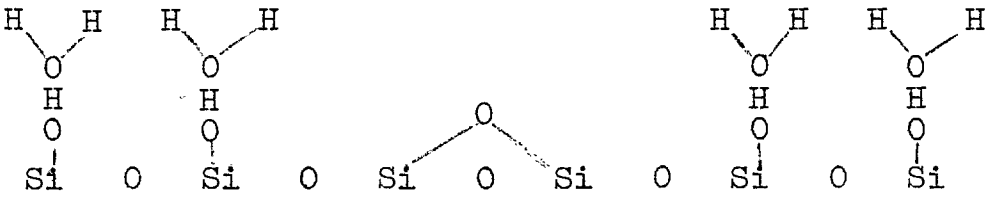
7.3.1. Theoretical considerations.

Most metals or metal oxides adsorb water when exposed to water vapour. The extent of the adsorption depends upon the relative humidity or water vapour pressure[29,40,41].

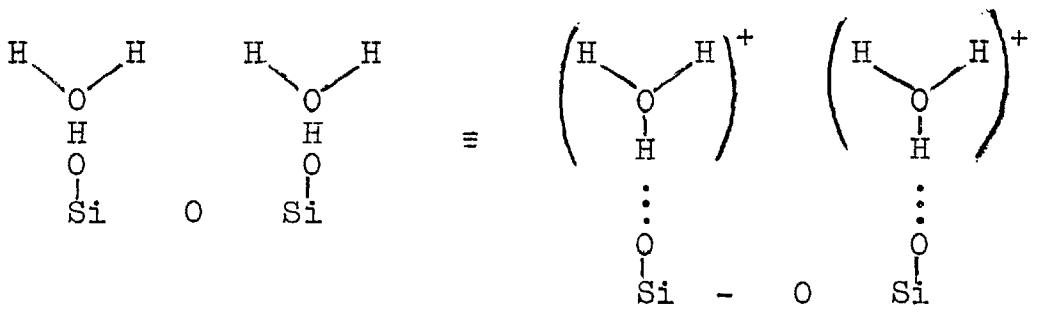
Hydroxyl groups bound to silicon atoms are known to be the species active in the physical adsorption of water vapour on quartz. From infra-red spectroscopy studies,

McDonald[35] was able to state, "These changes (from absorbance studies of the adsorbed species) are unequivocal proof that adsorbed water molecules interact with surface silanol groups through the agency of hydrogen bonds". He was not able to determine whether all the water molecules are adsorbed at silanol sites, or even whether they are adsorbed first at silanol groups. The existence of hydrogen bonding has been confirmed by Gleniser and Rieck[37].

There is further evidence that water adsorption will only take place at silanol sites. Iler has shown[29] that for every OH group lost from the surface by dehydration, about one less molecule of water was adsorbed at low pressure. In addition, Shapiro and Kolthoff[42] and others[39] found that silica gel loses some of its capacity to adsorb water as the gel is dehydrated. Thus the first adsorbed water on a partially dehydrated surface may be represented by



According to McDonald[35], the adsorbed water molecules rearrange slightly to form $(H_3O)^+$ groups associated with an oxygen site, thus



Dehydration of a silica surface can result in the removal of the surface hydroxyls. The geminal groups are not easily removed below 200°C.[39] The removal of the single surface hydroxyls has been visualised by Hockey and Pethica[39] as the elimination of one molecule of water and the simultaneous formation of a strained Si - O - Si bridge. Water which is initially physically adsorbed on the surface hydroxyls of a partly dehydrated silica migrates to react with nearby strained surface groups. The formation of new silanol groups on partly dehydrated surfaces is time-dependent and is only possible when the samples are covered with multilayers of adsorbed water.

After a quartz or silica surface has been dehydrated, lost silanol groups can be regenerated on exposure to water vapour. McDonald has shown that a silica sample heated at 950°C in vacuo for 90 hours, and then left for 2 weeks still under very low pressure, experienced a partial rehydration of active sites. This was confirmed by Hackerman[36] who found that a quartz sample heated at 700°C for 48 hours in

air and then exposed to saturated water vapour for two weeks, produced silanol groups with a subsequent increase in the number of adsorption sites. It is possible[34] that silanol groups are regenerated by a mechanism of water dissociation which leads to the adsorption of protons at oxygen sites and hydroxyl groups at silicon sites.

7.3.2. Experimental procedure.

(i) Apparatus.

Because of the large size (-52 +100 mesh) of the mineral particles used and the corresponding low surface areas, i.e. approximately 250 to 350 cm^2 per g. for quartz, the standard methods of measuring small weight changes due to adsorbed water were considered as too insensitive. For example, a quartz spring balance with a maximum capacity of 2 g. of sample can detect weight changes of the order of 0.05 mg. which is well above the average weight of water adsorbed by the quartz at low to moderate air humidities. On the other hand, increasing the surface area of the minerals by comminution, would lead to the formation of new surfaces with properties that may well be completely different from those of the original surface.

The difficulty was partly overcome by increasing the weight of the sample to 100 g. The change in weight

on exposure to air at four constant relative humidities was read continuously on a chemical balance, using the following equipment.

A Mettler multi-purpose balance, model H5, capacity 160 g. ± 0.2 mg. accuracy and 0.1 mg. precision was firmly fixed on top of a large perspex glove box containing air at the required relative humidity. Air humidity was controlled by means of saturated salt solutions placed in the box. The balance had an extension stirrup pan suspended beneath it, inside the glove box, and attached to the balance by means of thin steel wire passing through a 1/16 in. hole in the top of the box.

(ii) Preparation of materials.

Since the water adsorbing capacity of quartz and kyanite depends on the condition of their surfaces, a standard procedure was adopted for the preparation of the materials prior to the water adsorption measurements. 100 g. samples of acid-cleaned quartz and kyanite were weighed into petri dishes of 9 cm. diameter and were dried for 4 hours at a temperature of 120° - 125°C. The samples were cooled overnight in a desiccator containing silica gel.

The preparation of amine-treated quartz was as follows: Acid-cleaned quartz was reacted with a hexadecylammonium chloride solution under conditions known to

render the mineral surface completely hydrophobic (Section 9.3), i.e. a reagent concentration of 100 mg/l. at a solution pH of 9.0 and a 6/1 liquid to solids ratio. After a reaction time of 15 mins., the solution was decanted, the solids dried at 85°C. for about 3 hours and then cooled as described above.

(iii) Procedure.

After a cooling period of 18 to 20 hours, a petri dish holding a 100 g. sample was transferred to a smaller desiccator which was placed in the glove box. The petri dish was then removed to the stirrup pan and the time at which the solids first became exposed to the moist air was noted because an average of 75 to 90 seconds elapsed between the first exposure of the sample to air and the first weighing. The gain in weight of the solids, as registered by the balance, was recorded at appropriate intervals. After the solids had reached equilibrium with the moist air, the sample was returned to the large desiccator and allowed to dehydrate for about 48 hours. The sample was then weighed on the same balance at very low air humidity to determine the initial weight. Standardisation of all measurements was undertaken by the use of an A grade 100 g. weight. At the start and finish of each weighing the balance was so standardised.

Blank runs were carried out to determine the

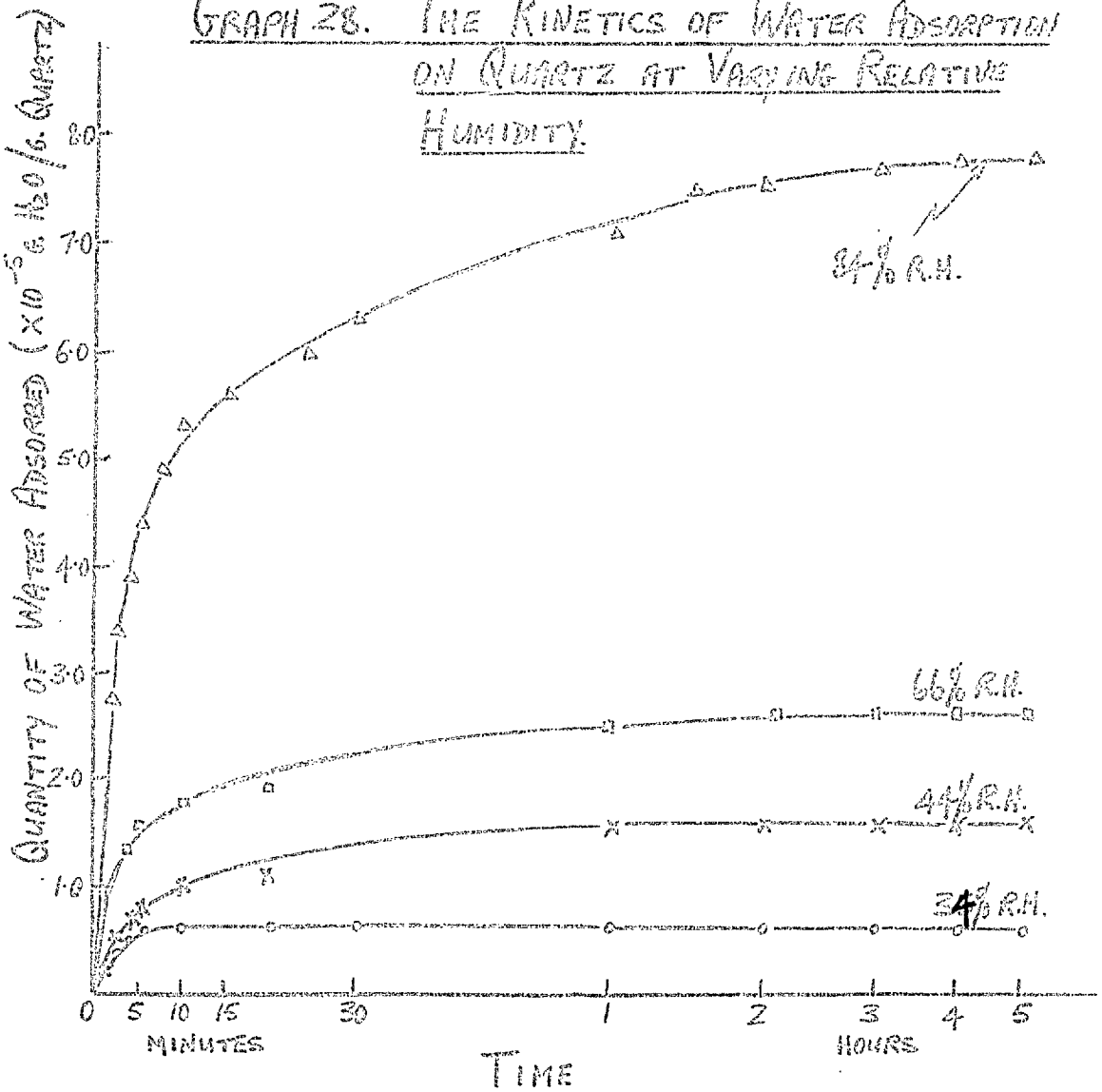
adsorption of water on the petri dishes. No detectable increase in weight could be observed. The temperature was not controlled and averaged about 19°C ± 1°C.

No great accuracy can be claimed for this method of measuring the adsorption of water because of the small increments of weight on large initial weights, i.e. 0.1 to 7.8 mg. variation on about 140 g. weight (100 g. samples and approximately 40 g. for the petri dish). However, with the standardisation, reproducibility of weighings was good and duplicate tests at each relative humidity revealed small standard deviations.

7.3.3. Results and discussion.

At the four relative humidities studied, the adsorption of water is time-dependent, i.e. the rate of water adsorption is initially very rapid, falling off as saturation amounts are approached. The higher the moisture content of the air, the longer the solids take to reach saturation water take-up (graph 28). At 34% relative humidity the adsorption of water on quartz attains an equilibrium value in about 5 to 10 minutes, while at 84% relative humidity the solids continue to increase in weight for 4 hours. The adsorption of water on kyanite is also time-dependent but to a much lesser extent, i.e. at 84% relative humidity kyanite takes 15 minutes to reach equilibrium with the moist air.

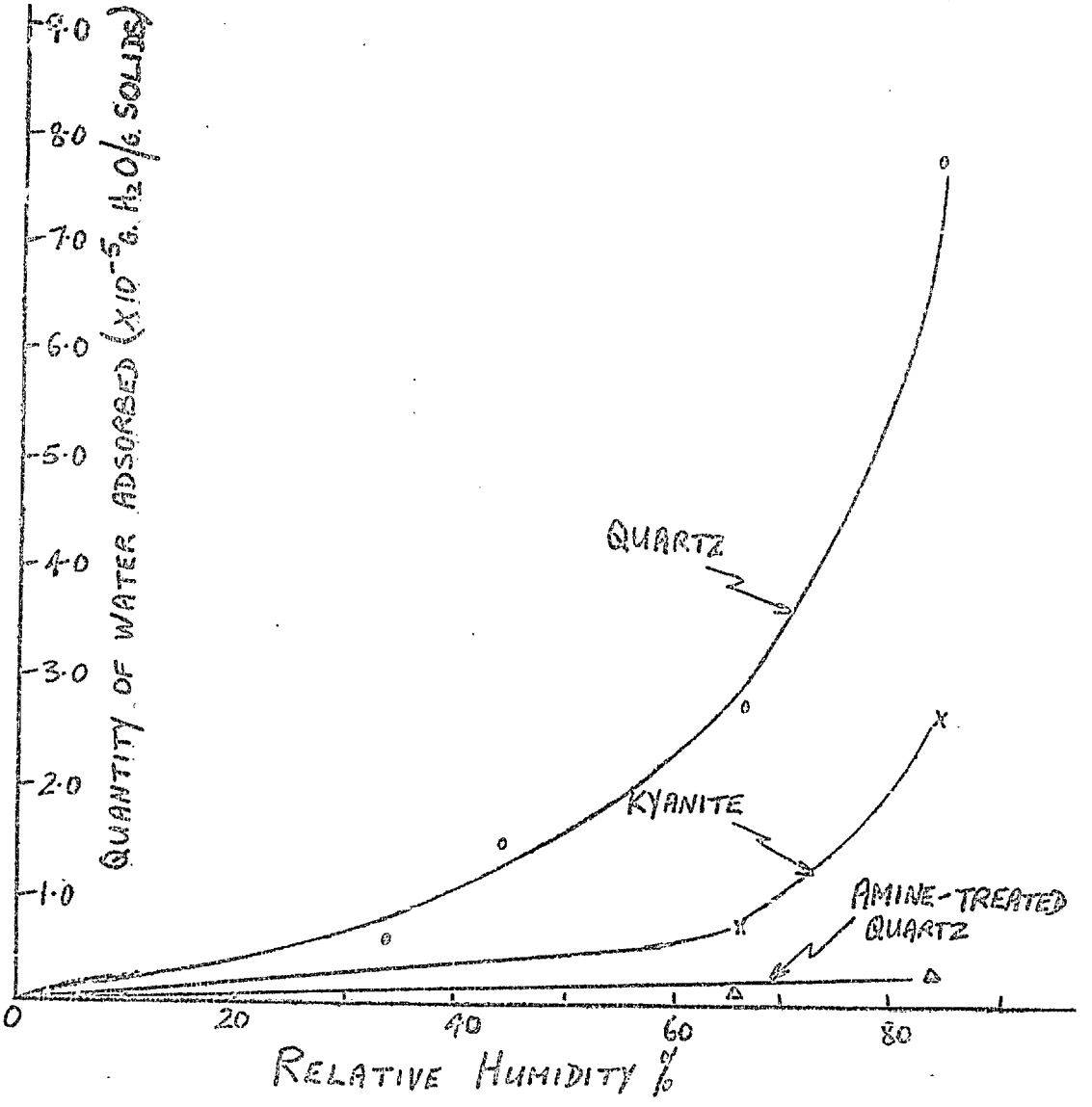
GRAPH 28. THE KINETICS OF WATER ADSORPTION ON QUARTZ AT VARYING RELATIVE HUMIDITY.



The water adsorption isotherm of quartz, kyanite and amine-treated quartz, representing saturation water take-up as a function of relative humidity, is shown in graph 29. As is generally accepted, the quantity of water adsorbed by each mineral species increases with moisture content of the air. The chemically-treated quartz is almost completely hydrophobic, adsorbing only 0.3×10^{-5} g. H_2O per g. quartz at the highest water vapour content studied. The shape of the curve for clean quartz is similar to that for the silica gels studied by Kurosaki[43] and Hackerman[36]. The rapid increase in water take-up at high air humidities is attributed to the formation of multilayers and capillary condensation[44].

The dynamics of water adsorption on quartz and silica has not received much attention. Klassen[45] reported that at a water vapour pressure equivalent to 83% of the saturation value, a film of water 45 ^{o}A thick is adsorbed instantaneously on quartz. Hockey and Pethica[39] indicated that adsorption became time-dependent when silica gel was exposed to moist air at a relative humidity in excess of the level at which there are two water molecules per pair of surface hydroxyls. This was attributed to the slow chemisorption of water by partly dehydrated silicas. For the silica they used, the critical relative humidity was 11%.

GRAPH 29. WATER ADSORPTION ISOTHERMS.



Other authors[4,19,24,46] have noted that the increase in surface conductivity of insulators improved with time when exposed to moist air, i.e. Kakovsky[4] showed that the resistance of apatite, when exposed to air at 70% relative humidity, decreased at a rapid rate initially, reaching a constant value after 60 minutes.

The observation in this work that the adsorption of water on quartz and kyanite increased with time may be explained as follows:

(a) The 100 g. samples were spread over an area of 63.6 sq.cm. in the petri dish, corresponding to a depth of sample of 10.4 mms. This could have caused a time lag for the penetration of water vapour to the bottom of the bed of particles. However, the electrical properties of the upper and lower layers of the particle column were determined separately and no variation was found. This is described in greater detail below (Section 7.5).

(b) In preparing the quartz and kyanite samples, drying was at 120° to 125°C. This could have resulted in the loss of silanol groups, the regeneration of which increases slowly with time, as envisaged by Hockey et al.

The quantity of water required to form a monolayer on the surface of the quartz was calculated from the equation[42], $S = NqA/M$,

where S = specific surface area expressed in sq.cm. per g. adsorbent

N = Avogadro's number

A = Cross-sectional area of a single molecule expressed in sq.cm.

M = Molecular weight of adsorbate.

With a surface area varying between 250 and 350 sq.cm./g., the amount of water necessary to form a monomolecular layer on the quartz surface was calculated as 0.7 to 1.0 X 10^{-5} g. per g. mineral. These theoretical amounts of water correspond to the water take-up on quartz at 34 to 40% relative humidity (graph 29). Shapiro et al[42] found monomolecular coverage of water on silica gel at 44% relative humidity.

7.4 The increase in the surface conductivity of quartz and kyanite due to adsorbed water.

7.4.1. Introduction.

Much work has been reported[4,6,16,24,47,48] on the influence of surface water on the electrical conductivity of insulating materials. It is generally accepted that the presence of an extremely thin layer or film of water on the surface of the mineral can considerably increase the conductivity. Since the adsorption of water on to metal oxides is dependent on the moisture content of the surrounding atmosphere, many of the above authors studied the influence of relative humidity on the surface conductivity of insulators and found a linear relationship, as expressed by the general formula:

$$\text{Log}_{10} S = a - b H \qquad (23)$$

where S = surface conductivity, H = relative humidity and a,b are constants.

Kurosaki[43] studied the dielectric behaviour of water adsorbed on silica gel and was able to show that the properties of the adsorbed water depended on the amounts involved. The relation between apparent dielectric constant and the weight of adsorbed water, a (expressed in mg.H_2O per g. silica), was divided into three stages occurring at a less than 15 mg./g., 15 - 94 mg./g. and greater than 94 mg./g. In the first stage the water is strongly bound to the silica surfaces as confirmed by the extremely high heat of sorption. In the second stage interaction between adsorbed water molecules is slight. De Boer[49] has shown that such weakly adsorbed water molecules possess a considerable degree of lateral mobility. In the third stage the adsorbed water is in a firmly bound condition and is considered to have a much more strongly developed hydrogen bond than pure water, the molecules being arranged in an orientation approaching the structure found in ice. In the vicinity of a moisture content of 100 mg./g., the heat of adsorption coincided with the heat of condensation, suggesting that sorbed water at this point is thermodynamically in the same state as liquid water. Kurosaki concluded that a quantitative explanation

of the observed results is possible if the adsorbed water in excess of 94 mg./g. is considered as a phase having the same dielectric constant, specific gravity and conductivity as liquid water. In addition, he showed that increased ion conduction resulted on gels on which large quantities of water had been adsorbed.

Many authors[6,50,51] have corroborated Kurosaki's statement that water adsorbed on silica surfaces and on many other types of material increases the surface conductivity. According to Bikerman[6] the temperature and humidity-dependence indicate that the surface conductivity may be considered that of a thin film of ionically conducting material spread on the surface of the solids. The calculated bulk conductivity of a water film would be 8×10^{-6} mho/cm. which is greater than the conductivity of pure water. In the calculation it was assumed that hydrogen ion is the only mobile species, i,e. the dominant charge carrier, and that the mobility of the hydrogen ion is the same in the surface film as in bulk water[52].

Sarakhov[53] measured the volume and thickness of water adsorbed on quartz and calculated that the hydrogen ion concentration in the adsorbed film varied between 3×10^{-6} and 8×10^{-6} mole/l depending on the humidity. His estimated average conductivity is 1.5×10^{-6} mho/cm. which compares well with Bikerman's 8×10^{-6} mho/cm. The calculation failed at humidities below 80% since water

adsorbed at low humidities does not have the properties of bulk water.

It has been shown[6] that as the thickness, ℓ, of the adsorbed water layer increases, the surface conductivity, S, increases as well, so that the ratio S/ℓ is nearly independent of ℓ. This ratio was 8×10^{-6} mho/cm. on quartz, i.e. a few times that of distilled water; on glass it was 10^{-3} mho/cm., i.e. equal to the conductivity of NaOH solutions containing a few millimoles in one liter. The thickness of the gel film on glass was 5×10^{-7} cm.

It is concluded that the increased surface conductivity of quartz at multilayer coverages of adsorbed water may be quantitatively accounted for by the assumption that it is the volume conductance of a thin layer of water on the mineral surface.

7.4.2. Experimental Procedure.

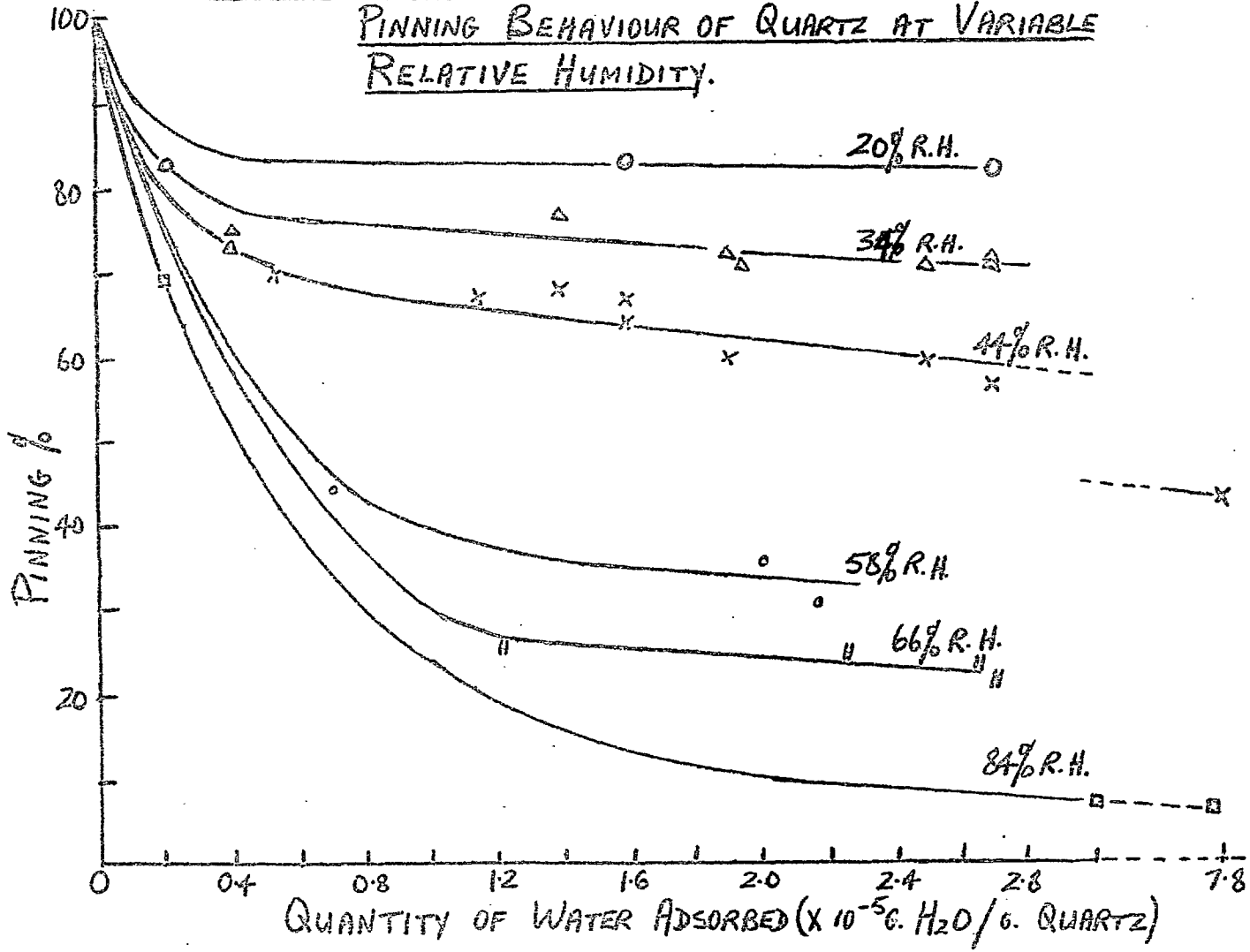
In this section of the work the surface conductivity of quartz, kyanite and quartz treated with amine was determined as a function of the variables (a) relative humidity and (b) water adsorption density. The determination of changes in conductivity by means of the plug resistance measurements described earlier (Section 4.5), proved to be insensitive to the small increments of resistance involved. Hence, changes in surface conductivity were assessed through the pinning behaviours of the materials

under standard high tension conditions.

Quartz samples of 50 g. weight, contained in petri dishes, were dried under conditions identical to those outlined above (Section 7.3.2.), i.e. 4 hours at 120° - 125°C. followed by cooling overnight over silica gel. The samples were then placed in a glove box containing air of the required moisture content. The amount of adsorbed water was varied by (1) changing the air humidity and (2) adjusting the time of exposure to such relative humidities. The quantity of water adsorbed by the quartz samples was estimated by referring to graph 28, which shows the relationship between the rate of water adsorption and air humidity. After attainment of the requisite take-up of moisture, the samples were transferred to the high tension separator, through which air of the required relative humidity was being circulated. Pinning values were determined over a range of relative humidities (graph 30).

The effects of small amounts of adsorbed water, i.e. 0 - 4 mg. water per 100 g. solids, on the pinning of clean quartz could not be determined by this method. During a period of about 4 minutes, representing the passage of the dry samples through the separator, water adsorption on dry quartz could be extensive, particularly at high relative humidities. The difficulty was overcome by rendering the quartz hydrophobic, using hexadecylamine treatment under

GRAPH 30. THE EFFECT OF ADSORBED WATER ON THE PINNING BEHAVIOUR OF QUARTZ AT VARIABLE RELATIVE HUMIDITY.



the conditions specified on page 127. The concentration of the amine was 100 mg./l, obviating the possibility of the formation of multilayers of adsorbed reagent on the quartz surface. Hence, any decrease in the conducting properties of the quartz particles is unlikely to have been due to the presence of a thick insulating layer of reagent. The increase in pinning is attributed almost exclusively to the water-repellency of the surface of the mineral. The pinning behaviour of the hydrophobic quartz was determined over a range of relative humidity (graph 31).

Adjustments to the quantities of water adsorbed on the mineral surfaces were estimated after each test to allow for additional adsorption or desorption of moisture during the passage of the mineral through the separator. It was assumed that desorption was reversible. Attempts to measure the adjustments quantitatively failed due to the inconsistencies of the results.

The effect of changes in relative humidity on the pinning behaviour of kyanite was determined in similar manner for comparison with the above results. Pinning values were determined under saturation conditions of water adsorption at each of the air humidities studied. The results (graph 31) indicate that the conductivities of kyanite and the amine-treated quartz are similarly affected by the presence of water vapour.

7.4.3. Reproducibility of results.

In relating the pinning of quartz to the water adsorption density, good reproducibility of results was essential, because only small changes in pinning value result from the increased water adsorption. An example of the reproducibility is given below. Several quartz samples were humidified at 66% air humidity for varying times and the resultant pinning values noted at a separation humidity of 34%. (table 11).

TABLE 11.

Humid. Time (Mins.)	Pinning Values %	Average % Pinning	Standard Deviation.
0	75.3 77.2 75.4 74.1	75.5	1.6
15	72.6 71.6 71.9	72.0	0.3
60	70.4 71.2 70.8 70.3	70.7	0.2
120	69.2 69.9 69.9	69.7	0.2

The small standard deviations shown in table 11 indicate the reliability of the method for determining

changes in the electrical conductivity of quartz with increasing water take-up. Comparable reproducibilities were found throughout the work described in the thesis.

7.4.4. Results and discussion.

(i) The effect of water adsorption density on the pinning of quartz.

Graph 30 shows that at a constant relative humidity, the increasing coverage of the quartz surface with adsorbed water increases the conductivity of the mineral. Pinning decreases initially at a rapid rate until the completion of a monolayer of adsorbed water is approached. Thereafter, pinning falls at a much slower rate.

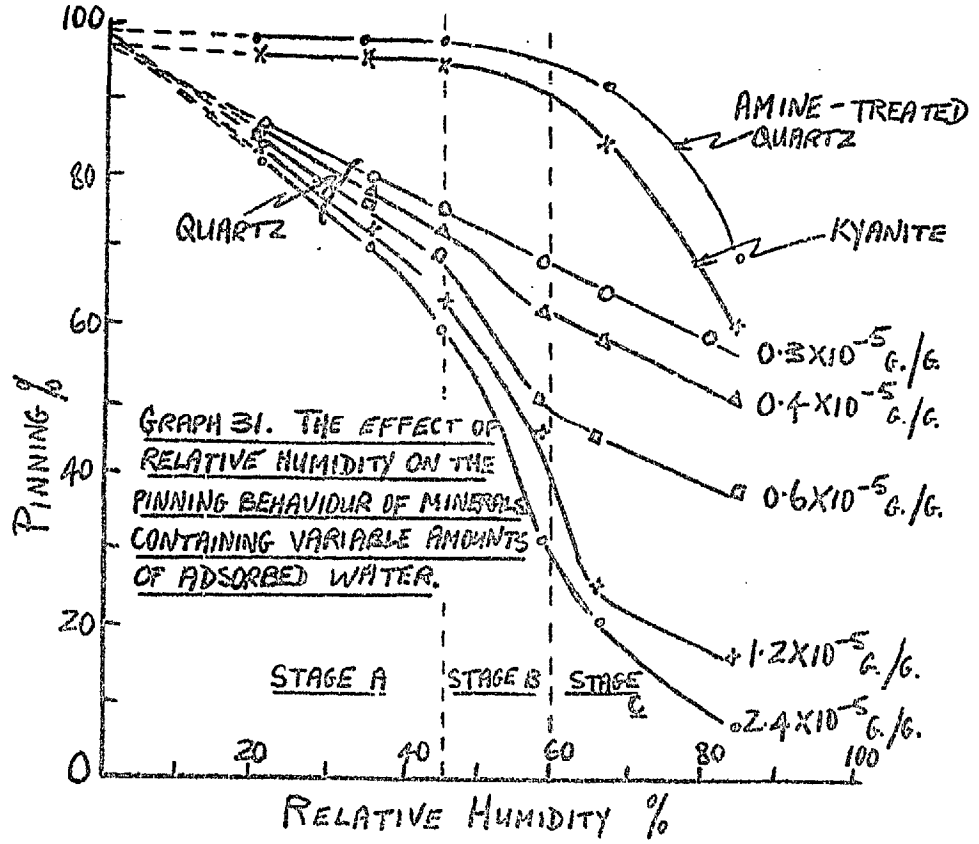
The increased conductivity of the quartz particles at constant relative humidity can therefore be safely ascribed to the presence of the adsorbed water. It is envisaged that the initial random adsorption of water molecules at active silanol sites provides many conducting paths along which ions can travel when the particles are under the influence of the static field of the high tension separator. In addition, the initially adsorbed water molecules possess considerable lateral mobility and can increase the surface conductivity by acting as charge carriers. After saturation of the surface with a monolayer of adsorbed water, further increase in moisture take-up leads to a slower rate of increase in conductivity

due to (a) the water molecules being attached more stably to the silicon atoms and contributing less to the surface conductivity and (b) the adsorbed water behaves as bulk water and the conductance of charge carriers now depends on the thickness of the moisture film.

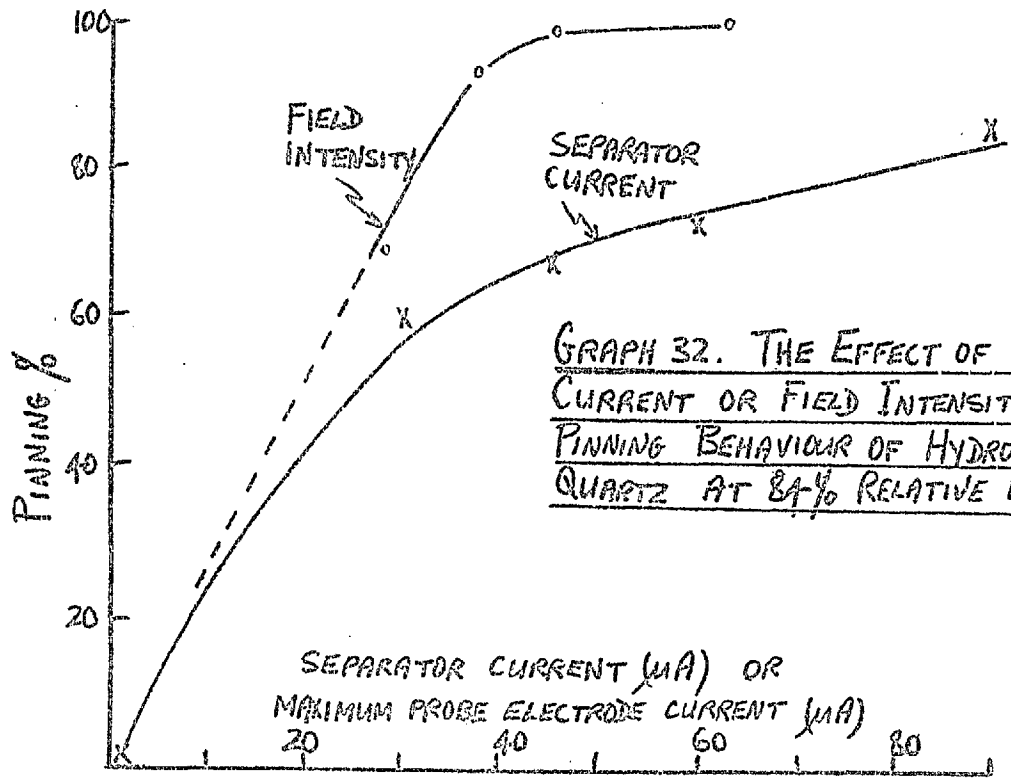
(ii) The effect of relative humidity on the pinning behaviour of minerals.

The influence of relative humidity on the electrical conductivity of quartz is shown (graph 31) as a function of constant water adsorption density, using interpolated values from the family of curves in graph 30. Also included on the graph are the pinning vrs. relative humidity relationships of kyanite and amine-treated quartz. It is apparent that the moisture content of the air in contact with the minerals is a factor of considerable importance in determining their pinning behaviours. The effect of increasing relative humidity is a decrease in the insulating properties of the minerals, more markedly so in the case of hydrophilic solids.

All the curves of graph 31 tend to converge to a narrow range on the ordinate axis corresponding to about 97 to 99% pinning. This suggests that most minerals of small bulk conductivity report as perfect insulators at very low air humidities. This has been confirmed elsewhere[54]. With increasing water vapour content of the



GRAPH 31. THE EFFECT OF RELATIVE HUMIDITY ON THE PINNING BEHAVIOUR OF MINERALS CONTAINING VARIABLE AMOUNTS OF ADSORBED WATER.



GRAPH 32. THE EFFECT OF SEPARATOR CURRENT OR FIELD INTENSITY ON THE PINNING BEHAVIOUR OF HYDROPHOBIC QUARTZ AT 84% RELATIVE HUMIDITY.

atmosphere the pinning behaviour of the minerals alters at a rate dependent on the quantity of water adsorbed by the surface of the solids. The hydrophilic quartz particles increase considerably in conductivity with rise in air humidity, while the pinning of the hydrophobic kyanite and amine-treated quartz samples remains unaffected up to about 45% relative humidity, thereafter decreasing sharply.

The change in the pinning behaviour of quartz with increasing air humidity can be divided into three stages, corresponding to ranges of relative humidity of (a) 0 to 45%, (b) 45 to 60% and (c) greater than 60%. Over stage (a) a linear decrease in pinning is maintained to about 45% air humidity, where pinning diminishes sharply (stage b). The rapid fall in pinning is checked over stage (c). A similar result was observed at Warren Spring Laboratory[54], where an identical quartz sample was tested on a high tension separator of the disc-type.

Stage (a). Over this region a linear relationship exists between pinning and relative humidity, as expressed by the equation

$$P = -aH + b \qquad (24)$$

where P = pinning value, H = relative humidity expressed as a percentage, a and b are constants. The slope of the lines (numerically equal to constant, a) depends on the

degree of coverage of the mineral surfaces with adsorbed water. When the surface coverage is increased from zero to an amount exceeding a theoretical bimolecular layer, i.e. 2.4 X 10^{-5} g. H_2O per g. quartz, the slope varies from nil to 0.8. Constant, a, therefore indicates the hydrophilicity of the surface of the mineral.

In the preliminary study of the effects of relative humidity on the pinning behaviour of the chemically-treated mixture of quartz and kyanite (Section 4.3), relationships similar to equation (24) were found, i.e.

$$P_c = 138 - 2.0\,H \qquad (25)$$

$$P_I = 105 - 0.4\,H \qquad (26)$$

where P_c and P_I are the pinning values of the conducting and insulating fractions respectively. Equation (26) holds for values of H up to 60%.

When an insulating particle is under the influence of the static field of the high tension separator, leakage of charge is primarily along the solid-gas interface[6]. The rate of discharge is determined by the electrical conductance of this interface. The results of graph 31, stage (a), therefore suggest that the quartz-air contact resistance decreases when (a) the water vapour content of the surrounding air is raised or (b) the quantity of water adsorbed on the mineral is increased.

The pinning value of kyanite and the hydrophobic quartz is unaffected by changes in relative humidity over stage (a). It appears that the weak attraction of molecules of water vapour to the water-repellent surface prevents any increase in the conductivity of the solid-gas interface.

Stage (b). The pinning of clean quartz decreases sharply above a relative humidity of 45%, more particularly so at high coverages of the surface with water. The strong increase in surface conductivity of the particles is attributed to the adsorption of water on to the drum surface. It is suggested that monomolecular coverage of water occurs on the metal surface at air humidities existing over stage (b). This adsorption of water results in (i) an increase in the area of contact between the particles and the drum, facilitating charge leakage between the two and (ii) the adhesion between the surfaces of the mineral particles and the metal is increased (Section 7.6), so that the particle-drum contact resistance is lowered. The presence of large amounts of adsorbed water on the mineral increases both the area of contact and the adhesion envisaged above[6]. The fall in the pinning behaviour of quartz is therefore more pronounced at high densities of adsorbed water.

The pinning values of the more hydrophobic minerals decrease over stage (b), slowly at first and then more

sharply on entering stage (c). This is attributed to the following:

High moisture contents of the atmosphere result in (a) a small increase in the quantity of water adsorbed by the two materials (graph 29), thereby improving their surface conductivities, and (b) a fall in the intensity of the ionising field, thereby causing a decrease in the pinning behaviour (Section 5.5).

The latter postulation was checked by increasing the strength of the ionising field at high water vapour contents of the surrounding air and determining the effect on the insulating properties of the hydrophobic quartz. The standard high tension conditions were retained, except that the voltage and current were altered in order to modify the field intensity.

The influence of current on the pinning behaviour of the mineral was investigated at 84% relative humidity (graph 32). The field intensity, as represented by the maximum values of the probe electrode currents prevailing at the four air humidities studied (graph 24), was also plotted against pinning values on the same graph 32. The results demonstrate that the pinning of the water-repellent material improves with rising separator current or strength of the ionising field, reaching a maximum value in a fashion similar to that found for the pinning of insulators as a function of current (graph 3). It appears that above

45% relative humidity, the field intensity falls below the critical value required to bring about maximum pinning of the mineral particles (Section 6.3).

The reduced pinning values of kyanite and the amine-treated quartz can therefore be ascribed to decreased charging in the ionising field and adsorption of a small amount of water. The latter factor is probably of minor importance. The lower field strengths also aid in the decline of the pinning of clean quartz over stages (b) and (c).

Stage (c). It is suggested that the rise in surface conductivity due to the enlarged areas of contact and greater adhesion between mineral particles and the surface of the drum, reaches a limiting value. Thereafter, the particles rely on the continued improvement in the conductivity of the solid-gas interface for a further fall in pinning. Hence, pinning decreases at the slower rate found over stage (a). The slopes of the curves in stages (a) and (c) tend to be equal.

7.5 The effect of the depth of the sample bed on the pinning of quartz.

Reference was made (Section 7.3.3) to the possibility that the depth of the sample in the petri dishes may account for the time-dependence of the adsorption of water on quartz surfaces. If this were the case, the pinning

behaviour of the particles at the bottom of the bed could be expected to be higher than that of the particles at the top, when humidification times were kept shorter than needed for attaining saturation water adsorption. This line of evidence was checked as follows:

A circular strip of thin cardboard, about one inch wide, was placed around the inner circumference of a shallow petri dish, thus doubling its capacity from 50 to 100 g. Quartz samples of 100 g. weight were dried as before, placed in this petri dish and exposed to air at 66% relative humidity for 15 or 60 minutes, as listed in table 12. At the end of the period of humidification, the cardboard strip was lifted and the top half of the sample was removed by means of a spatula. Either the top or the bottom fraction was then immediately tested in the high tension separator at 34% relative humidity. The other half of each sample was discarded. The resulting pinning values are compared with those of the complete 100 g. samples (table 12).

TABLE 12.

Sample	Humid Time (mins.)	Pinning Values %	Average % Pinning	Standard Deviation
Complete 100 g.	15	72.6 71.6	72.1	0.5
Complete 100 g.	60	70.4 71.2	70.8	0.4
Top 50 g.	15	72.8 71.8 72.0	72.2	0.3
Top 50 g.	60	71.8 69.0 71.7	70.8	2.5
Lower 50 g.	15	72.7 69.8 69.9	70.8	2.7
Lower 50 g.	60	70.3 68.4	69.3	1.0

The results indicate that the conducting properties of the two fractions of quartz are equal within the limits of experimental error, suggesting that the adsorption of water is uniform throughout the bed of particles.

7.6 The adhesion of quartz particles to the surface of the drum in moist atmospheres.

In support of the statement that the adhesion between mineral particles and the surface of the drum increases at high air humidities, the following experimentation was performed:

100 g. samples of acid-cleaned quartz were dried under standard conditions and humidified for 60 minutes at 66% relative humidity. The samples were passed through the separator under conditions of gravitational trajectory, i.e. no applied voltage. The weight distribution of the trajected samples was noted at varying air humidities. The drum speed used was 50 rpm. At each relative humidity studied, tests were carried out either in duplicate or triplicate and the average distributions were noted (table 13). In this series of tests, the tray positions did not conform with the nomenclature outlined in Section 3.1. Tray 1 corresponded to a position 7.8 in. from the vertical tangent to the drum. Each tray was 0.6 in. apart.

The total quantity of material found in trays 1 to 4 decreases with increasing moisture content of the atmosphere, i.e. a reduction from 5.7 to 4.3% on increasing the relative humidity from 34 to 66%. This confirms that a small degree of adhesion had occurred, causing the weight distribution to be shifted towards the vertical tangent to the drum.

When the mineral particles are strongly pinned to the surface of the drum under operational conditions, the force of adhesion can be considerably increased[6]. The total quantities of material reporting in trays 7 to n

are in the inverse order to that in trays 1 to 4, i.e. at low humidities some of the quartz is actually pinned to the drum. This phenomenon can be attributed to the contact charging of the particles at low humidities, resulting in a weak electrostatic attachment to the metal surface of the drum.

TABLE 13.

Tray Number	Weight Distribution %		
	34% Relative Humidity	44% Relative Humidity	66% Relative Humidity
1	0.2	0.2	0.2
2	0.5	0.5	0.4
3	0.8	0.8	0.7
4	4.2 ± 0.1	3.4 ± 0.0	3.0 ± 0.3
5	74.6 ± 1.4	73.7 ± 0.5	78.8 ± 2.0
6	16.6 ± 0.9	18.6 ± 0.4	14.8 ± 0.6
7	1.4	1.5 ± 0.2	1.1
8	0.7	0.6	0.5
9	0.4	0.3	0.2
10	0.2	0.2	0.1
11	0.1	0.0	0.0
12	0.0	0.0	0.0
12 → n	0.3	0.2	0.2
	100.0	100.0	100.0

7.7 The effect of humidifying time on the electrical conductivity of quartz.

In the water adsorption studies it was observed that the take-up of water on quartz is time-dependent. Published literature has indicated that the surface conductivity of insulating materials attains an equilibrium value after the passage of finite times (usually 5 to 60 minutes) when exposed to atmospheres of high moisture content.

In the present work it was observed that when quartz was humidified at various relative humidities, it continued to decrease in pinning with time in excess of that required to obtain saturation water adsorption. This phenomenon was particularly noticeable at air humidities greater than 44%. Three examples are given below (table 14).

Quartz samples, humidified and then separated at the same relative humidity of 44%, show a slight decrease in pinning values up to 2 hours after the first exposure to the moist air. Investigations after 24 and 166 hours humidification revealed no further change in conductivity. When the quartz particles were exposed to air at 66% relative humidity and separated at 44 or 66% air humidities, the pinning values fell steadily with time. Quartz attains saturation water adsorption in 1 and 3 hours when exposed to the above humidities (graph 28).

TABLE 14.

Humidification R.H. (%)	Humidification Time (hours)	Separation R.H. (%)	Average Pinning Values (%)	Standard Deviation
44	0	44	69.6	1.2
	¼		67.4	1.6
	1		68.0	1.7
	2		66.3	0.7
66	0	66	25.8	0.2
	½		25.1	0.4
	2		24.1	0.4
	24		21.8	1.1
	48		22.0	0.2
66	0	44	69.6	1.2
	¼		59.4	0.4
	1		59.5	0.1
	3		56.3	0.7
	4½		57.6	0.8
	92		52.2	-
	265		38.6	1.6

7.8 Conclusions.

The moisture content of the surrounding atmosphere and the quantity of adsorbed water can modify considerably the electrical conductivity of insulating materials. Relative humidity has a more profound influence and affects the pinning behaviour of the minerals by controlling the intensity of the ionising field and the conductivity of the solid-air interface. The adsorption of water on the solid surfaces increases the surface conductivity by virtue of the ionically conducting properties of the components of the water.

From a knowledge of the time-dependence of (1) the increase in water adsorption on quartz particles exposed to moist atmospheres and (2) the continued increase in surface conductivity after saturation water take-up, the following mechanism is proposed for the reaction of water with a quartz surface: Drying the quartz samples at 120° - 125°C. for 4 hours leads to the loss of some silanol groups and the simultaneous formation of strained Si - O - Si bridges. Water molecules are physically adsorbed at existing silanol sites when the partly dehydrated surface is exposed to water vapour. The water molecules possess lateral mobility and migrate along the surface to react with adjacent siloxane bridges, thereby regenerating silanol groups. The regeneration of silanol

sites causes an increase in the water adsorbing capacity of the surface of the mineral. The water adsorption isotherm of a partly dehydrated quartz surface therefore displays an initial sharp rise in water take-up, followed by a slower rate of increase ascribed to the sluggish formation of additional adsorption sites.

When water adsorption attains an equilibrium value, it is suggested that the regeneration of silanol groups continues, but at a slower rate, as reflected by the continued increase in the surface conductivity of the mineral well after it has been saturated with water vapour. The extent of the formation of silanol sites depends on the degree of coverage of the surface with water molecules. At 44% relative humidity, where the coverage is theoretically of monomolecular dimensions, the number of silanols regenerated is relatively low, i.e. saturation water take-up is obtained after 60 minutes, while the pinning value decreases for at least 2 hours. When a multimolecular water layer is present at 66% relative humidity, the adsorption of water attains equilibrium after 3 hours. Humidification of the mineral for 265 hours at the same air humidity results in a pinning value of 38.6% compared with the 56.3% after 3 hours contact with the moist atmosphere. Although the samples in both these cases had the identical quantities of water adsorbed on their surfaces, ageing at 265 hours produced

a marked increase in surface conductivity and is attributed to the larger proportion of active silanol sites on the surface.

The validity of the above mechanism depends on the assumption that the surface conductivity of a quartz sample in equilibrium with a moist atmosphere, depends on (i) the quantity of adsorbed water and (ii) the number of silanol sites on the surface of the mineral. The first assumption has been verified, both elsewhere and in this thesis, while the second does not appear to be unreasonable as the regeneration of a silanol group involves the dissociation of a water molecule leading to the existence of free H^+ ions which can markedly improve the conductivity of the surface. In addition, the silanol sites may provide the paths along which mobile water molecules or $(H_3O)^+$ groups migrate.

The conductivity of quartz may also be increased by the following:

(1) Any alkali impurities present on the mineral surface will react chemically with the adsorbed water to form an alkaline film of good ionic conductance.

(2) The moist air surrounding the mineral particles contains carbon dioxide which can be dissolved by the adsorbed water to form H_2CO_3. This electrolyte can readily increase the surface conductivity.

Both the above mechanisms are not possible at low coverages of the quartz surface with adsorbed water.

8.0 MODIFICATION OF THE SURFACE CONDUCTIVITY OF MINERALS BY METAL SALT TREATMENT.

8.1 Introduction.

Metal ion activation has been widely employed to improve the floatability of quartz, silica and silicates using anionic collecting agents. In the field of high tension separation however, modification of the electrical properties of minerals by treatment with solutions of metal salts has not found extensive application.

One of the earliest references to metal ion conditioning to modify the surface conductivity of a mineral can be found in a 1910 patent attributed to Swart[2]. He rendered sphalerite conducting by treating it with dilute solutions of copper sulphate. The increased conductivity was later attributed to the formation of cuprous sulphide.[8] Sutherland and Wark[63] reported that the resistance of a plug of sphalerite particles decreased twelve fold after treatment with a solution containing 10 mg. $CuSO_4 . 4H_2O$/l. Using the same system, Pocock[17] demonstrated that the pinning of sphalerite fell after treatment with copper sulphate. Sun[64] reported the use of barium chloride and copper sulphate to modify the electrical properties of quartz. Linari-Linholm[65] studied the effect of various concentrations of salt solution on the recovery of diamonds from the gangue. He found a nearly parabolic

relationship between the concentration ratio and the salt concentration with an optimum value of the latter at about 0.5%. Above this value, the salt solution wetted the normally hydrophobic diamonds. Bikerman[6] reported that wool soaked in a solution of sodium chloride and then rinsed with water had a higher conductance than wool which had no contact with the salt.

In flotation practice, pretreatment or "activation" of mineral surfaces with solutions containing metal ions is undertaken in order to obtain selectivity and/or enhance the collecting power of a collector reagent. Various researchers[45,63,66,67,68] have indicated that heavy metal salts so alter the surface of silicate minerals that they may be floated by collectors which normally have little effect. It is presumed that the mechanism is one of adsorption of a film of some less soluble substance able to adsorb the collector. The effectiveness of the activation is dependent on the pH of the solution, i.e. maximum recovery of activated quartz occurs in the pH region of precipitation of the relevant metal hydroxide [63,69,70,71,72,73]. Iler[29] observed that the adsorption of polyvalent ions from solution on to silica surfaces is a maximum at similar pH's. Vail[58] pointed out that salts of heavy metals have a particular affinity for colloidal silica at hydrogen ion concentrations at which precipitation of the metal hydroxide is incipient. The

resultant products are hydrous mixtures of varying composition and water content.

Metal ion activation is not used only to facilitate the flotation of silicates. In some cases it is used to depress minerals, e.g. potassium chromate, although not affecting the adsorption density of the collector, inhibits the flotation of quartz probably due to the high degree of hydration of the chromate ion adsorbed on the mineral[45,66]. Similarly, Al^{3+} and Fe^{3+} ions strongly depress quartz in the presence of lauryl amine[45].

In the present work the scope of the methods of modifying the high tension behaviour of quartz and kyanite by treatment with heavy metal salts was explored. A wide range of the important variables was studied in each instance in order to obtain optimum conditions. It appears that an increase in surface conductivity of the minerals can be attributed to the thickness of the hydrate layer and the water adsorbing capacity of the adsorbed matter and/or deposited salts. A decrease in conductivity is ascribed to the formation of insulating oxides by dehydration of the adsorbed metal hydroxides.

8.2 The electrical characteristics of the surface of minerals.

8.2 (a) Introduction.

The interaction of water molecules with different

ions occurring in the surface layer of a mineral varies, so that some ions are transferred into solution in greater amounts than others. The preponderant transfer into solution of ions of one charge causes a disturbance of the electrical equilibrium and the surface becomes electrically charged. Some of the ions transferred into the solution are concentrated in the immediate vicinity of the mineral by the action of the charge on the surface and partially balance this charge. In this way space separation of charges occurs, forming the electrical double layer. The ions constituting the inner layer are strongly anchored to the mineral surface and are presumably dehydrated. The outer layer or diffuse double layer is mobile and of low tenacity.

Klassen[45] and de Bruyn[74] have demonstrated the existence of two forms of adsorption of ions at interfaces, i.e. in the internal and in the external part of the double layer, the two forms of adsorption being interrelated. Klassen further reported that the simultaneous presence of different ions is possible not only at the interface but throughout the electrical double layer.

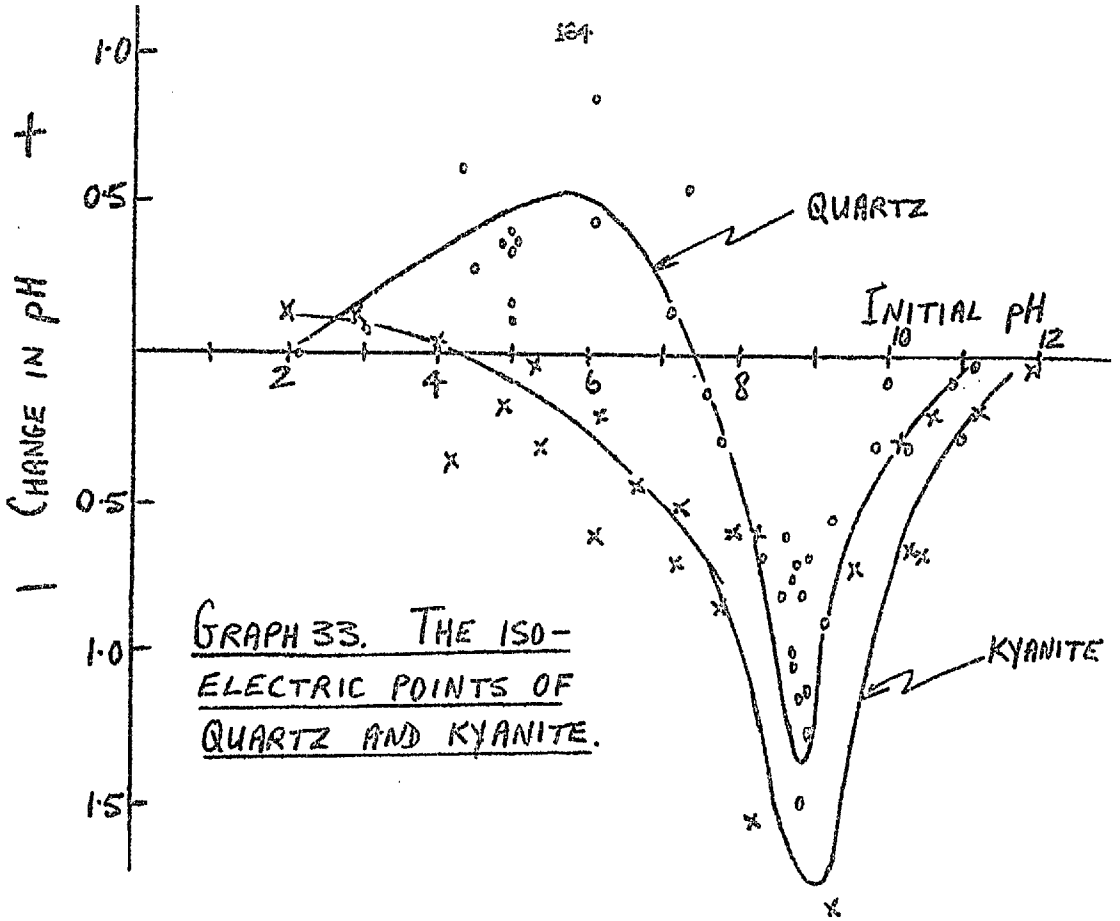
8.2 (b) The charge on a quartz surface.

All investigators are united in finding that quartz has a negative surface when in contact with pure water. It is postulated[75] that the freshly fractured

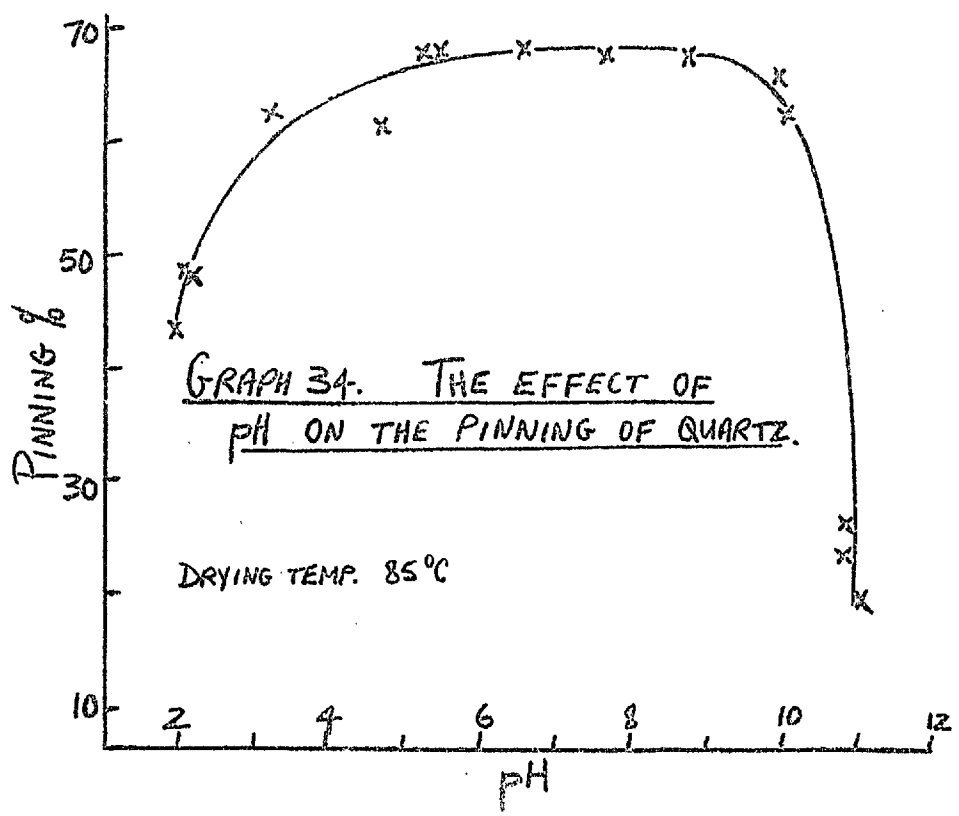
surface of quartz undergoes reaction with water to form a surface silicic acid. Ionisation of this surface silicic acid gives rise to the presence of H^+ at oxygen sites and OH^- at silicon sites[76]. On an average there is a preponderant transfer of H^+ into solution, causing a disturbance of the electrical equilibrium and the surface becomes negatively charged. H^+ and OH^- are the potential determining ions since pH controls the extent of the surface ionisation.

There is considerable confusion as to the iso-electric point or zero point of charge of quartz and silica[29]. For example, Aplan et al[77] and Gaudin[76] have reported that the iso-electric point is between pH2 and 3.7, while other researchers[29] have found it around pH7.

Measurement of the iso-electric point was ***not*** attempted in the present work. However, the observation that the equilibrium pH of solutions containing only added HCl or NaOH, changed after reaction with quartz, leads to the suggestion that the zero point of charge occurs at pH 7-7.5. Similarly, it is postulated that the corresponding value for kyanite is at pH4. After quartz or kyanite have been agitated in a solution, the pH changes to a higher or lower value depending on the initial hydrogen ion concentration. Graph 33 shows the increase or decrease in pH plotted against the initial pH.



GRAPH 33. THE ISO-ELECTRIC POINTS OF QUARTZ AND KYANITE.



GRAPH 34. THE EFFECT OF pH ON THE PINNING OF QUARTZ.

DRYING TEMP. 85°C

At the iso-electric point of quartz there is an equal amount of H^+ and OH^- on the mineral surface. On decreasing the pH by HCl additions, the surface becomes positively charged due to the preponderance of H^+ over OH^-, i.e. H^+ is either adsorbed or OH^- emitted[78]. In either case the pH of the system will increase. In alkaline pH's produced by NaOH additions, the mineral becomes negatively charged due to loss of H^+ from the surface[29] i.e. OH^- is either adsorbed or H^+ emitted, resulting in a decrease in pH. A similar argument was put forward by de Bruyn et al[74] for Fe_2O_3, where ~~above~~ below the iso-electric point (pH 8.5), the surface was positively-charged due to the presence of excess H^+ over OH^- and vice versa at pH's ~~below~~ above 8.5.

Further evidence of the occurrence of the zero point of charge of quartz at neutral pH is provided by the observation in this work (Section 9) that cationic surface active agents increase the hydrophobicity of quartz most effectively above pH 6-7. Similarly, an anionic reagent has maximum efficiency below pH6. For quartz treated in solutions of dodecylammonium chloride and sodium oleate, the pinning vrs pH curves intersect at pH7 (graph 53). It is widely accepted in flotation practice[63,76] that cationic and anionic collectors produce optimum flotation of minerals respectively above and below the zero point of charge of the solids.

8.3 The materials and reagents used in the study.

The quartz and kyanite minerals used in this study have been described in Section 2.2.

The literature has shown that over twenty metal cations have been used in the metal ion activation of silica and silicates. From this list, twelve of the more readily available metal salts were chosen for a preliminary study of the modification of the electrical conductivity of quartz. As a result of this work (not described in this thesis) six of the ions which gave the widest range of results, viz. Pb^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Sn^{2+} and Ca^{2+}, were investigated more thoroughly.

The metal salts were used in the chloride form and were of Analar grade, except the zinc chloride which had a minimum $ZnCl_2$ content of 95%. Dilute solutions of Analar sodium hydroxide and hydrochloric acid ($\frac{M}{40}$ concentrations) were used as pH regulators.

The distilled water was not de-aerated and had a pH ranging from 5.4 to 6.6

8.4 The variables studied.

In deciding the course of the investigation, emphasis was placed on the variables which influence the adsorption of metal ions on quartz. In electrolyte solutions the adsorption of ions is mainly dependent on reagent concentration, temperature and time of contact with the solids.

However, when charged precipitates of metal hydroxides or hydrated metal oxides are formed, they are subjected to electrostatic attraction by the oppositely-charged mineral. In this case pH is an important variable as it determines the magnitude and sign of the charges acquired by the minerals and the precipitates.

The rapid precipitation of a metal hydroxide sol can result in charges quite different in magnitude from those obtained by the slower formation of the same sol[55]. In addition, ageing can influence the surface charge density. If ferric hydroxide sols are left standing for some time, they begin to discharge and hence their interaction with mineral particles will be lowered. A standard procedure was therefore adopted for the precipitation of the metal hydroxides. The addition of sodium hydroxide to the agitated solutions of metal salts was spread over 5 minutes. The agitation was at a constant rate and carried out by means of a magnetic stirrer. The solutions were used within 45 minutes of their preparation.

Another variable examined was the effect of washing the minerals after treatment with the metal salts. Soluble salts deposited on the surfaces of the mineral particles during drying can influence the pinning behaviour.

The temperatures at which the metal salt treatments

were performed were not controlled and averaged about 20.0° ± 2.0°C. The reaction time and the liquid/solid ratio were kept constant at 15 minutes and 3/1 respectively. Investigations were therefore confined to a study of the following variables:

(I) pH of the solutions.

(II) metal ion concentration of the solutions.

(III) washing the solids after chemical treatment.

8.5 Experimental procedure.

Fresh stock solutions of the metal salts were prepared immediately prior to use by dissolving appropriate amounts of salt in 1 litre of distilled water. Aliquots of sufficient quantity to give approximately 1.75×10^{-3}M metal ion concentration in 300 ml. distilled water were measured. The pH of the solutions was adjusted by additions of $\frac{M}{40}$ HCl or NaOH solutions. On attainment of the desired hydrogen ion concentration, 50g. acid-cleaned quartz or kyanite were added to the solution and the pulp was agitated for 15 mins. at a stirrer speed just sufficient to maintain all the particles in suspension. At the end of each treatment the solids were allowed to settle, as much as possible of the solution was decanted and its pH was noted. In this and the following section of the thesis, the pinning value of treated minerals is related

to the pH which is an average of the initial and final hydrogen ion concentrations. The solids were then dried at a temperature not exceeding 115°C. It became subsequently apparent that the drying temperature influenced the surface conductivity of conditioned minerals and the maximum temperature was lowered to 85 °. (The temperature of drying used for each series of tests will be specified on the appropriate graphs illustrating the results). Excessive drying causes a dehydration of the layers attached to the mineral surfaces, resulting in increased pinning values.

When the investigations included washing the conditioned minerals, the following standard procedure was carried out. After decantation of the salt solutions, 300mls. of either distilled water or water adjusted to the pH at which chemical treatment had taken place, were slowly added to the solids. The bed of solids was gently raked with a glass rod to facilitate mixing of the liquid phases. The liquor was decanted and the procedure was repeated once. On an average 6% of the solution was retained by the solids after each decantation. Hence the soluble salt content of the liquor in contact with the mineral particles was reduced to a theoretical 0.0036 of its initial concentration.

After drying for 2½ to 3 hours, the samples were

cooled overnight in a desiccator containing silica gel. The pinning behaviour was then determined under the standard high tension conditions described earlier in Section 4.5.

The method used in this thesis for assessing the pinning behaviour of minerals has led to results of good reproducibility (Sections 4.1 and 7.4). In the experimentation involving the modification of the electrical properties of minerals by chemical treatments (Sections 8 and 9), single tests were performed at each level of the variables studied. Throughout the series, however, random tests were repeated and in every case the deviation of results was small.

8.6 The contamination of the high tension separator by chemically-treated minerals.

It was considered that there was a risk of material loosely attached to the surfaces of chemically-treated minerals contaminating the high tension separator, thereby affecting the pinning behaviours of minerals tested subsequently. An investigation was undertaken to examine this possibility.

A 200g. weight of -52 +100 mesh quartz was conditioned with a solution containing 5.83×10^{-3}M sodium chloride concentration at pH 9.0. After drying, the material was divided by riffling into four representative

samples of 50g. each. In addition, four aliquots of 50g. of clean, untreated quartz were prepared. Alternating samples of the treated and untreated quartz were passed through the separator under standard high tension conditions and the pinning behaviours determined. (Table 15).

TABLE 15.

Test No.	Material	% Pinning
1	NaCl - treated quartz	14.3
3		13.3
5		13.0
7		12.9
2	Clean quartz	69.2
4		67.7
6		67.7
8		68.4

The reproducible pinning values for both materials indicate that contamination of the high tension separator by chemically-treated samples is unlikely.

8.7 Results and discussion.

8.7.1 The effect of Na^+, H^+, Cl^- and OH^- ions on the surface conductivity of quartz.

The modification of the electrical conductivity of quartz after treatment with the ions common to all the

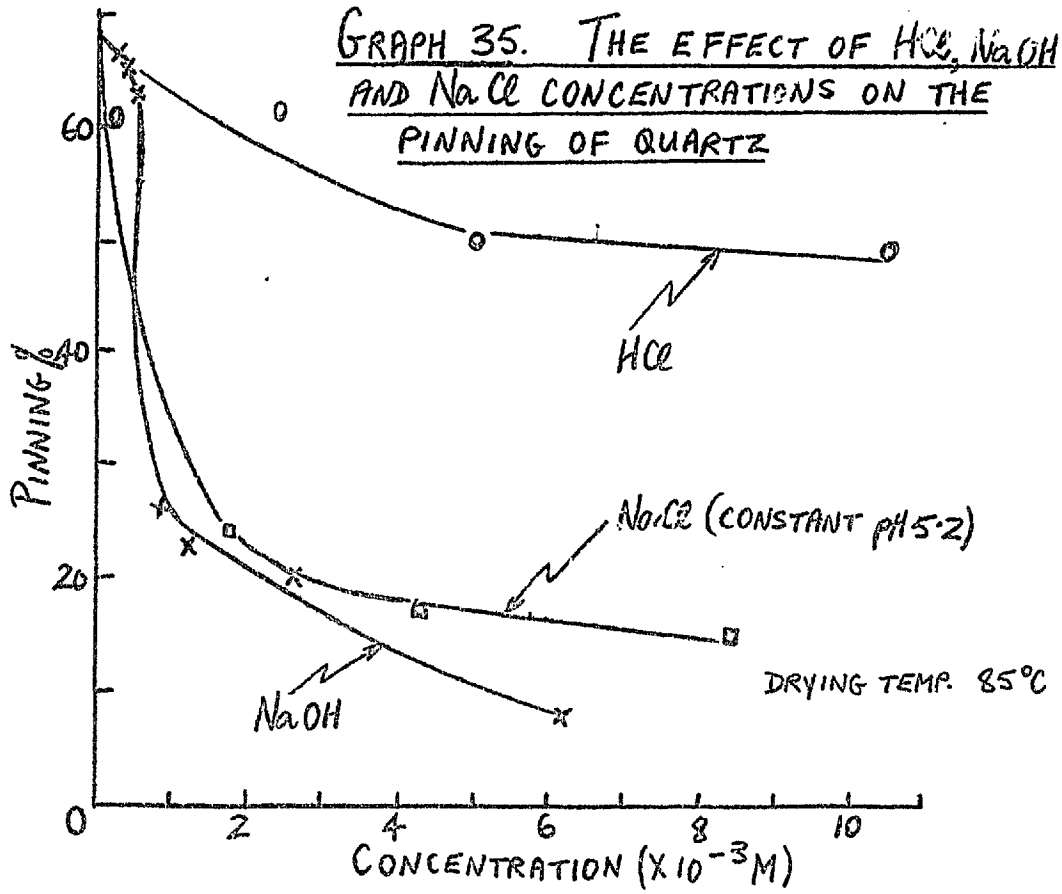
solutions used in this work was investigated. This preliminary step was undertaken to obtain some measure of the relative effects of these ions and the metal ions studied. The ions are Na^+, H^+, Cl^- and OH^- derived from

(1) ionisation of the metal salts, and

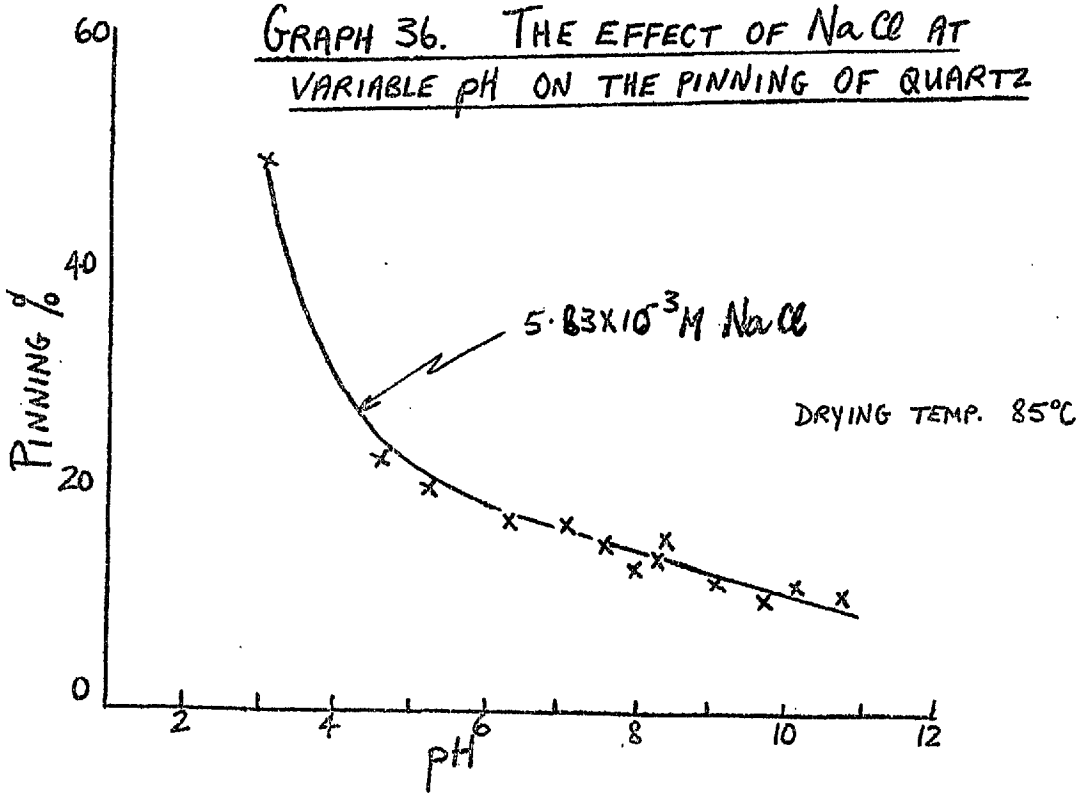
(2) the HCl and NaOH used as pH regulators.

The pinning behaviour of quartz, after reaction with solutions of varying hydrogen ion concentration, remains relatively unaltered through a wide range of pH, namely 4 to 10 (graph 34). On departure from this range the pinning decreases, more markedly so in the alkaline region. When the abscissa of graph 34 is changed to NaOH or HCl molar concentrations, the resultant curves (graph 35) show that the acid has only a slight influence on the surface conductivity of quartz. On the other hand, NaOH strongly affects the pinning behaviour of the mineral. Na^+ is adsorbed on the surface of quartz[80-85] and the thick hydration sheath associated with the adsorbed ion can increase the conductivity of the mineral. At low concentrations there is not much difference between the relative effects of NaOH and NaCl (at pH 5.4). At higher concentrations NaOH has a stronger tendency to decrease the pinning of quartz and this is attributed to the larger water adsorbing capacity of deposited NaOH.

Klassen[45] has demonstrated that the degree of



GRAPH 35. THE EFFECT OF HCl, NaOH AND NaCl CONCENTRATIONS ON THE PINNING OF QUARTZ



GRAPH 36. THE EFFECT OF NaCl AT VARIABLE pH ON THE PINNING OF QUARTZ

hydration of a mineral is related to the magnitude of its surface charge. Furthermore, he indicated that H^+ and OH^- ions adsorb on the surface of quartz under favourable conditions and change the stability of the hydrated layer. The adsorption of potential-determining ions can have a pronounced effect on the hydrophobicity of the surfaces of minerals. The increased surface charge density (positive or negative) on quartz, at pH's far removed from the zero point of charge, is associated with a high degree of surface hydration, accounting for the decreased pinning values. Similarly, Gaudin and Fuersteneau[84] measured the zeta-potential of quartz as a function of various electrolyte concentrations. At a reagent concentration of 10^{-3} equivalents per litre, the resulting zeta-potential values were approximately -110, -75 and +30 mV in solutions of NaOH, NaCl and HCl respectively. The corresponding pinning values of quartz, treated under similar conditions, are 24, 30 and 62%, thereby confirming the suggestion that the increased hydration of the surface of a mineral leads to improved conducting properties.

In addition, O'Connor et al[75] and others[60] measured the surface charge density of quartz in various electrolytes. The addition of either acid or alkali to the solution resulted in an increase in the density of the positive charge in the diffuse layer. Alkaliis appeared to have a greater effect in increasing this charge. Th

observations could account for the greater increase in the surface conductivity of quartz after treatment with NaOH (graph 35).

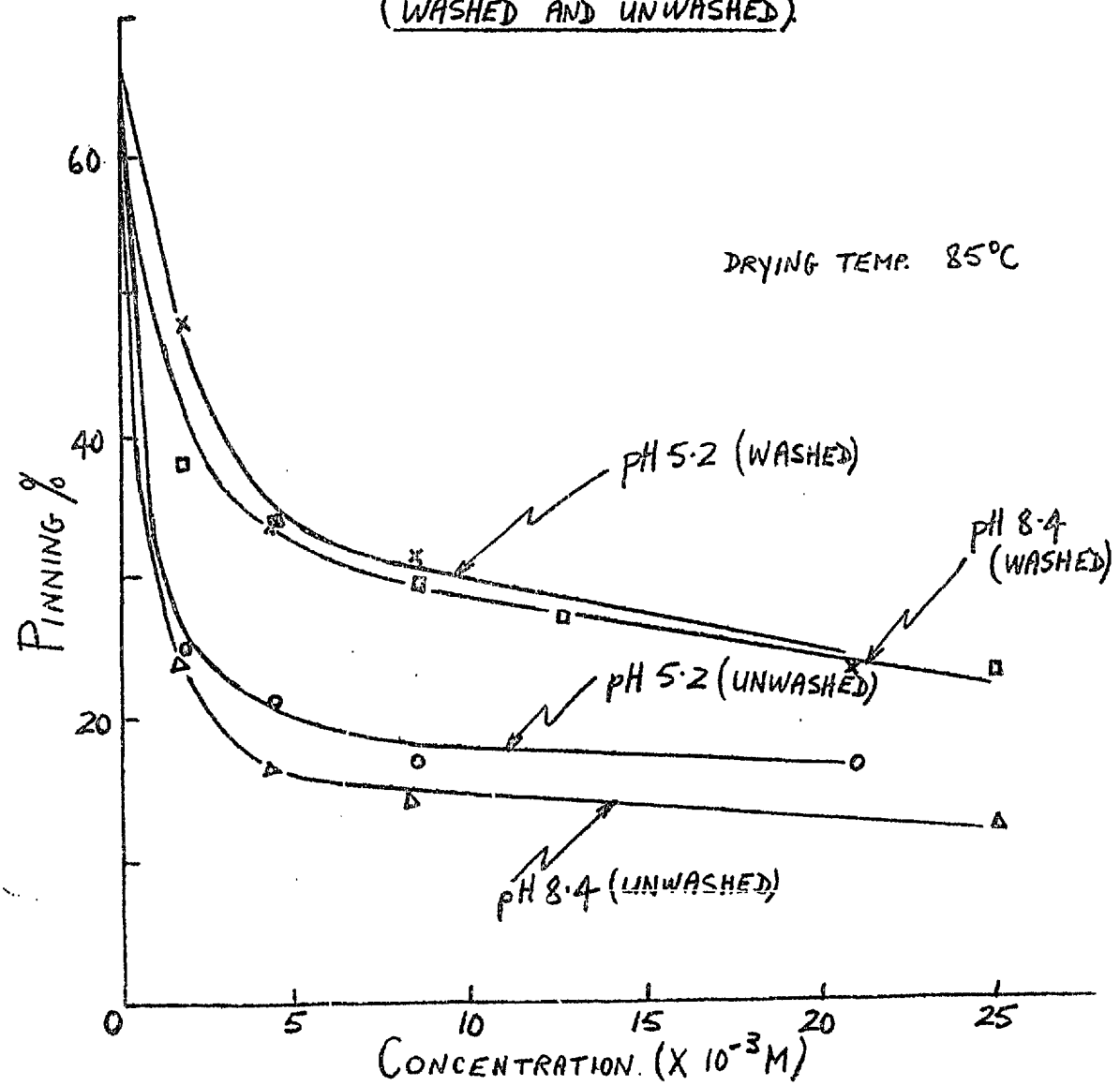
8.7.2 The effect of NaCl treatment on the surface conductivity of quartz.

The influence of NaCl at variable concentration and pH on the pinning of quartz is shown in graphs 36 and 37. With rising pH and increasing salt concentration, pinning decreases sharply at first and thereafter relatively slowly. The adsorption of Na^+ on quartz depends on the pH of the solution and the concentration of NaCl. The initial rapid decrease in pinning therefore represents an increase in surface conductivity due to the high rate of adsorption of hydrated Na^+ ions. As the completion of a monolayer is approached, the adsorption of Na^+ is at a slower rate and pinning decreases accordingly.

In the present work, a similar situation was envisaged for the adsorption of water on quartz (Section 7.4). Gregg[44] demonstrated that in dilute solutions of two components, i.e. A dissolved in B, the isotherm of concentration change in the presence of solids resembles graphs 36 and 37. He maintained that an approach of this kind is often taken to denote the formation of a completed monolayer of component A on the surface of the solid.

The continued decrease in pinning at high

GRAPH 37. THE EFFECT OF NaCl CONCENTRATION AT CONSTANT pH ON THE PINNING OF QUARTZ (WASHED AND UNWASHED).



concentrations and pH's can also be ascribed to the deposition of NaCl salt on drying the solids. The deposited salt increases the water adsorbing capacity of quartz (Section 8.11).

Washing the quartz after treatment with NaCl at the two pH's studied, weakened the original improvement in the conducting properties of the mineral (graph 37). It is reported[55,79] that strong electrolytes are adsorbed on solids, generally in equal amounts with respect to anion and cation. The adhesion of the ions is much stronger than in the case of simple apolar adsorption of molecules. It is frequently impossible to reverse the process by treating the adsorbent with the pure solvent. It appears that washing serves the sole purpose of reducing the salt content of the residual liquor, thereby minimising its deposition on the solids.

8.7.3 The effect of $FeCl_3$ treatment on the surface conductivity of quartz and kyanite.

(a) Quartz

(i) The effect of pH

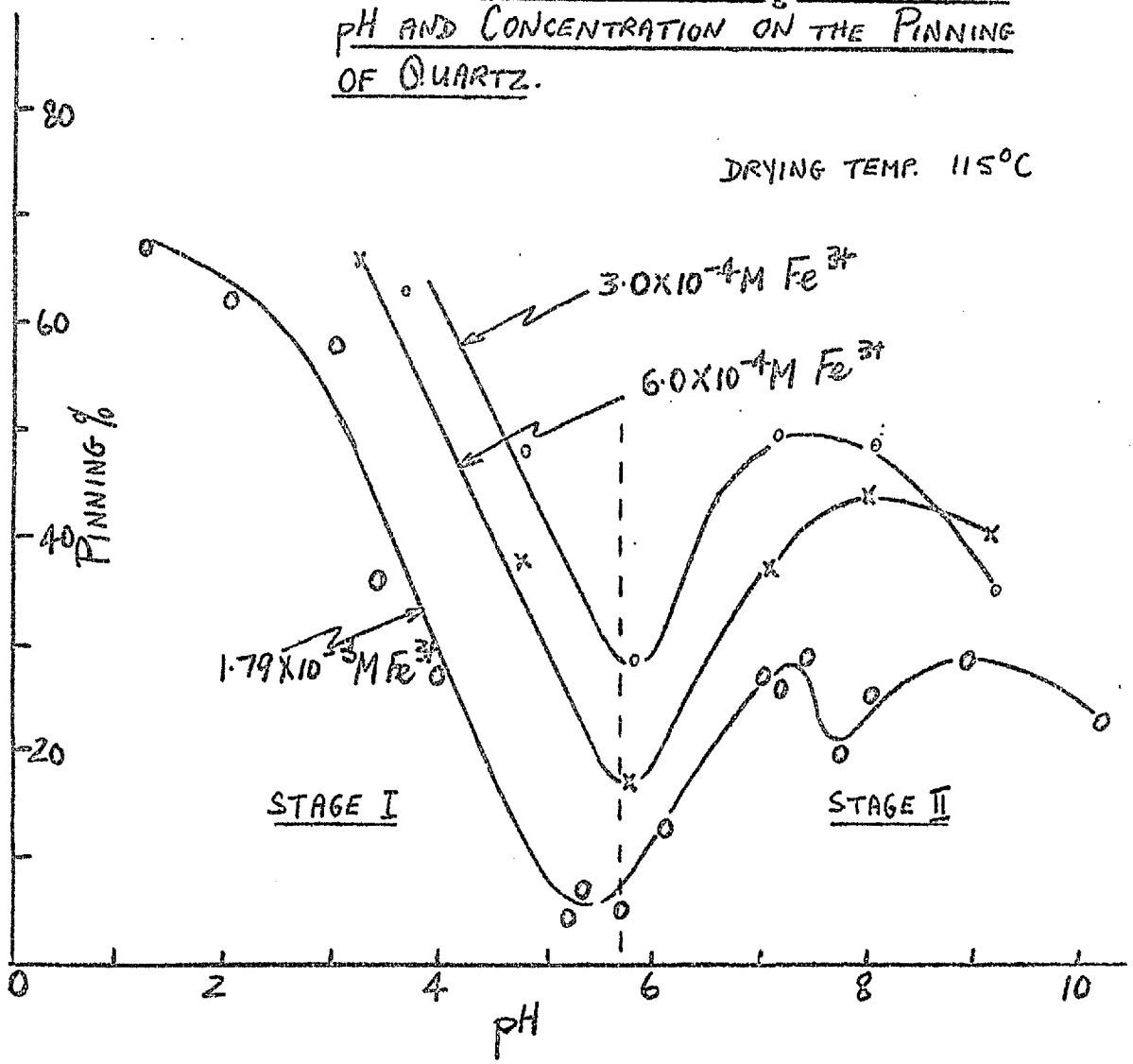
The treatment of quartz in $FeCl_3$ solutions brings about the most marked change in the pinning behaviour of the mineral, reducing it from 68% to 5% under optimum conditions. At a constant Fe^{3+} concentration, the effect of pH on the electrical conductivity of quartz can be

divided into two stages (graph 38).

Stage (i). The addition of NaOH to an acidic $FeCl_3$ solution results in (i) an increased concentration of NaCl in solution, the Cl^- ions resulting from the dissociation of the $FeCl_3$ (ii) precipitation of the hydroxides or hydrated oxides of iron. Feitknecht[57] reported that upon rapid precipitation, amorphous ferric hydroxide is first formed which becomes incompletely crystalline depending on the experimental conditions. The products formed are chiefly $\alpha FeOOH$ and under certain conditions, αFe_2O_3. The ferric hydroxide exists as a micellar colloid and is positively-charged.[55,56] The particles in the ferric hydroxide sol contain in addition to ferric oxide and water, the oxy-chlorides, e.g. FeOCl, which dissociates into FeO^+ and Cl^-.[55] The chloride ions remain in the diffuse double layer, thereby making the colloid particles positive. The adsorption of ions can also cause charging of the precipitates.

The sharp decrease in pinning over stage (i) is ascribed to the combined effects of NaCl adsorption (probably in toto) and the attachment to the mineral surface of one or more of the various hydroxo-complexes of iron present in solution. The following complexes have been identified:[57] $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe_2(OH)_2^{4+}$ and $Fe(OH)_4^-$. Iler[29] reported that Fe^{3+} can fit into the surface of silica in tetrahedral coordination. At hydroxyl ion concentrations approaching the iso-electric

GRAPH 38. THE EFFECT OF $FeCl_2$ AT VARIABLE pH AND CONCENTRATION ON THE PINNING OF QUARTZ.



point of quartz, positively-charged ferric hydroxide sols adhere to the surface of the quartz. The attachment of colloidal particles to solid surfaces has been demonstrated experimentally.[55] Vail[58] pointed out that the interaction between metal hydroxides and silica gives rise to hydrous compounds of varying composition and water content.

The high surface conductivity of the quartz particles in the pH region 5.0 to 5.5 results from the thick hydrous layer associated with, and the water adsorbing capacity of, the adsorbed ferric hydroxide (Section 8.11). Dehydration of the hydrous layer by excessive heating or prolonged exposure to relatively low air humidities, tended to restore the conductivity of the mineral to its original pinning value (Section 8.9).

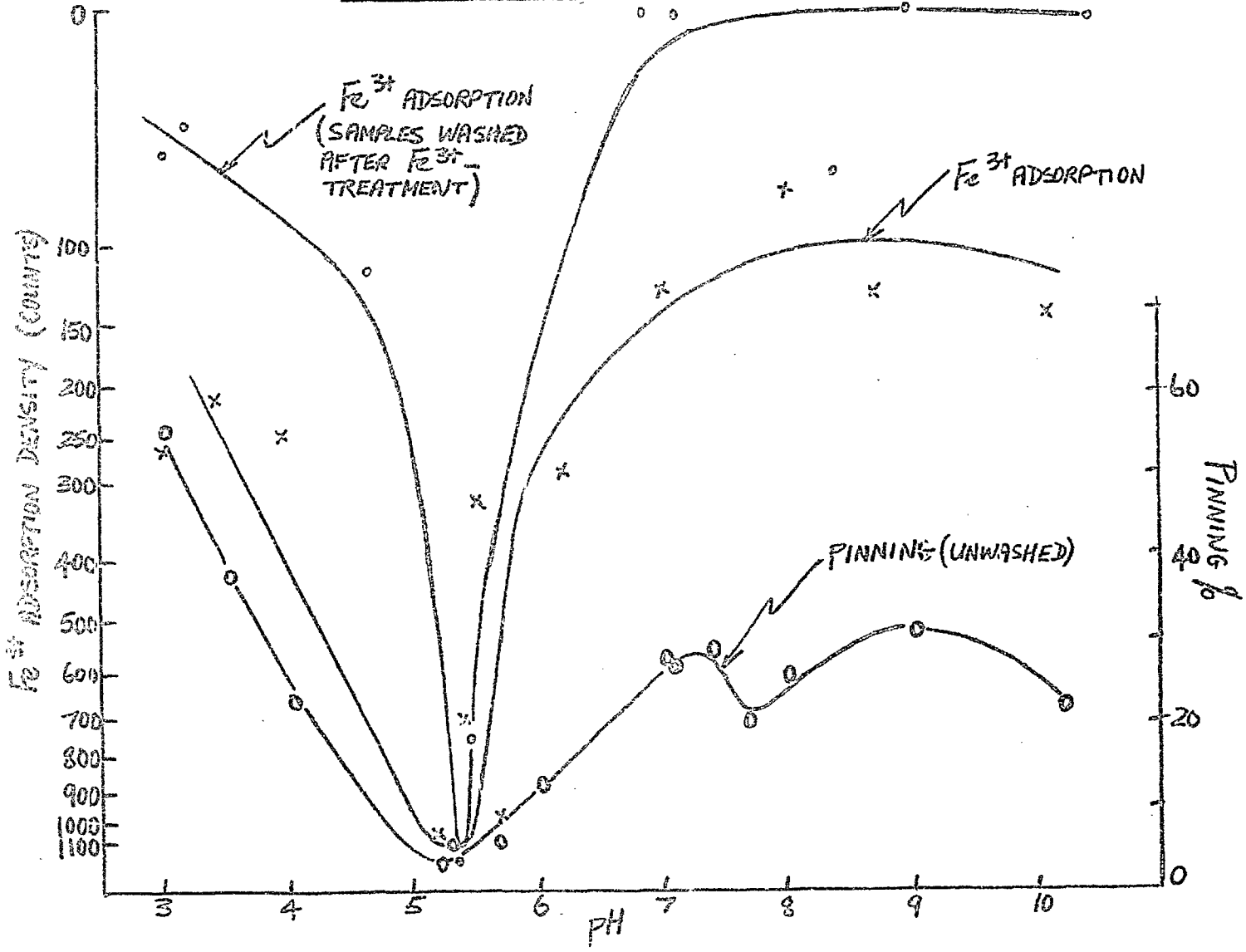
Stage (ii). The stability of metal hydroxide sols is dependent on the solution pH and the presence of electrolytes.[55] At high NaCl concentrations and pH's exceeding that at which precipitation occurs, the sols discharge rapidly. In stage (ii) the stability of the ferric hydroxide precipitates decreases considerably as deduced from the observation that flocculation occurred above pH 6. The pinning of quartz therefore increases due to the diminishing electrostatic affinity of the precipitates for the surface of the mineral. The rise in pinning is checked above pH 7, where NaCl adsorption is sufficiently high to restore an increase in the surface conductivity. Above this pH pure NaCl

solution lowers the pinning behaviour of quartz in a comparable fashion (graph 36). It is not known why a distinct depression occurs in the curve of highest Fe^{3+} concentration at about pH 7.7. A factor which may be connected with the problem is that at this pH, Na^{+} and Cl^{-} ions are present in stoichiometric amounts. Similar phenomena were observed in the treatment of quartz with solutions containing Sn^{2+}, Cr^{3+} and Zn^{2+} ions.

(ii) The measurement of Fe^{3+} adsorption density.

In this work, it was qualitatively observed that optimum Fe^{3+} adsorption on quartz occurs at pH's at which the ferric hydroxide sols display considerable stability. The maximum metal ion take-up is attained at the pH a little less than that at which flocculation of the sols is incipient. When the pH of maximum stability of ferric hydroxide is lowered to about pH 4.4 by additions of organic surfactant, the pH of maximum Fe^{3+} adsorption is shifted accordingly (Section 9.7). The quantity of Fe^{3+} adsorbed by the quartz particles was measured by X-ray fluorescence spectroscopy and the results are plotted on graphs 39 and 40. The quantity of metal ion adsorbed can be qualitatively correlated with the decreased pinning of treated-quartz up to about pH 6.0 (graph 39). Thereafter, the adsorption diminishes at a much sharper rate than the corresponding increase in pinning, testifying to the effect of NaCl at

GRAPH 39. THE RELATIONSHIP BETWEEN THE DENSITY OF ADSORBED Fe^{3+} AND THE PINNING OF QUARTZ.



pH's exceeding 6 or 7. Above pH 8, the adsorption of Fe^{3+} reaches a limiting value and appears to increase once more. Kruyt[56] has pointed out that ferric hydroxide sols peptised with HCl, are flocculated on addition of an amount of NaOH equivalent to the HCl present. A more than equivalent addition of the flocculating electrolyte leads to a second region of stability, where the charge on the sol proves to be inverted in sign. At still higher electrolyte concentrations, the second region of stability is closed by a new flocculation value. The second region of stability of the ferric hydroxide sols above pH 8 is likely to increase Fe^{3+} adsorption on the surface of the quartz. Double flocculation was particularly noticeable in the study of the organic reagent treatment of quartz using a combination of Fe^{3+} and oleate ions (Section 9.7).

(iii) <u>The effect of washing the Fe^{3+}-conditioned quartz samples</u>.

Washing the quartz samples after treatment with 1.79×10^{-3} M Fe^{3+} concentration through the pH region 3 to 10.8, results in a decrease in the improved surface conductivities originally produced. Distilled water or water adjusted to the relevant pH at which conditioning had taken place, give the same result. It is inferred that the rise in pinning produced by washing can be ascribed to a decrease in the salt content of the residual liquor and desorption of some ions loosely held on the surface of the

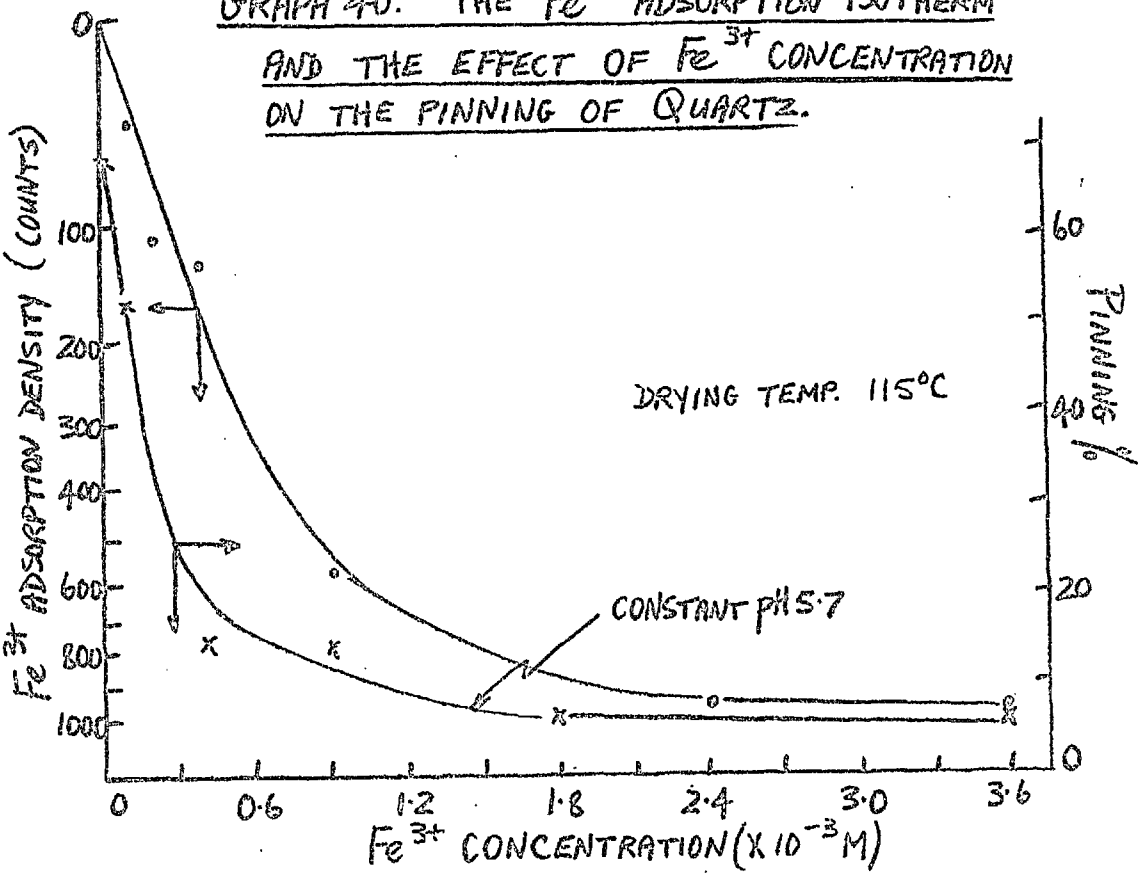
quartz. Adsorption densities were measured on the washed samples (graph 39). A comparison with the adsorption isotherm of unwashed quartz on the same graph show that in the pH region of about 5 to 6, the Fe^{3+} content is unaltered by washing. However, on departure from this region, the Fe^{3+} counts approach zero, due to the low degree of tenacity or solubility of the adsorbed matter.

(iv) The effect of Fe^{3+} concentration.

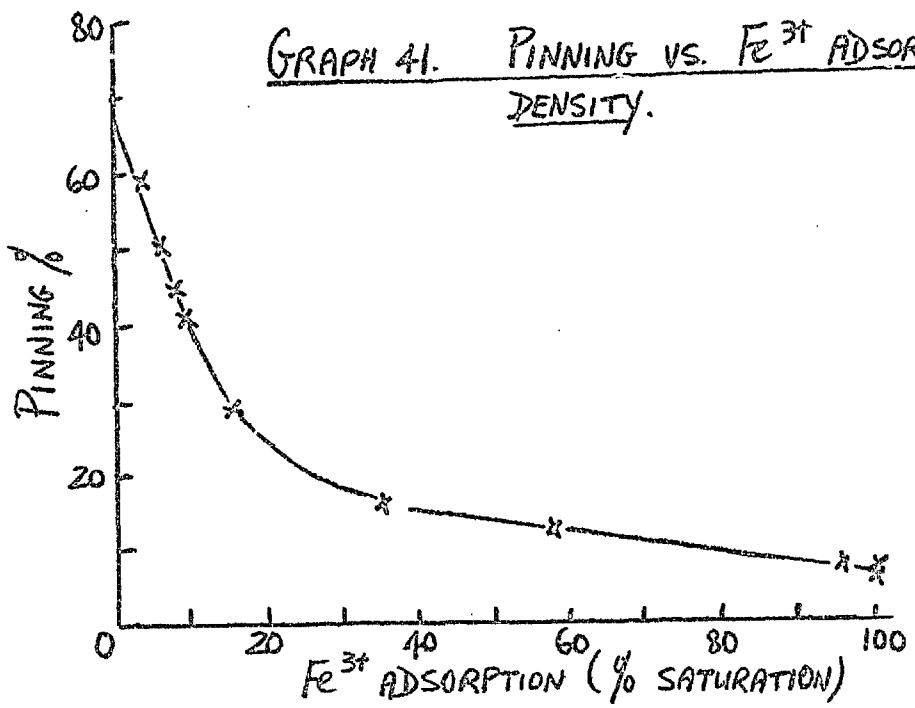
The effect of Fe^{3+} concentration on the electrical conductivity of quartz was investigated (graphs 38 and 40). Graph 38 shows a family of curves at Fe^{3+} concentrations of 1.79×10^{-3} M and less, with pH variable. The solutions of highest concentration have the most profound influence on the pinning of quartz. The depression at pH 7.7, reffered to above (page 181) is not evident at the lower concentrations due to the scarcity of points.

At a constant pH 5.7, pinning decreases sharply with rise in Fe^{3+} concentration, reaching a minimum value which persists up to 3.6×10^{-3} M concentration (graph 40). An investigation at 7.16×10^{-3} M revealed a tendency for the pinning to increase. The corresponding Fe^{3+} adsorption densities are plotted on graph 40 and illustrate that the pinning behaviour of quartz, after treatment with $FeCl_3$ solutions, is directly related to the quantity of adsorbed Fe^{3+}. The relationship between pinning and Fe^{3+} adsorption

GRAPH 40. THE Fe^{3+} ADSORPTION ISOTHERM AND THE EFFECT OF Fe^{3+} CONCENTRATION ON THE PINNING OF QUARTZ.



GRAPH 41. PINNING VS. Fe^{3+} ADSORPTION DENSITY.



(expressed as a percentage of the saturation value) was determined (graph 41). At low surface coverages, pinning decreases at a sharp rate. As the saturation figure is approached, pinning falls more slowly. This phenomenon can best be explained by reference to the model of film thickness increase with rising adsorbate concentration, as suggested by Bogdanov[66] and Klassen[45].

During the chemical interaction between reagents and minerals, the reagent ions have first to diffuse to the solid surface through the relatively immobile liquid layer. Approaching the mineral surface these ions are adsorbed, forming either a monolayer or a multilayer of interaction products on the surface. On approaching completion of the monolayer the interaction products interfere with further penetration of reagent ions and therefore the adsorption rate will depend on the rate of diffusion through the product layer.

The kinetics of film formation is as follows: In the initial stage when the surface is readily accessible to the solution, the rate of the process will be determined by the rate of the reaction forming the film. When the surface is partially covered by a film, the rate of further growth is determined by the rate of diffusion of the solution through the film pores.

The velocity of film formation can be expressed by

$$\frac{dx}{dt} = KC_2 \qquad (27)$$

where x = thickness of the film, t = time and K = rate constant of film formation, C_2 = concentration of the solution at the internal portion of the film.

When the rate is determined by the rate of diffusion,

$$\frac{dx}{dt} = D\,\frac{C_1 - C_2}{x} \qquad (28)$$

where D = diffusion coefficient, C_1 = concentration of active reagent on the external surface of the film.

The first of the two functions is represented by a straight line, the second by a parabola i.e. a curve representing the relation between the thickness of the film and time of its formation should be comprised of two portions, as shown in figure 12.

The shape of the curves in figure 12 and graph 41 are closely similar and suggests that the pinning behaviour of quartz after treatment with $FeCl_3$ solutions at pH 5.7, is directly related to the thickness of the hydrated layer formed on the surface of the mineral.

It is likely that at Fe^{3+} adsorption densities in excess of that corresponding to about 20% saturation, multi-layers of Fe^{3+} are present on the surface of the quartz. Above this figure, the dry mineral particles display a faint yellow colour which increases in intensity with

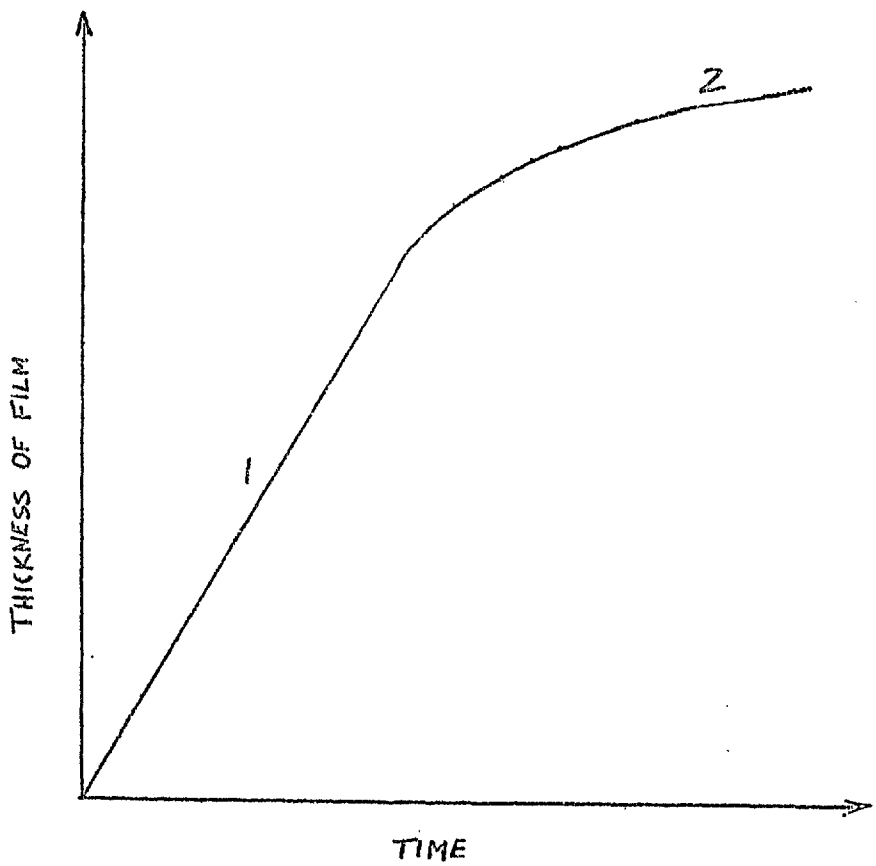


FIG. 12 THE KINETICS OF FILM FORMATION

increasing saturation.

(b) Kyanite

The conditioning of kyanite in solutions of 1.79 x 10^{-3} M Fe^{3+} content, results in a relationship between pinning and pH similar to that found for quartz, but at a higher level of pinning (graph 42). It appears that the affinity of Fe^{3+} for kyanite is less than that of the metal ion for quartz (Section 8.12).

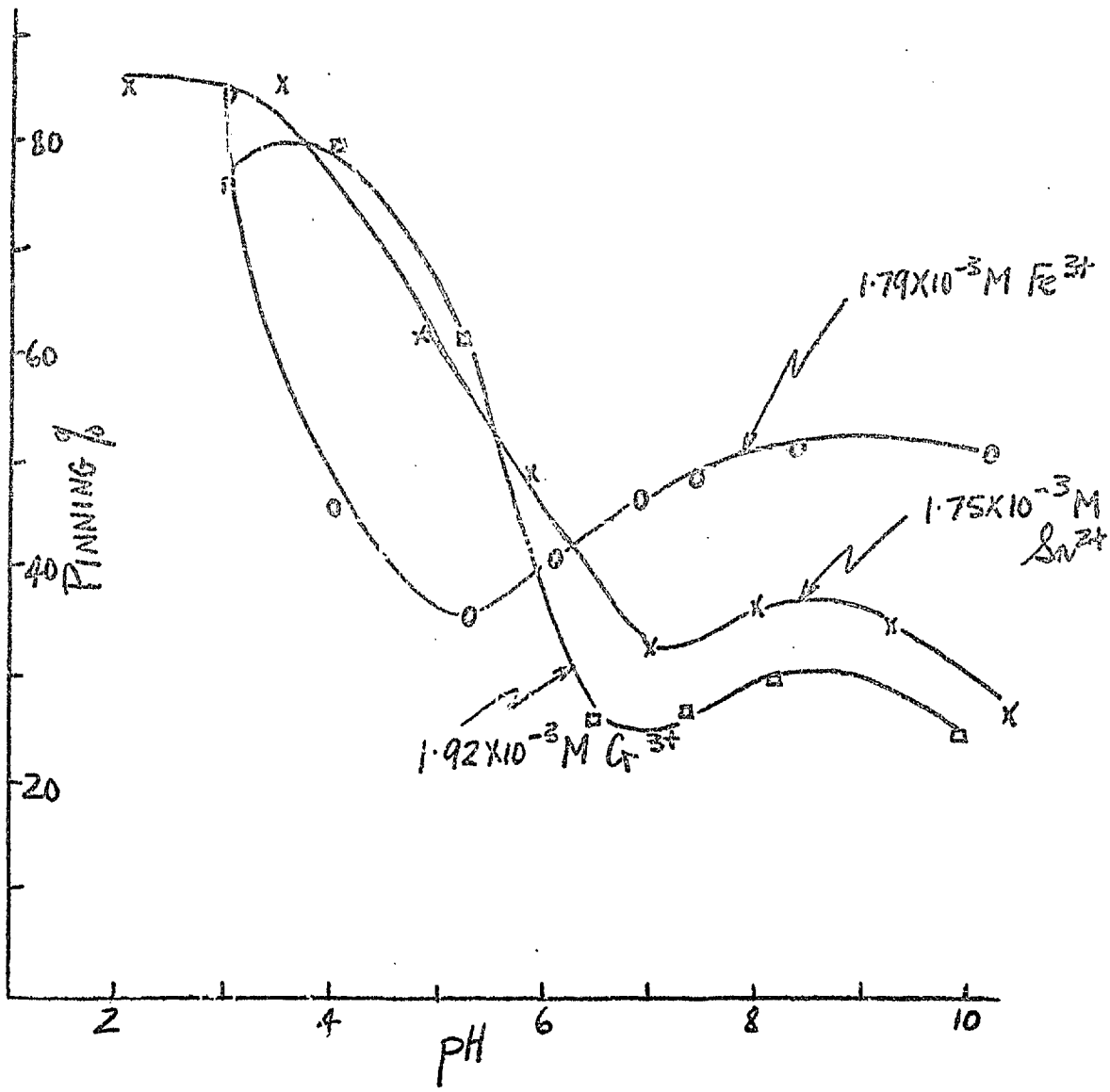
8.7.4 The effect of $SnCl_2$ treatment on the surface conductivity of quartz and kyanite.

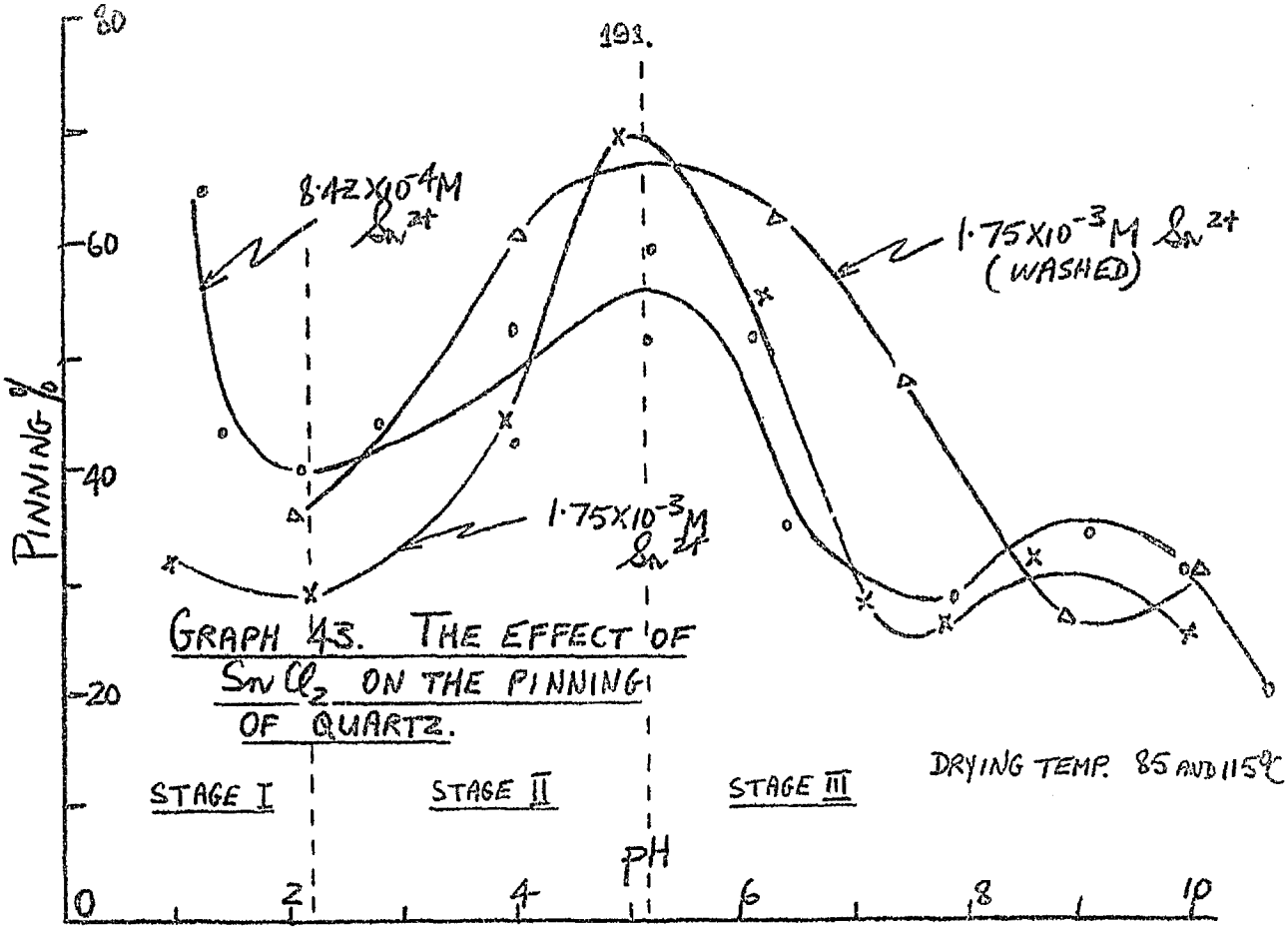
(a) Quartz.

(i) The effect of pH.

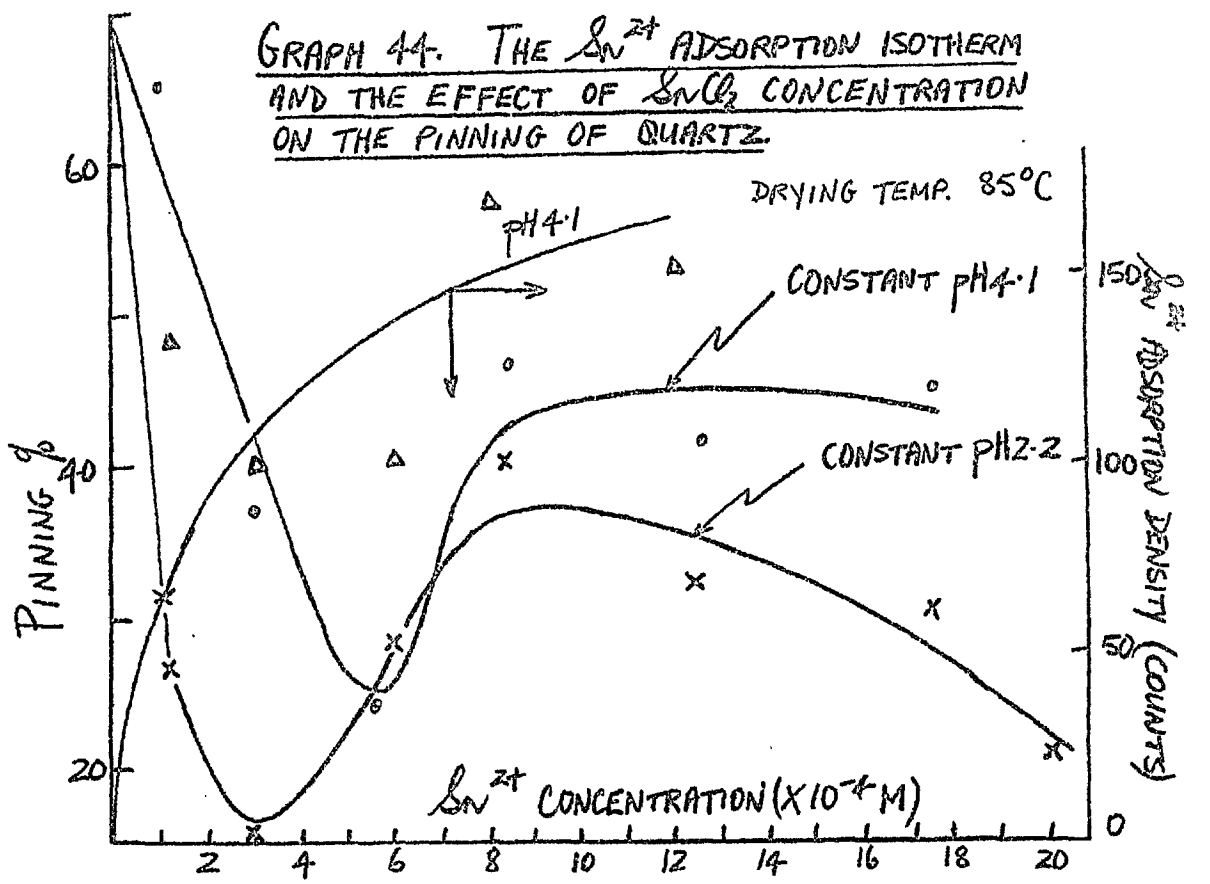
The curves of pinning vrs pH for quartz conditioned in $SnCl_2$ solutions at two concentrations, each display two maxima and two minima (graph 43), similar to those shown by the Fe^{3+}-treated mineral. The similarity is limited since the two Sn^{2+} curves overlap, the higher concentration curve having a larger pinning value in the pH region 5 - 5.5. Measurements of Sn^{2+} adsorption (table 16) indicate that maximum adsorption occurs in the same pH range. Feitknecht[57] pointed out that the precipitation of Sn^{2+} salt solutions yield initially $Sn_3O_2(OH)_2$, which invariably has a low Sn^{4+} content. The oxide-hydroxide is unstable and is easily converted into stable SnO. It is therefore envisaged that the increase in the pinning behaviour of quartz after

GRAPH 42. METAL ION CONDITIONING OF KYANITE





GRAPH 43. THE EFFECT OF $SnCl_2$ ON THE PINNING OF QUARTZ.



GRAPH 44. THE Sn^{2+} ADSORPTION ISOTHERM AND THE EFFECT OF $SnCl_2$ CONCENTRATION ON THE PINNING OF QUARTZ.

TABLE 16.

Metal Ion	Conc. $X10^{-3}M$	pH	Mineral Washed or Unwashed	Metal Ion Adsorption Densities (Counts)
Sn^{2+}	0.84	3.9	Unwashed	115
		5.2		200
		6.4		231
		7.9		60
		9.4		77
		10.0		124
		10.8		74
Sn^{2+}	0.84	2.2	Washed	108
		3.3		129
		4.6		96
		5.8		240
		7.0		175
		8.3		21
		10.2		96
Zn^{2+}	1.52	3.2	Unwashed	755
		4.3		792
		5.5		1986
		6.5		2079
		7.5		1756
		8.2		3150
		9.4		1552
		10.3		1213

treatment in $SnCl_2$ in the pH region of maximum Sn^{2+} take-up, is due to the attachment of $Sn_3O_2(OH)_2$ to the surface of the mineral. Subsequent dehydration yields SnO, which increases the hydrophobicity (Section 8.11) and insulating properties of the solids. At the smaller concentration, a lower level of pinning is attributed to a reduction in the adsorption of Sn^{2+} and a greater hydration of the mineral surface (Section 8.8).

Washing the samples conditioned with 1.75×10^{-3}M Sn^{2+} up to pH 5, brings about little change in the original pinning values produced (graph 43). At higher hydroxyl ion concentrations pinning is increased by washing, due to the reduction in the soluble salt content of the residual liquor. There is little change in the density of metal ion adsorption after washing the samples that had been conditioned in 0.84×10^{-3}M $SnCl_2$ solutions of variable pH (Table 16).

The relationship between pinning and pH for quartz particles conditioned in 1.75×10^{-3}M Sn^{2+} concentration, can be divided into 3 regions (graph 43).

Stage (i) The hydroxo-complexes identified in $SnCl_2$ electrolyte are $Sn(OH)_2$, $Sn(OH)^+$, $Sn_2(OH)_2^{2+}$ and $Sn(OH)^-$. The decreased pinning from pH 1.0 to 2.2 is attributed to the adsorption of one or more of these complexes, increasing the hydration of the mineral surface.

Stage (ii). The precipitation of $Sn_3O_2(OH)_2$ is incipient at the start of stage (ii). The sols are positively-charged and, on approaching the iso-electric point of quartz, are electrostatically attracted to the mineral surface. Subsequent dehydration increases the pinning by the mechanism outlined above.

Stage (iii). A further increase in pH diminishes the affinity of $Sn_3O_2(OH)_2$ for the surface of quartz due to the discharge of the sols, as observed by flocculation at about pH 7.5. Thereafter, Na^+ adsorption begins to rehydrate the surface and pinning decreases once again.

The above mechanism of the change in conductivity of quartz resulting from Sn^{2+} treatment, applies equally well at the lower 0.84×10^{-3}M Sn^{2+} concentration. The depressions in the two curves at pH 7.5 correspond to the pH at which Na^+ and Cl^- are present in solution in equivalent amounts.

(ii) The effect of Sn^{2+} concentration.

The pinning behaviour of quartz after treatment in varying concentrations of $SnCl_2$ electrolyte (pH 2.2) was investigated (graph 44). Pinning falls to a minimum with increasing concentration; thereafter, it rises to a maximum value before decreasing again. Klassen[45] and others[59,60] have reported that the surface charge density of quartz generally increases with rising electrolyte

concentration. Thus, the initial decrease in pinning can be accounted for by assuming that the higher surface charge results in an increased hydration of the surface of the mineral. At higher concentrations, the hydration is lowered. The effect of electrolytes on the hydration of solid surfaces is described in greater detail under Section 8.8.

It appears that the action of $SnCl_2$ electrolyte up to a limiting concentration is to affect the hydration, and consequently the surface conductivity of quartz, in a fashion comparable to that envisaged by Klassen. In excess of about 1.2×10^{-3}M Sn^{2+} concentration, the decreased pinning is attributed to the adsorption of NaCl or the deposition of salts on drying the solids. Washing the quartz sample treated in a solution of 1.75×10^{-3}M $SnCl_2$ concentration, increased the pinning value from the original 29% to 37%, indicating the extent of the contributory effects of deposited salts.

The influence of Sn^{2+} concentration at a higher pH 4.1 (precipitation of $Sn_3O_2(OH)_2$ begins at about pH 2.5) was investigated (graph 44). The change in pinning behaviour is similar to that found at lower pH, but the overall effect is of a lesser magnitude because the precipitation of the tin-oxide hydroxide results in the attachment of the colloids to the solid surface, thereby

increasing its insulating properties. The quantity of Sn^{2+} adsorbed on quartz under these conditions was measured and is shown to increase with concentration (graph 44).

(b) Kyanite.

The influence of $SnCl_2$ solutions (1.75×10^{-3}M Sn^{2+} concentration and variable pH) on the pinning behaviour of kyanite was studied (graph 42). Comparison of the respective effects of Sn^{2+} treatment on the conducting properties of kyanite and quartz (graphs 42 and 43) open the possibility of using $SnCl_2$ to obtain a high tension separation of the two minerals. Sn^{2+} treatment is selective in the pH 2 region in that it reduces the pinning of quartz to about 25% and has little effect on the natural 95% pinning value of kyanite. At pH 6 and higher, selectivity disappears as the two minerals respond similarly to the treatment. It is suggested that the lack of response of kyanite to the $SnCl_2$ treatment at low pH can be attributed to the small affinity of Sn^{2+} for the surface of the mineral. Sn^{2+} adsorption densities were not measured on the treated kyanite.

8.7.5. The effect of $ZnCl_2$ treatment on the surface conductivity of quartz.

Vail[58] reported that $ZnCl_2$ reacts with silicates to form hydrous zinc oxides at pH's close to

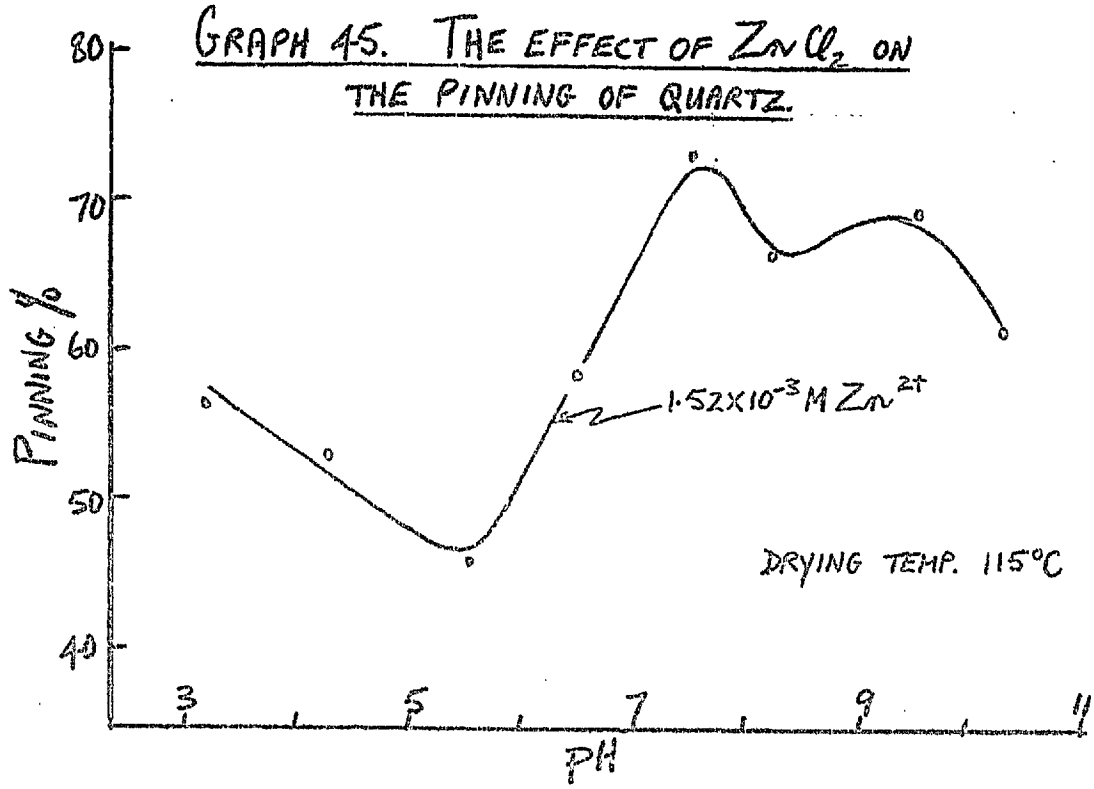
that at which zinc hydroxide precipitates. In addition, reference[45] has been made to the fact that zinc hydroxide has a particular affinity for quartz. In the flotation of sphalerite where colloidal $Zn(OH)_2$ is present, the recovery of the sulphide was considerably increased on the removal of the $Zn(OH)_2$ by the addition of quartz, on to which the sol was selectively attached.

The conditioning of quartz with 1.52×10^{-3}M $ZnCl_2$ solution does not produce as wide a range of pinning values as that obtained with solutions of the other metal salts. The pinning is reduced to 46% at about pH 5.4 and increased to 73% at pH 7.5 (graph 45). The pinning vrs. pH relationship is similar to that described above for Fe^{3+} and Sn^{2+} treatments.

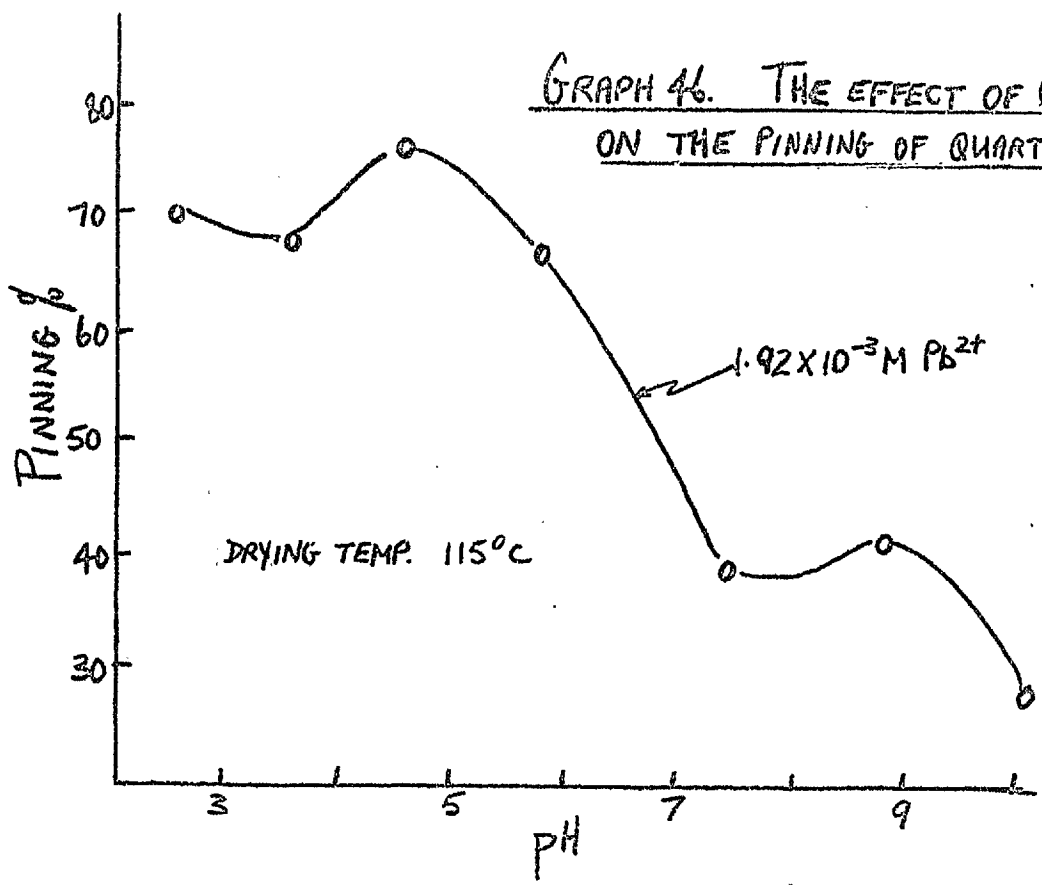
Maximum Zn^{2+} adsorption was found in the pH region of 7.5 - 8.5 (table 16). $ZnCl_2$ conditioning of quartz resembles treatment with $SnCl_2$ in that the pinning of quartz is raised above its normal 68% value in the pH region of maximum metal ion adsorption. In this work, investigations have shown closely similar effects with Pb^{2+}, while Cr^{3+} and Ca^{2+} can be classed with Fe^{3+}.

On precipitation of $ZnCl_2$ solutions, the following solid phases are produced:[57] Amorphous $Zn(OH)_2$ and various active and inactive forms of $Zn(OH)_2$. As a rule, upon the addition of less than an equivalent amount of

GRAPH 45. THE EFFECT OF $ZnCl_2$ ON THE PINNING OF QUARTZ.



GRAPH 46. THE EFFECT OF $CrCl_3$ ON THE PINNING OF QUARTZ.



alkali to zinc salt solutions, the hydroxide salts, e.g. $Zn(OH)_{1.6}Cl_{0.4}$ are precipitated. In the case of complete precipitation amorphous $Zn(OH)_2$ is formed, which on ageing at room temperature results in the production of ZnO.

It is envisaged that the relatively high pinning of quartz after treatment in the pH region of maximum Zn^{2+} adsorption, is a result of the formation of a non-conducting layer of ZnO. The mechanism whereby the surface conductivity of quartz is modified after reaction with $ZnCl_2$ at variable solution pH, is very similar to that described above for $SnCl_2$. The depression in the curve (graph 45) at pH 8.2 coincides with the pH at which Na^+ and Cl^- are present in solution in stoichiometric amounts.

8.7.6. The effect of $CrCl_3$ treatment on the surface conductivity of quartz and kyanite.

(a) Quartz.

(i) The effect of pH. The treatment of quartz with $CrCl_3$ results in a pinning vrs. pH relationship that displays two maxima and two minima (graph 46). The quantity of Cr^{3+} adsorbed on the surface of the mineral was measured (table 17) and shown to increase sharply from pH 4, reaching a maximum in the pH region of 7 to 7.5, which corresponds to the pH range at which pinning is decreased to a minimum. This suggests that the trivalency

and small ionic radius of the adsorbed Cr^{3+} produces a high degree of hydration of the quartz surface. On further increase in the hydroxyl ion concentration, Cr^{3+} adsorption decreases strongly with a consequent increase in pinning until the Na^{+} begins to interfere, either in the form of NaCl adsorption or NaCl salt deposition on drying the treated-mineral.

At pH 4.5 the insulating properties of quartz are increased above the normal value of the clean mineral. Feitknecht[57] reported that dehydration of the precipitates of $Cr(OH)_3$ yields amorphous Cr_2O_3. The small increase in pinning is therefore attributed to the formation of insulating Cr_2O_3. Over the pH range corresponding to a marked increase in Cr^{3+} adsorption, the intense hydration and large capacity of the surface film to adsorb water (Section 8.11) overcome any tendency of the Cr_2O_3 to increase the pinning.

TABLE 17.

Metal Ion	Conc. $X10^{-3}M$	pH	Mineral Washed or Unwashed	Metal Ion Adsorption Densities (Counts)
Cr^{3+}	1.92	4.5 5.8 7.4 8.8 10.1	Unwashed	0 21 82 30 23
Pb^{2+}	0.48	4.0 5.0 5.6 6.8 7.9 10.3	Unwashed	18 42 135 20 49 92

(ii) The effect of Cr^{3+} concentration.

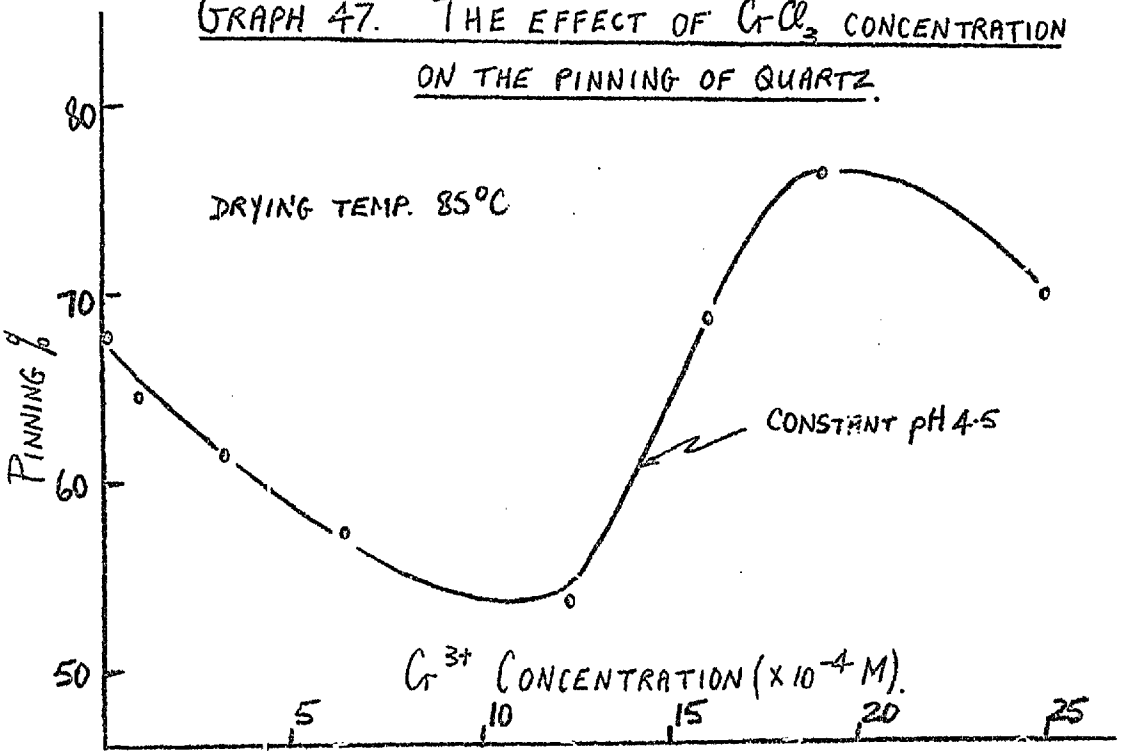
The effect of $CrCl_3$ electrolyte concentration (pH 4.5) on the pinning behaviour of quartz was determined (graph 47). Pinning decreases at low concentrations, reaches a minimum and increases to a maximum before falling once more. The reasoning applied to the similar effects of $SnCl_2$ may also hold for $CrCl_3$ solutions. A maximum pinning value of 77% is attained at 2.0×10^{-3}M $CrCl_3$ concentration.

Reference has been made[45] to the use of electrolyte solutions to float naturally hydrophobic minerals in the absence of collectors. It is not clearly understood why such minerals whose surfaces are weakly hydrated require additional dehydration by inorganic ions. Derjaguin[61] studied the flotation of antimonite in the absence of a collector and was able to postulate a mechanism whereby the wetting film on antimonite can be ruptured by suitable control of zeta-potential.

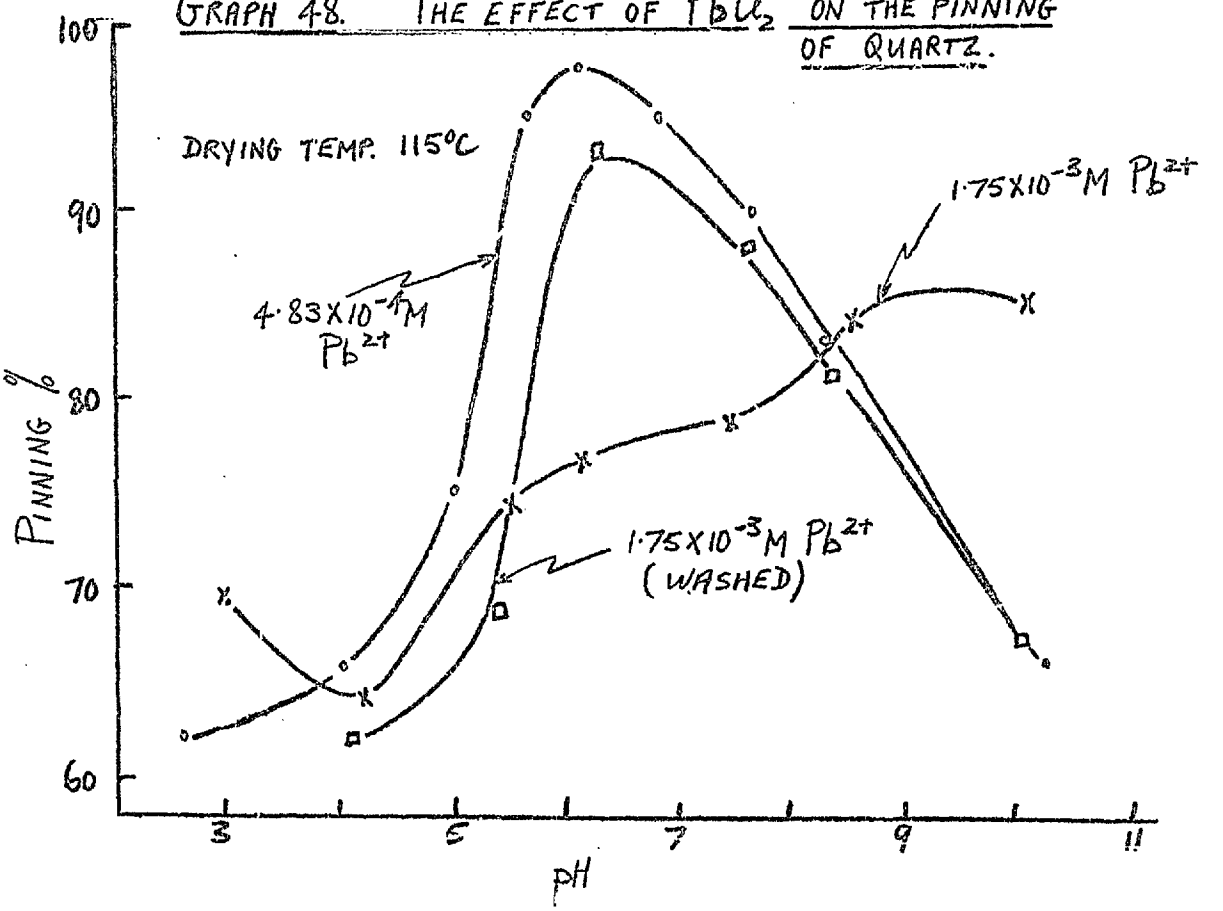
(b) Kyanite.

The reaction of kyanite with 1.92×10^{-3}M $CrCl_3$ solutions at variable pH results in a relationship between pinning and pH (graph 42) similar to that produced on quartz. At an optimum pH of about 6.8, Cr^{3+} appears to affect kyanite to a greater extent, i.e. the pinning of the mineral is reduced from 95% to 25% while the

GRAPH 47. THE EFFECT OF $CrCl_3$ CONCENTRATION ON THE PINNING OF QUARTZ.



GRAPH 48. THE EFFECT OF $PbCl_2$ ON THE PINNING OF QUARTZ.



corresponding figures for quartz are 68% to 37%.

8.7.7. The effect of $PbCl_2$ treatment on the surface conductivity of quartz.

(i) The effect of pH.

The influence of solutions of $PbCl_2$ on the pinning behaviour of quartz was investigated at two concentrations and variable pH (graph 48). At the higher concentration a slight initial decrease in pinning at pH 3 is followed by a slow increase to a maximum value at about pH 9.5-10. The curve of lower concentration displays a maximum at pH 6.0, about which the curve appears to be symmetrical. The mechanism whereby the conductivity of quartz is altered by treatment with $PbCl_2$ is surmised as follows: 4.83×10^{-4}M $PbCl_2$ concentration. At high hydrogen ion concentrations, i.e. pH 2.6 - 4.4, pinning is below the normal value of clean quartz and this is attributed to the action of the acid. In the absence of $PbCl_2$, the pinning value of quartz is reduced to 60% after reaction with a solution of pH 4 (graph 34). On approaching the pH of precipitation of the $PbCl_2$ solution, i.e. pH 5.6, pinning increases sharply reaching a maximum value at pH 6.0.

Upon addition of more than an equivalent amount of alkali to a Pb salt solution, $Pb_2O(OH)_2$ is precipitated[57]. Dehydration yields PbO (red) at elevated temperatures and PbO (yellow) at low temperatures. The measurement of

Pb^{2+} adsorption densities (table 17) demonstrates that Pb^{2+} take-up increases strongly from pH 4, reaching a maximum at about pH 6 where maximum pinning is observed. The rise in pinning can therefore be correlated with the increasing adsorption of Pb^{2+}. The large ionic radius of the Pb^{2+} ions causes the adsorbed species to be weakly hydrated and easily converted to insulating PbO. Iler[29] pointed out that Pb^{2+} adsorbed on glass became oxidised and in so doing, rendered the glass hydrophobic.

On departure from pH 6, the adsorption of Pb^{2+} decreases because the $Pb_2O(OH)_2$ sols discharge with a consequent lowering of the insulating properties of the mineral.

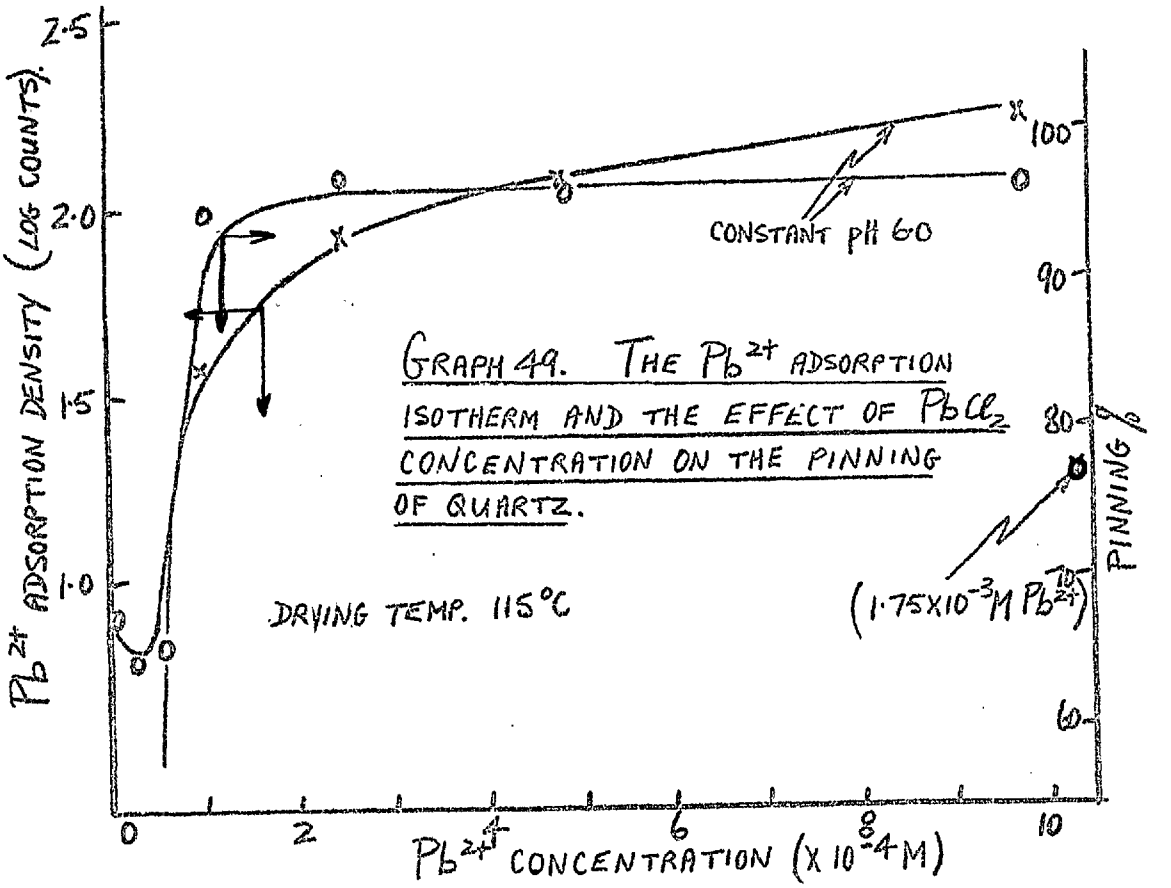
1.75 X 10^{-3}M $PbCl_2$ concentration. At the higher $PbCl_2$ concentration studied, the improvement in the pinning of quartz after the initial slight decrease (pH 3.0 to 4.4) is at a slow rate, approaching a maximum at pH 9.5 - 10. Washing the quartz samples after treatment under these conditions, results in a curve almost identical to that obtained for the unwashed samples at lower concentration (graph 48). It is therefore envisaged that the displacement of the maximum pinning value to higher pH's is due to the competition between Pb^{2+} to render the surface insulating and Na^{+} to render it conducting.

(ii) The effect of Pb^{2+} concentration.

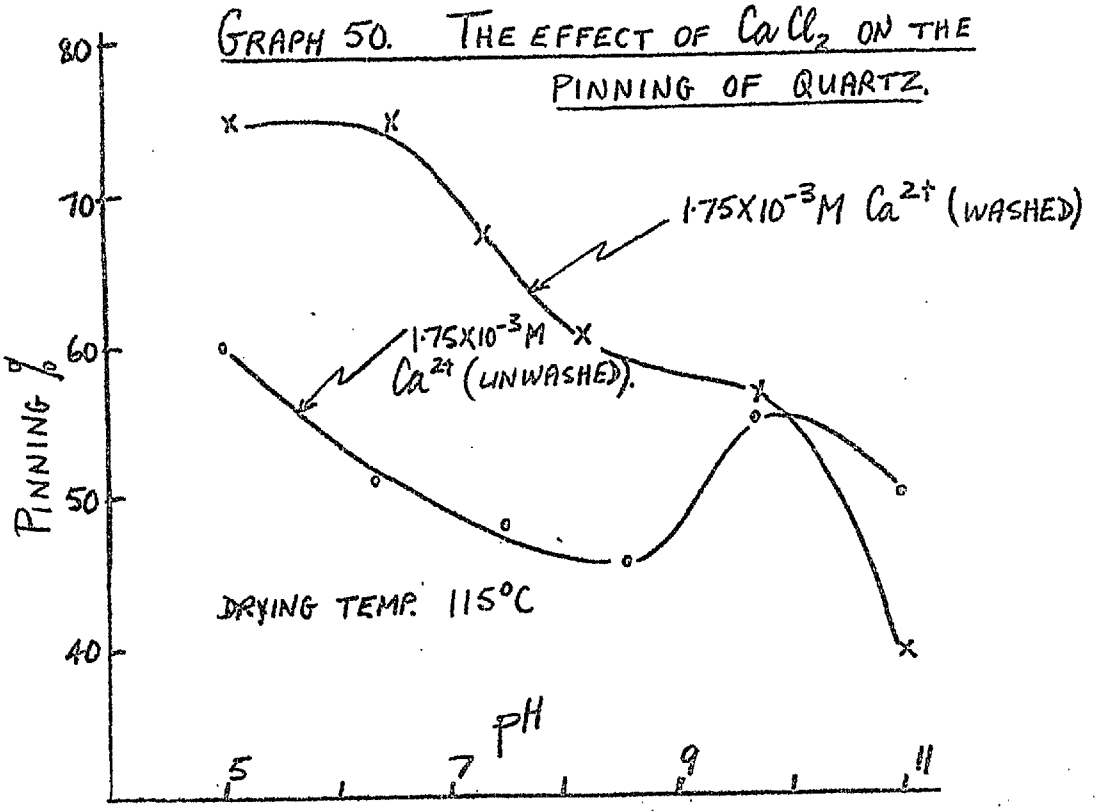
The influence of Pb^{2+} concentration (pH 6.0) on the pinning behaviour of quartz is shown in graph 49, which also includes the Pb^{2+} adsorption isotherm. The slight initial decrease in pinning at low concentration is ascribed to a slight hydration of the mineral surface by a mechanism similar to that caused by small concentrations of Cr^{3+} and Sn^{2+}. (This phenomenon is discussed in greater detail under Section 8.8). Thereafter, pinning improves rapidly in association with rising Pb^{2+} adsorption. Pinning remains constant at the high value of 97% until it decreases strongly at Pb^{2+} concentrations in excess of about 1×10^{-3}M, due to adsorption of Na^{+} and/or deposition of NaCl on drying. Washing the quartz sample conditioned at 1.75×10^{-3}M Pb^{2+} concentration results in a return to a high pinning value, i.e. 93%.

8.7.8. The effect of $CaCl_2$ treatment on the surface conductivity of quartz.

Ca^{2+} is regarded as the most efficient metal ion used in the activation of quartz and silica for flotation with anionic collectors. However, the $CaCl_2$ treatment of quartz did not produce a significant change in the surface conductivity. The influence of Ca^{2+} (1.75×10^{-3}M concentration) on the conductivity of the mineral was investigated (graph 50). Throughout the pH range studied, the



GRAPH 49. THE Pb^{2+} ADSORPTION ISOTHERM AND THE EFFECT OF $PbCl_2$ CONCENTRATION ON THE PINNING OF QUARTZ.



GRAPH 50. THE EFFECT OF $CaCl_2$ ON THE PINNING OF QUARTZ.

pinning values are reduced below the normal 68% value. This is attributed to the deposition of $CaCl_2$, which is extremely hygroscopic and can markedly increase the conductivity of the solid. Washing of the quartz samples treated in Ca^{2+} results in pinning values a little in excess of normal, except in the alkali range where the presence of Na^+ in the wash solution increases the surface conductivity. Ca^{2+} adsorption densities were not measured.

8.8. The hydration of mineral surfaces.

The formation of hydrated layers around ions, molecules and surfaces of minerals is a specific characteristic of water due primarily to its dipole structure. The hydration of mineral surfaces can result from:

(1) Molecules, ions or atoms on the solid surface attract dipoles of water as a result of free atomic or molecular forces[45]. The hydration of the interface is determined by the density of the electrostatic charges on the surface, i.e. if strong charges are present the surface is highly hydrated; however, if the charge is small the hydration is correspondingly lower.

(2) The adsorption of hydrated ions increases the hydration of the surface.

According to Klassen[45], it has been shown experimentally that hydrated layers possess definite thickness and stability. The layers constitute a distinct phase,

separated by a sharp boundary from the residual water surrounding the surface. He represented the effect of electrolytes on the hydration of surfaces in the following way. With an increase in the concentration of electrolyte, the volume adsorption of ions and the hydration of the surface of the solid increases toward a definite limit. When the adsorbed ionic layer is saturated, the subsequent increase in the concentration of electrolyte causes a compression of the electrical double layer. In this case, the electrical forces of the oppositely-charged ions are largely compensated by their interaction and the hydration of the interfaces is lowered. The effect of the ions becomes stronger with an increase in their valency and a decrease in the ionic radius.

In describing the effects of the various metal salt solutions on the electrical conductivity of quartz and kyanite, emphasis has been placed on the postulation that decreased pinning after chemical treatment can be attributed to (1) the capacity of the adsorbed matter to take-up water and (2) the thickness or stability of the hydrate layers associated with the species adsorbed on the solid surfaces. Kakovsky[4] relied on the same hypothesis while Bikerman, Kurosaki and others (Section 7.4) gave consideration to the fact that the surface conductivity of a hydrated quartz surface is that of a thin film of ionically

conducting material, presumably adsorbed water in equilibrium with the surface of the quartz. In the present work it was shown that the electrical conductivity of quartz at constant relative humidity is dependent upon the quantity of adsorbed water (Section 7.4).

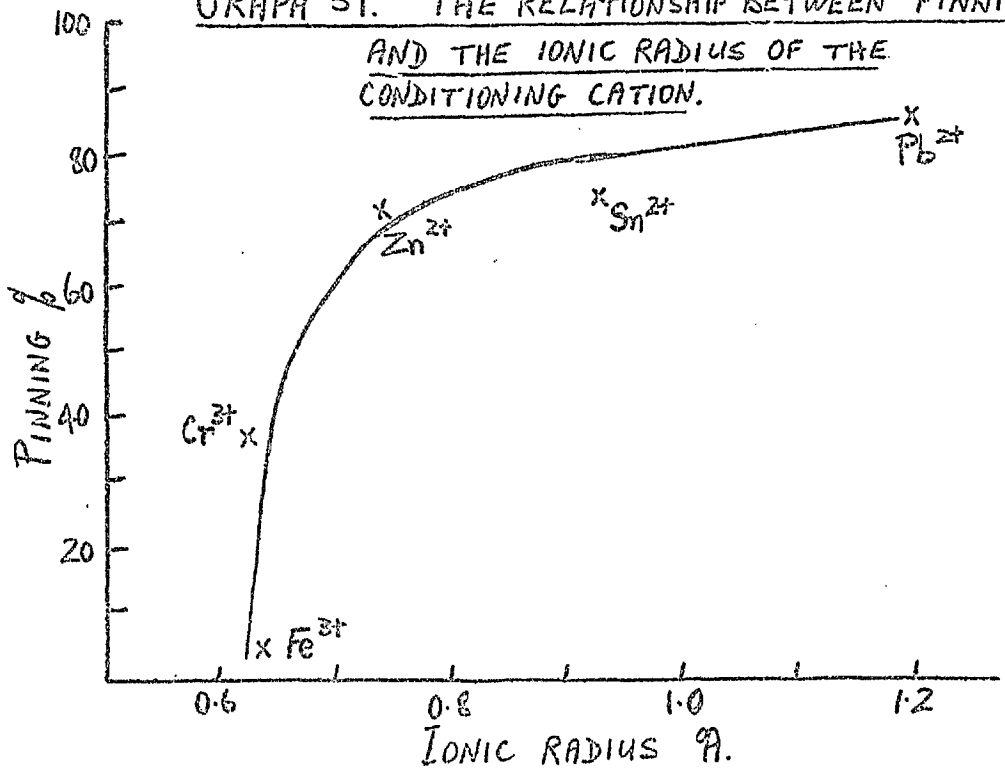
The degree of hydration of an ion depends on its valency and ionic radius.[45] A relationship was sought between the crystal ionic radius[86] of the cations studied and the resultant pinning behaviour of quartz conditioned with these metal ions. Such a correlation was found to exist and is illustrated in graph 51. The quartz samples were treated under conditions resulting in the maximum adsorption of the relevant cation. Ca^{2+} does not conform because maximum Ca^{2+} adsorption occurs above pH 11[85], where Na^{+} has a strong effect on the conductivity of the quartz. The monovalent cations Na^{+} and H^{+} do not conform.

8.9 The effect of the dehydration of chemically-treated quartz.

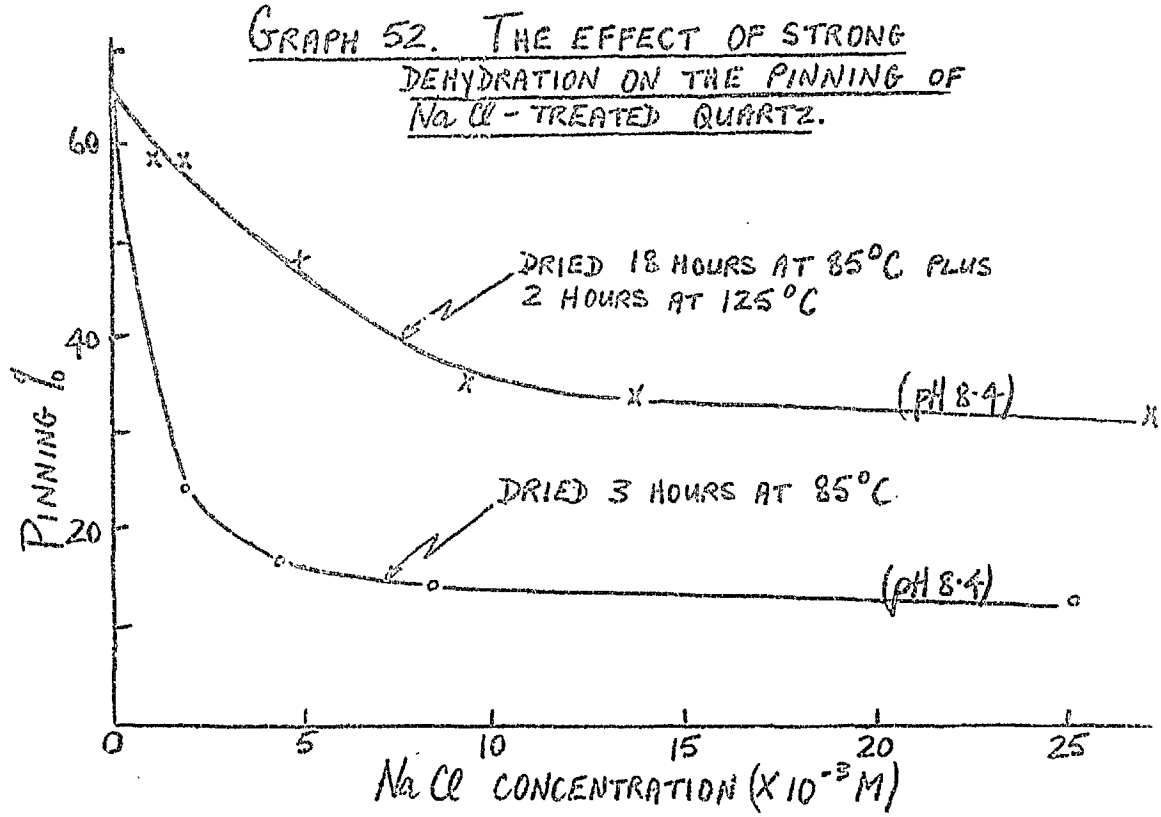
If increased surface conductivities are attributed to the presence of hydrated layers on the surface of the mineral, then dehydration of such layers should decrease the conductivities produced. The dehydrated adsorbed species can still influence the pinning behaviour by virtue of their water adsorbing capacity or insulating properties.

The dehydration of treated-quartz samples was carried

GRAPH 51. THE RELATIONSHIP BETWEEN PINNING AND THE IONIC RADIUS OF THE CONDITIONING CATION.



GRAPH 52. THE EFFECT OF STRONG DEHYDRATION ON THE PINNING OF NaCl - TREATED QUARTZ.



out by either exposing the samples to low air humidities (i.e. about 30% relative humidity,) or drying at elevated temperatures. The effects produced are shown in table 18 and graph 52. The graph demonstrates how excessive drying modifies the pinning behaviour of quartz treated with NaCl through a range of salt concentrations.

The results of table 18 show that dehydration causes a decrease in the surface conductivity of the conditioned quartz. It is likely that the process of dehydration not only decreases the hydration of the surface layers but also oxidises the adsorbed metal hydroxides, resulting in the formation of insulating oxides. Oxidation could account for the fact that in some cases drying results in pinning values exceeding the natural 68% for clean quartz.

8.10 A quantitative measure of the dehydration of chemically-treated quartz samples.

The dehydration of quartz, conditioned with solutions of $FeCl_3$, $SnCl_2$ and $CrCl_3$, was quantitatively measured. Quartz samples of 100 g. weight were reacted with the three solutions under the conditions (table 19) known to result in the maximum adsorption of the relevant cation on the mineral surface. After the treatment, the solids were washed twice with distilled water and dried at 80°C for 3 hours, followed by cooling for one hour in a desiccator containing air at 66% relative humidity. In turn, the

TABLE 18

SALT	CONC. X10^{-3}M	pH	WASHED OR UNWASHED	METHOD OF DEHYDRATION	PINNING AFTER DEHYD.%	†PINNING BEFORE DEHYD.%
$PbCl_2$	0.48	6.1	unwashed	↑	100	97.7
"	"	8.3	"		100	72.5
$Pb(NO_3)_2$	"	5.7	"		86.4	70.2
"	"	6.1	"	85°C for 17-19	88.9	70.0
$Pb(CH_3COO)_2$	"	6.1	"	hours plus 2	71.9	69.6
$SnCl_2$	0.84	4.0	"	hours at 125°C	81.8	48.0
"	"	6.0	"		66.9	48.5
$FeCl_3$	1.79	4.6	"		43.1	14.5
"	"	6.5	"		45.9	18.5
$CrCl_3$	1.92	8.1	"		64.4	38.5
"	"	10.0	"		50.0	28.5
$CaCl_3$	1.75	10.3	"		72.4	53.5
$PbCl_2$	0.48	6.0	washed		>90	96.5
"	"	8.2	"		93.2	62.9
$FeCl_3$	1.79	6.8	"		59.8	37.5
"	"	4.5	"		54.7	24.5
$CaCl_2$	1.75	10.0	"	↓	84.6	54.5
$FeCl_3$	1.79	5.7	unwashed	122 days at R.T.	21.9	5.2
"	"	5.4	"	62 "	29.9	5.5
"	"	5.4	washed	62 "	59.4	13.5
$CrCl_3$	1.92	4.5	unwashed	14 "	72.2	53.8
$SnCl_2$	1.75	8.8	washed	14 "	50.4	26.2
NaCl	20.9	5.1	"	20 "	31.2	23.5

† This column denotes the pinning values of the quartz treated under the conditions stipulated in the table and dried 2½ to 3 hours at a temperature never exceeding 85°C. The pinning behaviours were determined within 20 hours of drying the samples.

samples were transferred to the apparatus used for the water adsorption measurements (Section 7.3.2). The glove box contained dry air, maintained by the use of silica gel.

Over a 48 hour period, the samples lost 0.7, 1.5, and 0.3 mg. H_2O per 100 g. of the quartz conditioned in Fe^{3+}, Sn^{2+} and Cr^{3+} solutions respectively (table 19). It is unlikely that the three samples contained the same amounts of water when first exposed to the dry air. Hence the relative magnitudes of the water desorption are of qualitative importance only, but confirm the suggestion that loss of water occurs when chemically-treated samples are exposed to low humidities.

The three samples were removed from the glove box and dried for 22 hours at 90°C, followed by 2 hours at 125°C. When cool, they were weighed at low humidity. The strong dehydration resulted in losses of 11.9, 4.3 and 11.8 mg. respectively. The comparatively low 4.3 mg. loss in weight of the quartz sample treated in $SnCl_2$ suggests that the surface of the mineral had been weakly hydrated. The relatively large ionic radius of the Sn^{2+} i.e. 0.93 Å,(86) can account for the small degree of hydration. The trivalency and small size of the Cr^{3+} and Fe^{3+} ions cause a strong hydration of the solid surfaces.

TABLE 19

SALT	CONC $X10^{-3}M$	pH	AFTER MILD DRYING ADS. OF H_2O	AFTER MILD DRYING LOSS OF H_2O	AFTER STRONG DRYING ADS. OF H_2O	AFTER STRONG DRYING LOSS OF H_2O	PINNING %
$FeCl_3$	1.79	5.7	6.8 mg.	0.7 mg.	9.7 mg.	11.9	13
$CrCl_3$	1.92	7.5	1.5 "	0.3 "	3.3 "	11.8	38
$SnCl_2$	1.75	4.9	1.0 "	1.5 "	1.5 "	4.3	67
$PbCl_2$	0.48	6.0	0.7 "	-	-	-	98
NaCl	20.0	5.4	2.9 "	-	-	-	17

8.11 The water adsorbing capacity of chemically-treated quartz.

Quartz samples of 100 g. weight were treated with solutions of $FeCl_3$, $SnCl_2$, $CrCl_3$, $PbCl_2$ and NaCl under the conditions specified in table 19. After the reactions the five samples were each washed twice with distilled water. The materials were dried at 80°C for 3 hours, cooled overnight over silica gel and the water adsorption densities were measured at 44% relative humidity using the apparatus and method described earlier (Section 7.3). The samples gained weight in the order $FeCl_3$>NaCl>$CrCl_3$>$SnCl_2$>$PbCl_2$. The corresponding pinning values are in the inverse order (table 19). The results suggest that the surface conductivity of chemically-treated quartz is largely dependent on the water adsorbing capacity of the adsorbed species.

Strong dehydration of the samples conditioned in Fe^{3+}, Sn^{2+} and Cr^{3+} solutions (i.e. 22 hours at 90°C and 2 hours at 125°C) results in increased water-avidities, although the corresponding pinning values had risen (tables 18 and 19). It is therefore postulated that the improved surface conductivity of quartz, treated in salt solutions, depends on the quantity of water associated with, and the water adsorbing capacity of, the layer of material adsorbed on the surface of the mineral.

8.12 Conclusions.

In the modification of the electrical conductivities of quartz and kyanite by treatment with heavy metal salts, hydrogen ion concentration of the solutions is a variable of marked importance. pH influences the pinning behaviour of the minerals by precipitating charged metal hydroxide sols, which under optimum conditions can be electrostatically attracted to the oppositely-charged mineral surfaces. It has been shown in the present work that the maximum adsorption of metal ions on quartz occurs in the pH region of precipitation of the relevant metal hydroxide or hydrated metal oxide. Furthermore, the maximum change in the surface conductivity of quartz is produced in the same pH ranges. The correlation between the pH's of maximum adsorption of metal ions, of incipient precipitation of metal hydroxides and of maximum modification to the pinning behaviour of quartz ~~are~~ is shown in table 20.

TABLE 20

METAL ION.	pH FOR OPTIMUM ADSORPTION	pH FOR MAX. CHANGE IN PINNING BEHAVIOUR	pH FOR PRECIPITATION
Fe^{3+}	5.2-5.8	5.0-5.8	3.0
Cr^{3+}	7-8	7.5-8.0	6.0
Sn^{2+}	5.5-6.5	2.2	2.5
Pb^{2+}	5.5-6.0	6.0	5.6
Zn^{2+}	8.0	5.5	5.2
Ca^{2+}	11.0(85)	8.6	11.0

The concentration of the solutions of metal salt influences the surface conductivity of quartz by the dual action of (1) affecting the surface charge density of the mineral and (2) influencing the quantity of cation adsorbed. Both these factors determine the degree of hydration of the mineral surface and the consequent pinning behaviours. When the pH of the solutions is above the pH of precipitation of the relevant metal hydroxide, the electrostatic attachment of the charged sols to the solid surface can also affect the hydration. A comparison of graphs 40, 44, 47 and 49 demonstrates the similarity of the effects of Fe^{3+}, Sn^{2+}, Cr^{3+} and Pb^{2+} concentrations on the pinning of quartz. In each case pinning decreases with rise in concentration, reaches a minimum and increases to a maximum before falling once more. The Fe^{3+} curve (graph 40) does not display the final fall in pinning up to the highest concentration studied. The above phenomenon can be correlated with Klassen's postulate of the change in hydration of mineral surfaces with increasing electrolyte concentration (Section 8.8).

The reaction of heavy metal and alkali metal salts with quartz and kyanite can alter the surface conductivity of the minerals by one, or a combination of some, of the following:

(1) the adsorption of ions influences the hydration of

the mineral surfaces. The degree of hydration of the interface depends on the saturation of the adsorbed ionic layer and the valency and size of the ions. It is suggested that mild drying does not greatly reduce the thickness of the hydrated layers on the surface of the minerals.
(2) the electrostatic adhesion of colloidal metal hydroxides to the solid surface can increase the hydration of the surface. The hydrated layers are generally water-avid.
(3) dehydration of the metal hydroxides attached to the solid surfaces results in the formation of oxides which can increase the insulating properties of the minerals.
(4) dehydration of the treated-quartz decreases the water content of the adsorbed species, without reducing its water adsorbing capacity.
(5) the deposition of salt on drying the samples can increase the water-avidity of the solids.

The preponderance of any of the above factors controls the pinning behaviour of the mineral particles. It is concluded that the surface conductivity of quartz and kyanite, treated in solutions of metal salts, is a function of the degree of hydration and the water adsorbing capacity of the surfaces of the minerals.

A comparison of graphs 38, 43 and 46 with graph 42 shows that the pinning values of kyanite after treatment with Fe^{3+}, Sn^{2+} and Cr^{3+} salt solutions resemble those found for quartz under similar conditions. The curves

for kyanite appear to be displaced to the left of the corresponding curves for quartz so that the maximum increase in the conductivity of the aluminium silicate occurs at higher hydrogen ion concentrations. This is attributed to the lower iso-electric point of kyanite compared with that of quartz. The similarity in pinning behaviour suggests that the physical nature of the attachment of the metal hydroxides to the solids is non-selective and influences silicates to the same extent, the optimum effect being related to the zero point of charge of the mineral.

The minimum pinning behaviours of the two minerals are comparable in magnitude after Sn^{2+} and Cr^{3+} treatments. This indicates that the metal ions have a greater effect on kyanite since its natural pinning value is 95% compared with the 60% for quartz. It is suggested that the surface roughness of the kyanite particles aids in the attachment of the metal hydroxides to the mineral. The quartz particles are relatively smooth. Fe^{3+} ions have a greater affinity for the quartz surface, reducing its value to 5% compared with the 37% for kyanite. The selectivity may be connected with Iler's[29] observation that metal ions which are strongly acidic and are precipitated as metal hydroxides at pH's below 4, e.g. Fe^{3+} ions, adsorb on silica with the formation of a moderately strong metallosilicic acid. The development of acidity is supposed

to be due to the fact that the metal ions can fit into the surface of the silica in tetrahedral co-ordination. The close-packed structure of the alumino-silicate surface will not allow such a penetration by Fe^{3+} ions.

In the acid region, i.e. pH 2 to 4, the three metal ion solutions slightly decrease the pinning of kyanite to a relatively constant value suggesting that the small increase in conductivity is due to the effect of the acid on the surface of the mineral. The lack of response to metal treatment at low pH's is particularly noticeable in the case of Sn^{2+}, where at pH 2 the pinning of quartz is reduced to 25% while that of kyanite is relatively unaltered. It is not clear why Sn^{2+} lowers quite considerably the pinning of quartz in the highly acidic range, while Cr^{3+} and Fe^{3+} have minor effects.

9.0 MODIFICATION OF THE SURFACE CONDUCTIVITY OF MINERALS BY TREATMENT WITH ORGANIC REAGENTS.

9.1 Introduction.

In this thesis emphasis is placed on the importance of water as a means of rendering silica and silicates better conducting. The water may form part of the hydrated mineral surface or be present as "free" water molecules attached to the surface and associated with adsorbed matter. It is envisaged that water increases the surface conductivity of insulating minerals by virtue of its ionically conducting properties. Adsorbed moisture can also increase the conductivity of the solid-air interface. This section of the work deals with the methods of rendering mineral surfaces hydrophobic and studying the effects of such treatments on the pinning behaviour of the minerals. It is concluded that the complete absence of water from the surfaces of quartz and kyanite results in decreased surface conductivities. The bulk insulating properties of the adsorbed organic reagents appear to have a minor influence on the electrical conductivity of the minerals. For the purpose of this study, organic surface active agents were used, of types commonly employed as collectors in flotation practice.

In a paper presented in 1960 by Kakovsky et al[4], the possibility of deliberately manipulating the surface

electrical properties of minerals in a fashion comparable to that used in flotation practice was brought to light. They attempted to show that the theoretical principles of the treatment of a mineral surface before high tension separation and flotation are very similar.

Kakovsky was not the first to refer to the use of organic compounds to modify the electrical conductivity of minerals. In 1937 Johnson[87] patented the use of resorcinol, camphor, naphthalene and various inorganic chemicals to alter the surface conductivity of minerals and in 1943 extended his list to include cresylic acid, pine tar oil, kerosene, gasoline and turpentine, all of which aided the recovery of fluorspar from the accompanying gangue. In 1942 Fraas and Ralston[88] published information on the pretreatment of minerals using benzoic acid. In the separation of sillimanite from quartz and biotite, wet acid treatment (sulphuric and hydrofluoric acids) was used, followed by the addition of 1 lb/ton benzoic acid to the hot, dry feed. Similar results were obtained with kyanite in a quartz-muscovite-chlorite gangue and with kyanite in a quartz-zircon gangue. Fluorite was separated electrostatically from silica[89] by milling a siliceous fluorite ore with sodium silicate and then conditioning the milled product with oleic acid, a laurylamine collector and transformer oil. Sun[64] studied the effect of laurylamine hydrochloride on the

surface conductivity of quartz. In 1952 a patent by Fraas[91] claimed the use of a wide variety of organic acids in the vapour phase, e.g. normal aliphatic acids such as heptoic, propionic, crotonic and oleic acids; dibasic acids such as fumaric acid; and aryl acids such as benzoic, naphthenic, salicylic, phthalic and cresylic acids. In more recent years Brewis[5] managed to separate kyanite from a quartz-kyanite ore by means of sodium oleate treatment and finally a United States patent[92] claimed the use of chlorophenoxy acetic acid to separate kieserite electrostatically from mixed potash salts.

9.2 The effect of cationic surface active reagent treatment of minerals.

9.2.1 Introduction.

The cationic surfactants used in this study were dodecylamine and hexadecylamine. The two reagents have been widely studied in flotation practice and were readily available. Amines are organic compounds which represent derivatives of ammonium and ammonia[45] in which the hydrogen atoms are replaced by organic radicals, i.e. RNH_2. In flotation practice the reagent is normally used in the salt form, i.e. chloride or acetate, as these are more soluble than the amine. When hexadecylammonium chloride is dissolved in water, an equilibrium is set up between free amine (RNH_2) and aminium ion (RNH_3^+),

according to

$$RNH_2 + H^+ + OH^- \rightleftharpoons (RNH_3)^+ + OH^- \qquad (29)$$

The dissociation constant of hexadecylamine is 4.3×10^{-4} (45).

Equation (29) shows that the relative and absolute quantities of free amine and aminium ions present at any instant depend on the pH of the solution. The forms in which the amine salt can exist in solution are (1) ionically dissolved as RNH_3^+ (2) Molecularly dissolved RNH_2 and (3) precipitated RNH_2. Klassen(45) calculated the quantities of the three forms present in a solution containing 100 mg./l hexadecylammonium chloride as a function of pH. The amount of RNH_3^+ remains constant at 100 mg./l from pH 2 - 8, thereafter decreasing sharply to 10^{-2} mg./l at pH 11. Dissolved RNH_2 increases linearly from 10^{-7} mg./l at pH 2.5 to a constant 10^{-1} mg./l at pH 9. Undissolved RNH_2 increases rapidly from 10^{-7} mg./l at pH 8 to 10 mg./l at approximately pH 9, thereafter reaching a constant concentration of 100 mg./l at pH 10.

9.2.2 The adsorption of amine on silica and silicates.

It is generally agreed(76) that amines adsorb in the electrical double layer and do not interact chemically with the surface of the minerals. Sutherland and Wark(63) maintain that the interaction of amine with quartz is an exchange adsorption in which a cation originally present

on the quartz surface is exchanged for the cation of the collector.

There still exists some controversy concerning the identity of the active species adsorbing on a solid surface, i.e. ion or molecule. Various researchers[63,76,77,93,94] have shown that multilayer adsorption of amine occurs on glass and silicates at high reagent concentrations and high pH's. The observation that loss of amine from solution increases with pH indicates that the adsorption is favoured by the formation of free amine. The mechanism is one of ionic adsorption proceeding initially, until a sufficient proportion of hydrocarbon surface is presented to the solution, when molecular adsorption begins. In support of this postulation are the facts that ionic adsorption is favoured by the large negative charge of silica and the extent of molecular adsorption depends entirely on the quantity of free amine in solution, i.e. a function of pH.

Gaudin and Morrow[95] calculated the energy of adsorption of dodecylamine on quartz from measurements of contact angle as a function of collector adsorption. It appears that the rate and process of adsorption changes with surface coverage. The energy of the adsorption process on the most active sites corresponds initially to chemisorption changing to physical adsorption as the monolayer is completed. It has been suggested[96] that

dodecylammonium ion and dodecylamine molecule are both active species. However, the dodecylamine molecule is carried to the surface by capture by dodecylammonium ions.

Investigations have shown[45] that surface active reagents lower the stability of the hydrated layers surrounding minerals by decreasing the interaction between ions, atoms and molecules on the solid surface and in the surrounding liquid. Molecules of surfactant compounds adsorbing on particles through the hydrophilic group, have the hydrophobic portion of the molecule directed to the bulk liquid. Hence the interaction between dipoles of water and ions on the mineral decreases.

The adsorption of organic compounds on the surface of silica depends on the presence of polar groups in the molecule. The polar groups of the compound are attracted to the polar silanol surfaces, i.e. they form the primary point of attachment to the mineral surface[97]. The hydrocarbon chain or other non-polar parts of the organic molecule tend to escape from the aqueous medium in which they are embedded.

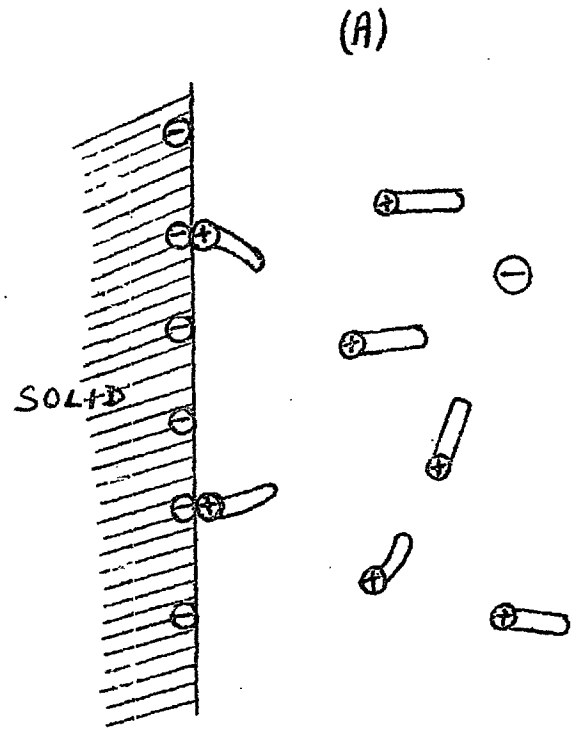
From a study of the change in zeta-potential of quartz in solutions of increasing aminium acetate concentration, Aplan and Fuersteneau[77] concluded that the organic electrolyte behaves initially as an indifferent electrolyte, but once a certain concentration is reached the ions begin to show a marked affinity for the surface.

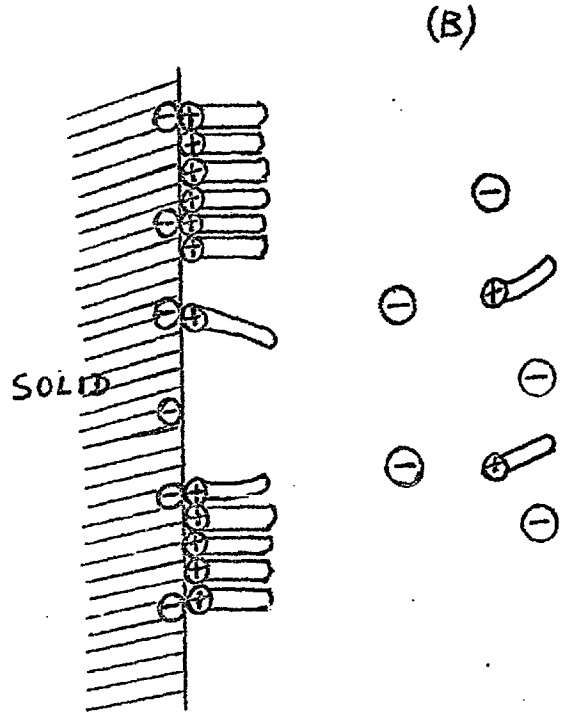
This phenomenon has been explained by considering the ions to be adsorbed as individual ions until their concentration in the Stern layer becomes sufficiently great for the hydrocarbon chains to begin to associate, a phenomenon akin to the formation of micelles. The adsorption mechanism is illustrated schematically in figure 13.

In support of the hypothesis above, de Bruyn[90] determined the adsorption isotherm of dodecylammonium acetate on quartz and illustrated that a sharp increase in adsorption was exhibited when association of the hydrocarbon chains occurred.

9.2.3 The flotation of quartz with amines.

Soane[98] has reviewed the literature pertaining to the flotation of quartz with long chain primary amines. It is generally agreed that at small concentrations of amine there is a critical pH at which flotation is a maximum. The critical pH varied from one system to another, but was never less than pH 5 or greater than pH 11. Flotation ceased outside these extremes of pH. The cessation of flotation at high pH values has been ascribed to competition of the collector with the added Na^+ resulting from the NaOH used as pH regulator. Many workers [63,98,99] have shown that the flotation of quartz and silicates with amines ceased at pH values approaching 12, e.g. Aplan and Fuersteneau[77] mentioned that pH 12.2 was





⊖ POTENTIAL DETERMINING IONS

⊖ HYDRATED COUNTER IONS

SURFACTANT CATION

FIG. 13 (A) THE ADSORPTION OF SURFACTANT IONS AT LOW REAGENT CONCENTRATION

(B) HEMI-MICELLE FORMATION AT HIGHER CONCENTRATIONS.

the highest possible pH for the flotation of quartz with primary amine salts. Under these conditions the concentration of dodecylamine was 2 X 10^{-5}M, whereas the concentration of dodecylammonium ion was but 4 X 10^{-7}M and that of Na^{+}1.6 X 10^{-2}M.

The contact angles on quartz in dodecylamine solutions were shown to increase with reagent concentration and then decrease as the concentration continued to rise (98). Soane was able to show that at constant pH 9 the flotation of quartz increased with dodecylamine hydrochloride concentration to a constant value.

9.3 The modification of the surface conductivity of quartz and kyanite by amine treatment.

9.3.1 Introduction.

In this section of the work the effects of amine conditioning on the surface conductivity of quartz and kyanite were studied. Treatments with dodecylamine and hexadecylamine were investigated through a wide range of concentration and pH. It appears that the resultant pinning values can be correlated with the flotation behaviour of the minerals. This correlation confirms the hypothesis enunciated earlier that a combination of the atmospheric humidity and of the water-repellency of the surface of an insulating mineral, determines the mineral's behaviour in a standard high tension field. The

floatability of the solids was not determined in the present work and the correlation was made from relevant flotation data presented in the literature.

9.3.2 The reagents.

The dodecylamine and hexadecylamine used in the study were supplied by the Armour Industrial Chemical Company, trade names Armeen 12D and 16D respectively. The compositions and formulae of the two amines are:
Dodecylamine $\left[CH_3 (CH_2)_{11} NH_2\right]$ consists of 95% n - dodecylamine, 2% n - decylamine and 3% n - tetradecylamine. The molecular combining weight is 195.
Hexadecylamine $\left[CH_3 (CH_2)_{15} NH_2\right]$ consists of 92% n - hexadecylamine, 7% n - octadecylamine and 1% n - octadecenylamine. The molecular combining weight is 250.

The two amines were used in the chloride form and were prepared as follows: 0.4000 g. amine was accurately weighed and then dissolved in a minimum amount of absolute alcohol. To this was added 12.0 mls. M/40 HCl. The solution was made up to 1000 mls. in a standard flask. The pH of the stock solution was about 3.2.

9.3.3 Experimental procedure.

50 g. samples of acid-cleaned quartz and kyanite were treated with solutions of dodecylammonium and

hexadecylammonium chlorides of variable concentration and pH. The reaction times were 15 minutes and in all cases the liquid/solids ratio was 6/1. After decantation of the liquor, the minerals were dried slowly at a temperature below 80°C to minimise vaporisation of the adsorbed amine. When dry, after about 2½ to 3 hours, the samples were cooled over silica gel. After an elapse of 18 to 20 hours, the pinning behaviour of the minerals was determined under the standard high tension conditions described in Section 4.5.

9.3.4 Results.

The effects of amine concentration and solution pH on the pinning of quartz and kyanite are shown in graphs 53,54 and 55. The surface conductivity of the minerals is decreased by treatment with amine, the pinning values depending on the reagent concentration and pH in analogy with the improved flotation of quartz under similar conditions. The depression in the hexadecylamine curve at pH 7 to 8 in graph 53 is apparent rather than real. It was qualitatively observed in some cases that if pinning was severe, a small amount of pinned material was "blown" into the thrown fraction, probably as a result of mutual repulsion between highly charged particles. This phenomenon could account for the scatter of points in the kyanite-hexadecylamine system (graph 55).

Under all the conditions studied hexadecylamine is more effective than dodecylamine in rendering the minerals insulating.

9.3.5 Discussion.

(a) The effect of pH on the pinning behaviour of quartz.

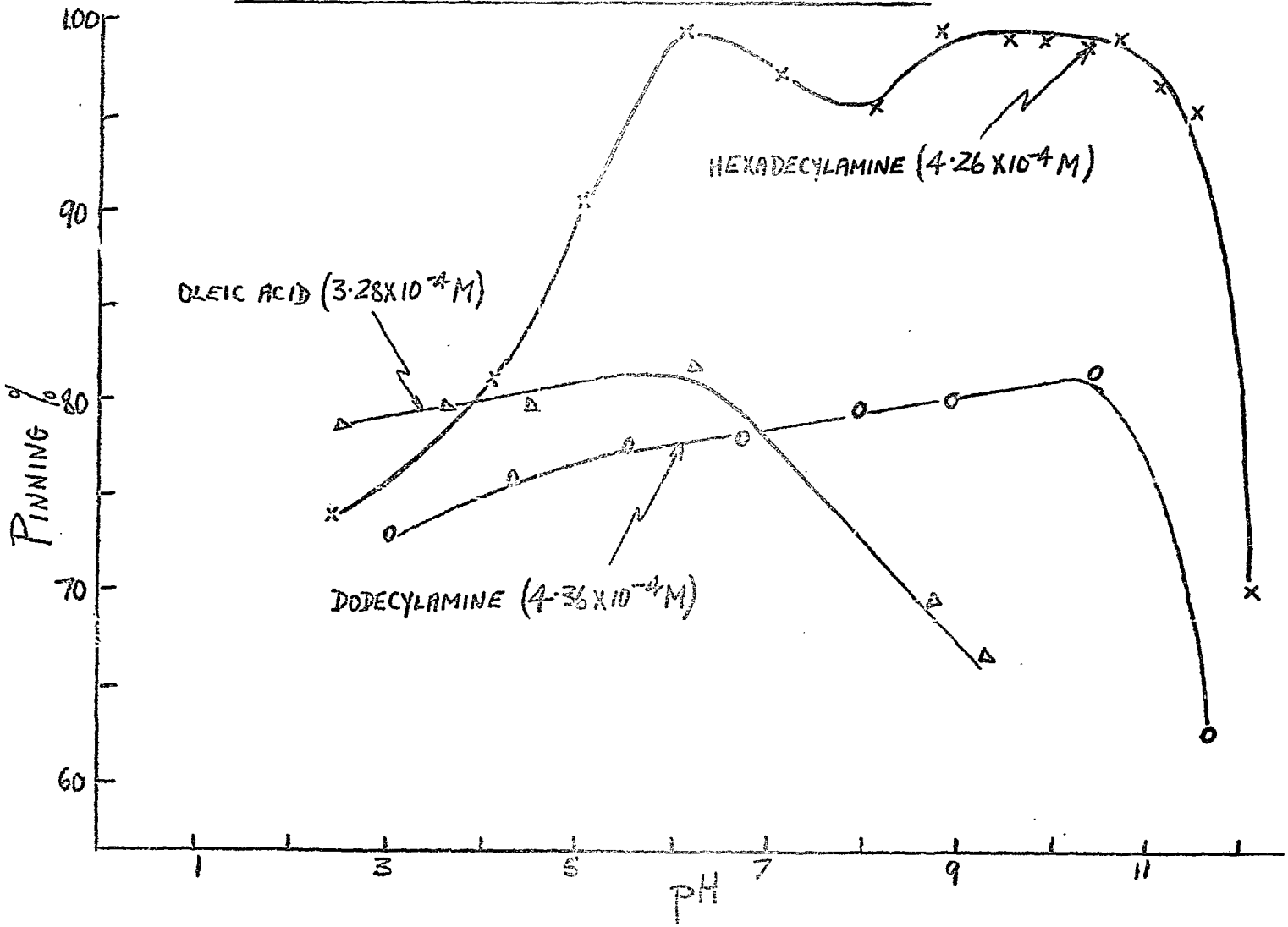
Hydrogen ion concentration influences the amount of amine adsorbed on the surface of quartz by one, or both of the following factors;

(i) The relative and absolute quantities of free amine molecules and ions present at any instant depend on the pH of the solution. The two species have variable affinities for the mineral surface.

(ii) Hydrogen ion concentration affects the surface charge density of a mineral surface. The adsorption of organic molecules is a maximum at the iso-electric point. On the other hand the adsorption of reagent ions depends on the electrostatic attraction of the ions for the oppositely-charged mineral surfaces.

At a constant amine concentration of 100 mg./l, increasing pH leads to the improved adsorption of amine on to the solid surface, presumably RNH_3^+ at low hydrogen ion concentrations and a combination of RNH_3^+ and RNH_2 molecules at pH's greater than 9 or 10. The rise in the pinning of quartz from pH 2 to 6 (graph 53) after reaction with hexadecylamine solution, is attributed to an increasing

GRAPH 53. THE EFFECT OF HEXADECYLAMINE, DODECYLAMINE AND OLEIC ACID ON THE PINNING OF QUARTZ.



surface coverage by RNH_3^+, which renders the mineral hydrophobic. Gaudin and Bloecher[100] reported that at a 100 mg./l. dodecylamine concentration, there is a 10% coverage of the surface of quartz. It appears therefore that the bulk insulating properties of the adsorbed amine cannot significantly effect the surface conductivity of the mineral.

Above pH 6, pinning remains at a constant high value probably due to saturation of the silanol sites with RNH_3^+. This does not necessarily imply that a complete monolayer of amine is present on the quartz surface. Gaudin et al[100] have shown that under similar circumstances, when using the same quartz-amine system, a fraction of a monolayer is formed but flotation was nevertheless good. If it is assumed that each hydrocarbon chain is horizontally orientated on the mineral surface, then a monolayer coverage is approached.

Over the pH range 6 to 10.6, the hydrophobicity of the samples after contact with the amine solutions was very obvious. After drying, the water-repellency was retained as demonstrated by the qualitative test of dropping the dry particles into distilled water and observing their failure to become wetted. The water adsorbing capacity of quartz treated at pH 9 was measured. The samples are almost completely hydrophobic even at high relative humidities. (Section 7.3).

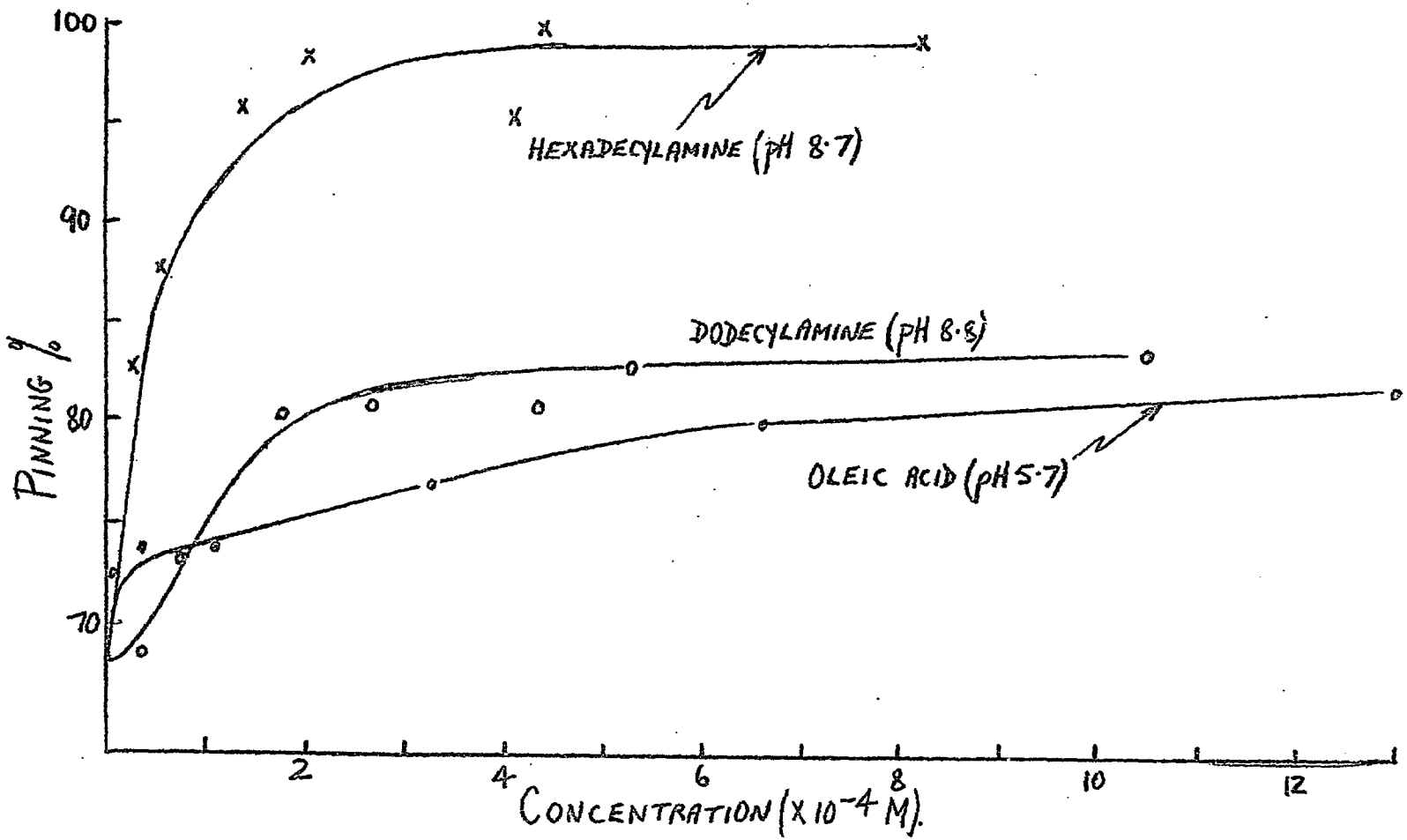
Above pH 9 the amount of RNH_3^+ in solution diminishes sharply, while the predominant species are molecular dissolved and undissolved RNH_2. The water-repellency of the mineral surface above pH 9 is therefore attributed to the physisorption of RNH_2. The hydrophobicity and resulting insulating properties are retained to about pH 10.6, where competition between the Na^+ and RNH_2 molecules results in an increased hydration of the quartz surface because of the predominant adsorption of Na^+ with its attendant water molecules of hydration. The cessation of flotation under these conditions has also been attributed[98] to the reverse orientation of the adsorbed collector species, i.e. with the hydrophilic polar head pointing towards the water.

Dodecylamine is not as effective as hexadecylamine in improving the insulating properties of quartz, because the shorter length of hydrocarbon chain results in a decreased adsorption density and a smaller coverage of the mineral surface.

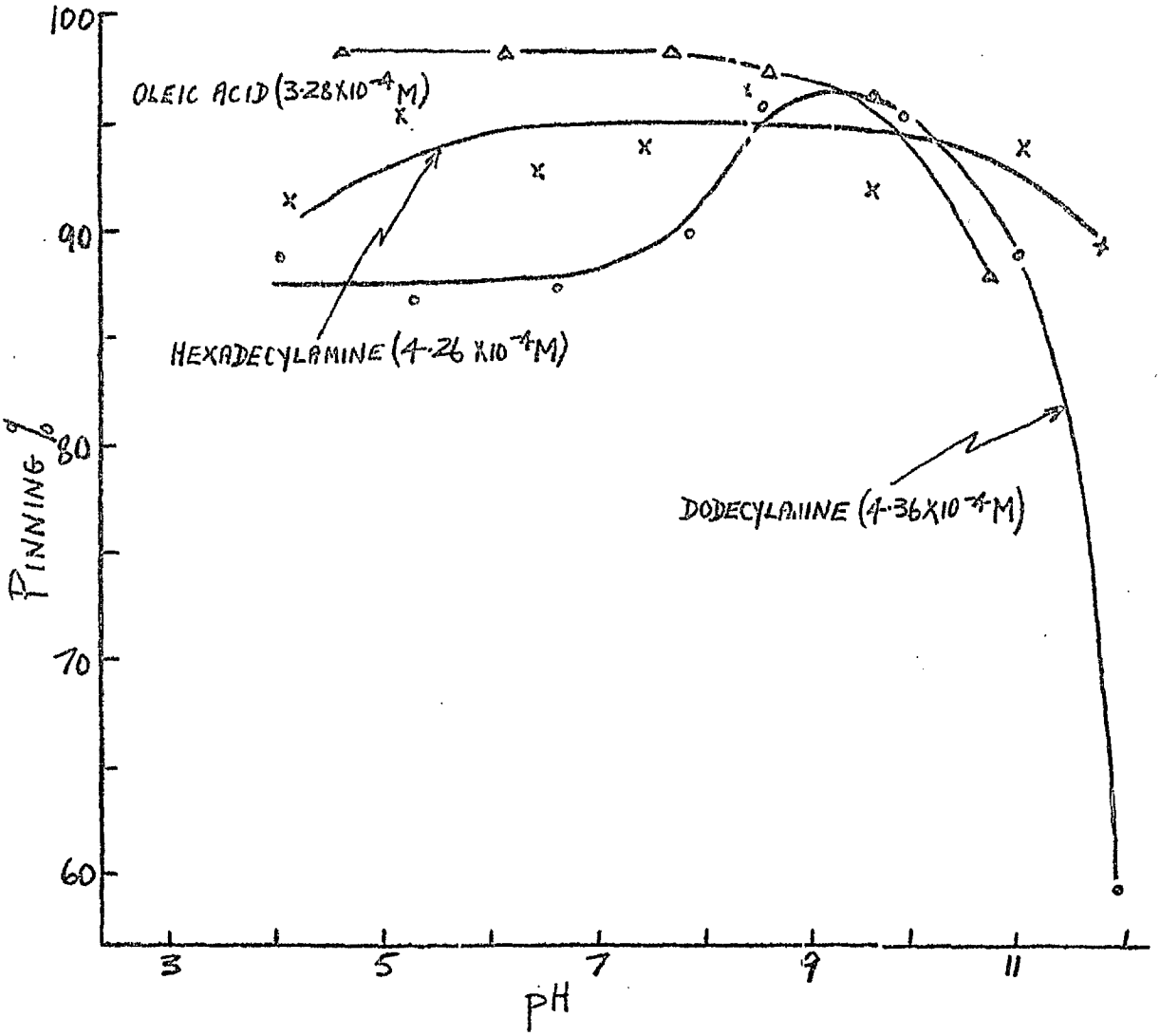
(b) The effect of pH on the pinning of kyanite.

The pinning of kyanite is not greatly altered from its normal value of 95% by the action of hexadecylamine (graph 55). Pinning remains relatively constant up to pH 12.1. Treatment with dodecylamine results in a maximum increase in pinning at about pH 9 to 10. Above pH 11 pinning decreases sharply. The reduction in the pinning behaviour from pH 4 to 8 cannot be accounted for.

GRAPH 54. THE EFFECT OF HEXADECYLAMINE, DODECYLAMINE AND OLEIC ACID CONCENTRATIONS ON THE PINNING OF QUARTZ.



GRAPH 55. THE EFFECT OF HEXADECYLAMINE, DODECYLAMINE AND OLEIC ACID ON THE PINNING OF KYANITE.



(c) <u>The effect of amine concentration on the pinning of quartz</u>.

The concentration of reagent is an important factor in influencing the adsorption of polar organic compounds on silanol surfaces. The amount of reagent adsorbed, Γ, is related to the initial concentration, C_o, by the gener formula,

$$\Gamma = aC_o^{1/n} \qquad (30)$$

where a and n are constants. The value of n varies between 0.1 and 1.

The pinning of quart after reaction with amine solutions at constant pH, increases sharply with rise in reagent concentration, reaching a constant value (graph 54). This behaviour is in analogy with the following:

(i) the increased quantity of RNH_3^+ in solution with rise in amine concentration[45]

(ii) the increased hydrophobicity of quartz (as determined by flotation tests under similar conditions)[98]

(iii) the increased adsorption of amine on quartz.[63,76]

It appears therefore that the rapid initial increase in pinning followed by a much slower rise to a maximum value, can be accounted for by assuming that a layer of hydrophobic RNH_3^+ is rapidly formed and thereafter, as the surface approaches saturation, adsorption is at a much slower rate. In corroboration of this statement, it may

be quoted that Alexander and Johnson[101] reported that the adsorption of long-chain organic compounds on sodium nitrate crystals was measured as a function of reagent concentration. It was observed that the surface was rapidly covered with adsorbed reagent until the theoretical monolayer was approached, when the rate of adsorption decreased considerably. In addition Wada[102] determined the surface coverage on quartz in aqueous solutions of dodecylammonium acetate as a function of concentration and found a relationship which can be closely correlated with that illustrated in graph 54.

In this work there was no evidence of reversed orientation of the adsorbed hexadecylamine. Two investigations performed at hexadecylammonium chloride concentrations of 2.13 and 4.26 x 10^{-3}M, revealed no change in the pinning of quartz, i.e. the pinning values remained constant at about 97%. It is likely that multilayer adsorption of amine results on the mineral surface at the high concentrations studied.[100]

9.4 Hexadecylamine treatment of conductor minerals.

The effect of hexadecylamine treatment on the electrical conductivity of conductor minerals was determined on the chromite and ilmenite described under Section 2.2. Clean chromite and ilmenite have pinning values of 12.5 and 5.1% under the standard high tension conditions. The

samples were conditioned with 100 mg./l. hexadecylammonium chloride at pH 9.0. After drying at 80°C, the pinning behaviours were determined. The pinning of chromite is increased to 19.2% while that of ilmenite remains completely unaltered. When investigations were performed at a higher amine concentration of 1000 mg./l., the resultant pinning values were 22.6 and 7.2% respectively.

In order to increase the insulating properties of a mineral whose bulk conductivity far exceeds its surface conductivity, it is necessary to attach to the mineral surface a thick insulating layer which is impermeable to the passage of ions and electrons. The increase in the pinning of the conductor minerals after treatment with amine, suggests that the bulk insulating properties of the adsorbed layer have an influence on the surface conductivity of the solids.

9.5 The effect of anionic surface active reagent treatment of minerals.

9.5.1 Introduction

The most widely used anionic surface active reagents in flotation practice are those which contain the carboxylic group $-C\overset{O}{\underset{OH}{<}}$, which represents the anion of all fatty acids. The fatty acid used in this study was oleic acid, chemical formula $CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, molecular weight 282.5.

Fatty acids are adsorbed less actively on oxides and silicates compared with amine adsorption, because of the like negative sign of the reagent ions and the mineral surfaces. Lapointe[3] measured the adsorption of oleic acid on quartz and found a linear relationship between fatty acid take-up and reagent concentration. It has been reported[104] that 35 g. sodium oleate per ton solids was adsorbed on -60μ quartz from an initial oleate concentration of 275 g/ton.

When sodium oleate is used as a collector in flotation practice, the collecting species may be undissociated acid, the oleate ion or possibly an acid soap or other complex group at higher concentration. Numerous attempts have been made to identify the species active in changing the hydrophobicity of a mineral surface when reacted with fatty acids. In the alkaline region where sodium oleate is almost fully ionised, it has been suggested[105] that the oleate ion is the collecting species for apatite. In the acid range undissociated oleic acid may be the active form. If oleic acid is the collecting species, adsorption of the fatty acid should be favoured at the iso-electric point of the mineral. Peck and Wadsworth[106] demonstrated by means of infra-red spectroscopy, that the optimum conditions for the flotation of fluorite corresponded to the peak of the curve relating chemisorption of oleate to pH. They also found that physical adsorption of oleic acid

increased with decrease in pH and was high under conditions where the mineral had low floatability.

The interaction of fatty acids with solid surfaces is strongly affected by the presence of activating cations on the mineral surface and by the ionic composition of the aqueous medium. Fatty acids react very strongly with ions like Ca^{2+}, Mg^{2+} and Fe^{3+}, forming insoluble soaps and increasing flotation ability. The mechanism whereby a collector is adsorbed by an activated quartz surface is complex and not well understood. It appears that the activating action of metal ions is related to the fact that they improve the adsorption of collectors on minerals, acting as a link between the two.(29,45)

Gaudin et al,(107) using radioactive sodium laurate and barium chloride, have established that quartz adsorbs Ba^{2+} and laurate ions independently, but in the adsorption of laurate ions by unactivated quartz, there is no flotation. He concluded that the adsorption of active cations on the surface of the mineral favours the transfer of collector ion from the diffuse layer to the surface, thus providing a sufficiently hydrophobic mineral surface.

In the adsorption of sodium oleate on Ba^{2+}-activated quartz, McGlashan(68) has identified the following sequence of events: the adsorption of potential-determining ions, the specific adsorption of Ba^{2+} ions and the adsorption of the fatty acid anions.

In the flotation of quartz and silica by oleic acid, the following metal ions have been used to activate the minerals; Fe^{3+} in the pH region 4 to 10[63,67,69]; Al^{3+} (pH 2 to 6 and 4 to 12[63]); Cu^{2+} (pH 6 - 10.5[63]); Ba^{2+} (pH 7 - 13[27,63,107]) and Ca^{2+} (pH > 11[29,67,69,80,103]). Cessation of flotation at pH's above and below the limits quoted has been attributed to the lack of metal ion adsorption. Monovalent cations do not activate quartz for flotation with anionic collectors and in fact can cause depression of the mineral. NaOH is a powerful depressant for quartz activated by Fe^{3+} and Al^{3+} compounds[67]. However, when Ca^{2+} is employed as the activator, quartz resists depression by NaOH and in the presence of the latter floats very well. At high pH's, although Ca^{2+} take-up has continued to increase[85], competition between Na^{+} and Ca^{2+} at the mineral surface results in the predominant adsorption of Na^{+} and flotation ceases.

9.6 Modification of the surface conductivity of quartz and kyanite by sodium oleate treatment.

9.6.1 Introduction

The use of oleic acid to modify the surface electrical properties of minerals has not received much attention. In this section of the work, methods of altering the surface conductivity of quartz and kyanite by treatment with sodium oleate were studied. The modifications

produced are explained on the basis of improved or decreased hydrophobicity of the solid surfaces in analogy with the flotation of the minerals under similar circumstances. Quartz samples were also treated with a combination of sodium oleate and metal ions.

9.6.2 Preparation of sodium oleate.

Hopkins and Williams "purified" grade oleic acid was used, as supplied by the manufacturers. Solutions of sodium oleate were made by saponifying the oleic acid with Analar NaOH to give a solution containing 0.4000 g./l. sodium oleate. The excess of NaOH maintained the pH of the stock solution at about 9.5.

9.6.3 Experimental Procedure.

Acid-cleaned quartz and kyanite samples were treated with sodium oleate solutions by the method described for the amine conditioning (Section 9.3.3). Pinning behaviours of the dried samples were determined under standard conditions.

9.6.4 Results and discussion.

The pinning behaviours of quartz and kyanite depend on sodium oleate concentration and solution pH (graphs 53, 54 and 55). At a constant reagent concentration of 3.28×10^{-4}M, the pinning of kyanite is slightly

increased to a value which is independent of hydrogen ion concentration from pH 2 to 9. Above pH 9, the insulating properties fall. Under identical conditions, the pinning of quartz is increased above its natural 68% value in the pH range 2.4 to 9.0, more decidedly so in the acid range. The maximum decrease in conductivity occurs in the region of pH 6, which approximates to the theoretical iso-electric point of quartz, (Section 8.2) and it is suggested that undissociated oleic acid adsorbing on the quartz surface at this pH contributes to the improved hydrophobicity. On departure from pH 6 the diminishing adsorption of oleic acid causes a decrease in the pinning (graph 53).

The improved insulating property acquired by quartz after treatment with sodium oleate is comparable in magnitude with the pinning produced by dodecylammonium chloride, but is markedly less than that obtained after conditioning with hexadecylammonium chloride.

The pinning of quartz, treated with sodium oleate at pH 5.7, increases slowly with reagent concentration to 81% at the highest concentration studied, i.e. 1.31×10^{-3}M.

9.7 Modification of the surface conductivity of quartz after treatment with a combination of inorganic metal ions and sodium oleate.

9.7.1 Introduction

The adsorption of metal ions on the surface of

minerals can result in more stable and more uniform collector attachment.[66] For example, tridecylate adhering to quartz surfaces activated by Fe^{3+}, could not be removed by washing with water, while 60% was removed in the absence of an activator. Bogdanov et al.[66] assumed that in linking themselves to the collector ions, the activator ions transfer from the solution layer near the surface on to the surface layer of the mineral. Gaudin[107] made the same suggestion. When metal ions are used as depressing agents, inhibition of flotation is caused by displacement of the collector from the mineral surface due to the preferential sorption of the depressing ions. In some cases depression is due to the high degree of hydration of the adsorbed metal ion, causing the hydrophobic effect of the sorbed collector to be neutralised.[67]

In this work small quantities of metal salt were added to sodium oleate solutions in order to increase the ability of the organic reagent to render quartz insulating. In the presence of Fe^{3+}, Sn^{2+} and Ca^{2+}, sodium oleate strongly increases the pinning of quartz at critical solution pH's and metal ion concentrations. When the mineral is pretreated with a metal salt prior to the reaction with sodium oleate, the increased pinning values are operative over a wider pH range.

9.7.2 Experimental procedure.

The procedure adopted in this study was as follows: Stock solutions of sodium oleate, $FeCl_3$, $SnCl_2$ and $CaCl_2$ were prepared immediately prior to use. The required aliquots of the organic and inorganic solutions were mixed in 400 ml. beakers and distilled water was added to make up the volume to 300 mls. The pH was adjusted by additions of M/40 HCl or NaOH. 50 g. samples of acid-cleaned quartz were added to the solutions and the mixtures agitated for 15 minutes. After decantation of the liquor, the solids were dried at 85°C and cooled for 18 to 20 hours over silica gel. The pinning behaviours were determined under standard conditions. The results are listed in table 21 and compared with the pinning values of quartz treated under similar conditions with (1) the relevant metal ion only and (2) sodium oleate only.

9.7.3 Results and discussion.

(a) The effect of pH

In the presence of Sn^{2+} or Fe^{3+}, sodium oleate has a strong influence on the electrical conductivity of quartz. Pinning values are increased to a maximum in the acid region, i.e. pH 2.6 to 4.4. The samples treated over this pH range are highly hydrophobic.

TABLE 21

METAL ION	CONC. X10^{-4}M	INITIAL pH	% PINNING		
			METAL ION ONLY	OLEATE ONLY	METAL ION PLUS OLEATE
Sn^{2+}	8.42	2.7	41.5	78.5	98.3
		3.5	45.0	80.0	99.8
		4.9	56.0	81.5	80.1
		6.5	36.5	79.5	77.0
		8.6	33.5	72.0	71.7
Fe^{3+}	6.00	3.0	-	79.0	97.2
		4.4	38.0	81.5	90.2
		5.6	17.0	81.0	70.8
		7.0	35.5	78.0	56.5
		9.1	43.5	69.5	68.3
Ca^{2+}	8.16	5.9	-	80.5	93.8
		8.3	-	73.5	91.5
		9.4	-	67.0	94.1
		10.2	-	59.0	93.0
		11.1	-	-	94.4

Fe^{3+} adsorption densities were measured on the five relevant samples listed in table 21. The resulting Fe^{3+} counts show that the maximum adsorption of metal ion occurs in acid solutions at about pH 4.4 (table 22) while in pure $FeCl_3$ solutions, the adsorption of Fe^{3+} on quartz attains a maximum at about pH 5.5 (graph 39). The difference in the critical pH's is ascribed to the observation that the addition of sodium oleate to the $FeCl_3$ solution shifts the pH of maximum stability of the $Fe(OH)_3$ sols to more acidic

pH's. Maximum Fe^{3+} adsorption can be correlated with the stability of the $Fe(OH)_3$ colloids (Section 8.7.3).

When flocculation occurs above pH 4.4, the take-up of Fe^{3+} decreases (table 22). Above pH 7, the metal hydroxide sols enter a second region of stability, and Fe^{3+} adsorption increases once more.

TABLE 22

Fe^{3+} CONC. X10^{-4}M	INITIAL pH	Fe^{3+} ADSORPTION DENSITY (COUNTS)	% PINNING OF TREATED QUARTZ
6.00	3.0	318	97.2
	4.4	367	90.2
	5.6	207	70.8
	7.0	241	56.5
	9.1	286	68.3
0.90	5.5	232	79.8
3.00	5.5	143	84.9
9.00	5.5	816	86.7
18.00	5.5	405	51.6

There appears to be only a semi-quantitative relationship between the quantity of Fe^{3+} adsorbed and the pinning values of the treated-samples. The adsorption of Fe^{3+} can severely hydrate the mineral surface (Section 8) and hence there is an opposing tendency for the adsorbed Fe^{3+} either to hydrate the surface or render it hydrophobic by increasing the adsorption of oleic acid.

Many researchers[45,63,66,67,68] have shown that the effectiveness of the metal ion activation is a maximum at

hydrogen ion concentrations at which precipitation of the metal hydroxides is incipient. Ferric and stannous hydroxides precipitate at pH 3.0 and 2.5 respectively. The maximum insulating effect produced in the acid range is attributed to the strong adsorption of Fe^{3+} or Sn^{2+} on the quartz surface, providing linkages for the adherence of the fatty acid with its associated hydrophobicity. The identity of the organic species is probably undissociated oleic acid because the adsorption of the metal ions can lower the zeta-potential of the mineral, thereby making it amenable to the physical adsorption of organic molecules. Bogdanov et al [66] observed that the presence of Ba^{2+} or Fe^{3+} on the surface of quartz markedly increased the adsorption of a fatty acid collector.

It is widely accepted in flotation practice that Ca^{2+} is very effective in activating quartz for flotation with an anionic collector. High hydroxyl ion concentrations are essential for efficient flotation because a monomolecular coverage of Ca^{2+} on a quartz surface is not possible below pH 11 [85]. In the present work it was found that the pinning behaviour of quartz, treated with Ca^{2+} and sodium oleate, is slightly less than the maximum obtained in the presence of Sn^{2+} and Fe^{3+} (table 21). However, in the case of Ca^{2+} the pinning values are independent of pH, a constant value being found from pH 5.9 to 11.1. At the highest pH studied the concentration of Na^{+} in solution is

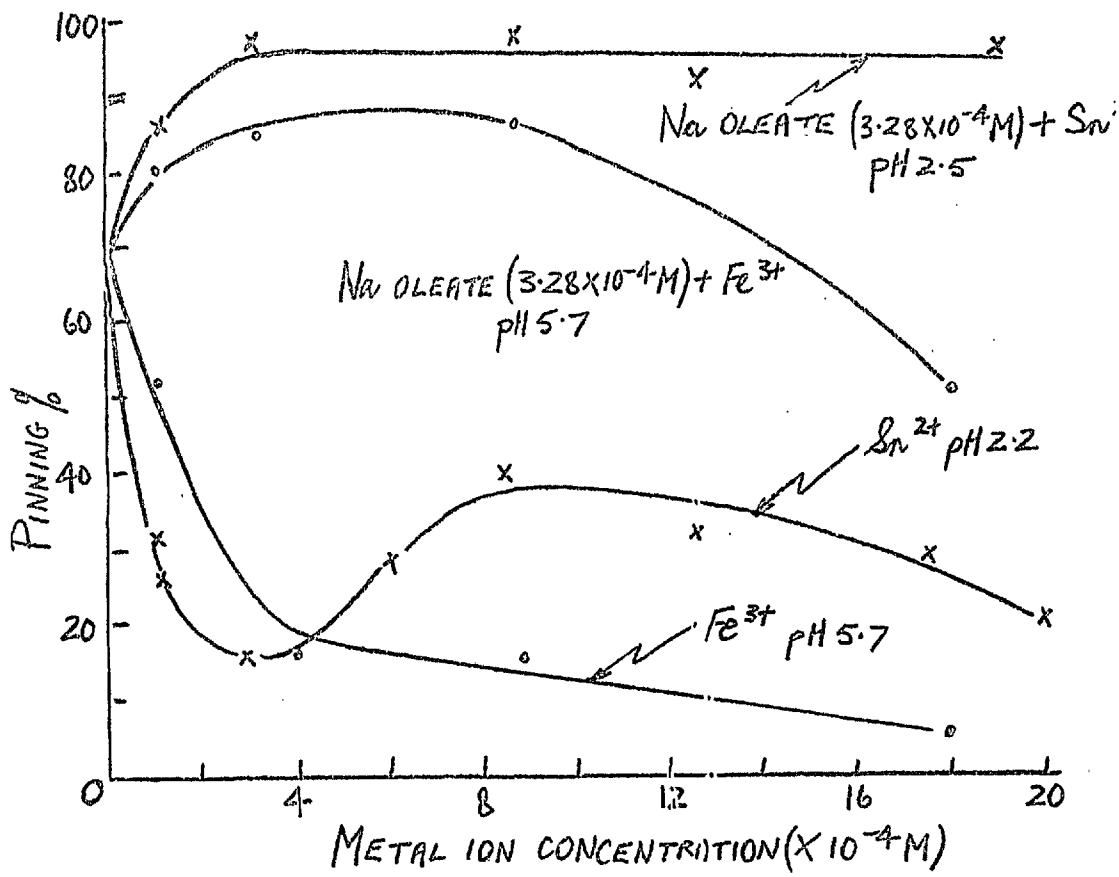
3.08×10^{-3}M, which is about 3.5 times greater than the concentration of Ca^{2+}. This ratio is well below the 400 to 800 suggested by Strathmore[80] for bubble pick-up on quartz to cease in the presence of $CaCl_2$ and sodium oleate.

(b) The effect of metal ion concentration.

The effect of variable metal ion concentration (at constant solution pH and sodium oleate content) on the pinning behaviour of quartz was studied. $FeCl_3$ and $SnCl_2$ solutions modify the surface conductivity of the mineral as illustrated in graph 56, which also includes the curves for quartz treated under similar conditions with pure solutions of $FeCl_3$ and $SnCl_2$.

In the case where the quartz is comparatively weakly hydrated by treatment with pure $SnCl_2$ solutions, the action of a combination of sodium oleate and Sn^{2+} is to render the quartz almost completely non-conducting through a wide range of metal ion concentration (graph 56). When Fe^{3+} is used, the increase in pinning is not so pronounced and at high metal ion concentrations, it decreases rapidly. The fall off in pinning at 1.8×10^{-3}M Fe^{3+} concentration is attributed to a reduction in the adsorption of Fe^{3+}, resulting in a decreased take-up of organic reagent. At this concentration, the Fe^{3+} adsorption density is half that found at 0.9×10^{-3}M Fe^{3+} concentration, i.e. 405 counts against 816 (table 22). The decreased adsorption

GRAPH 56. THE EFFECT OF A COMBINATION OF SODIUM OLEATE AND VARYING CONCENTRATIONS OF Sn^{2+} AND Fe^{3+} ON THE PINNING OF QUARTZ.



of the metal ion results from the severe flocculation of the ferric hydroxide sols by the sodium oleate.

The adsorption of Na^+ at high Fe^{3+} ion concentrations can contribute to the decreased pinning. At 1.8×10^{-3}M Fe^{3+} concentration, the quantity of Na^+ present in solution at pH 5.5 is 5.2×10^{-3} equivalents per litre. Assuming that this total amount of Na^+ is available in solution and not occluded with the flocs, the pinning of quartz can be reduced to about 20% at pH 5.4 (graph 37).

Polkin[104] studied the floatability of quartz with sodium oleate and found that small quantities of iron salts activate the mineral while an excess of these salts depress it. Using 0.55 mg. sodium oleate per g. solids, the flotation recovery of quartz was increased from 4% to 85% with a zero to 0.28 mg./g. addition of $FeCl_3$. On further increase in the concentration of salt, the recovery fell sharply to nil at 1.1 mg./g. $FeCl_3$ addition.

(c) The effect of metal ion pretreatment.

The mechanism whereby a combination of metal ion and anionic collector improves the hydrophobicity of quartz is complex and not well understood. The general consensus of opinion is that the metal ion adsorbs first on the mineral surface and serves as a link between itself and the collector species. The possibility also exists that the metal ion and the collector may react chemically to form a compound of limited solubility which is attached to the

surface of the mineral.

In an endeavour to elucidate this problem, quartz samples were pretreated with metal ion prior to their reaction with sodium oleate. The resulting pinning values are compared with those attained by the simultaneous treatment discussed above (Section 9.7.3(a)).

The samples were conditioned with $FeCl_3$ or $SnCl_2$ solutions at constant molar concentration and varying pH. After decantation of the liquor, residual salts were removed by washing the solids with distilled water. Sodium oleate solutions of 3.28×10^{-4}M concentration and at pH's identical to those at which metal ion pretreatment had taken place, were added to the solids and the mixture stirred for a further 15 minutes. After decantation the solids were dried and the pinning behaviours determined. The results are listed in table 23, which also includes the pinning values of quartz treated at similar pH's with sodium oleate alone, and also simultaneously with a combination of the relevant metal ion and the organic reagent.

The following observations are drawn from the results of table 23.

(a) The adsorption of Fe^{3+} and Sn^{2+} on to the surface of quartz prior to the sodium oleate treatment, increases the non-conducting properties of the mineral over a wide range of pH. When the inorganic and organic reagents are used

TABLE 23

METAL ION	CONC. X10^{-4}M	INITIAL pH	% PINNING		
			METAL ION FOLLOWED BY OLEATE	METAL ION SIMULTANEOUSLY WITH OLEATE	OLEATE ALONE
Sn^{2+}	8.42	2.5	97.4	98.3	78.5
		3.5	93.9	99.8	80.0
		4.9	99.3	80.1	81.5
		6.5	99.0	77.0	79.5
		8.6	75.5	71.7	72.0
Fe^{3+}	6.00	3.0	88.5	97.2	79.0
		4.4	98.4	90.2	81.5
		5.6	97.5	70.8	81.0
		7.0	87.9	56.5	78.0
		9.1	69.2	68.3	69.5

simultaneously, maximum pinning occurs over a relatively narrow pH range. It has been shown earlier (Section 8) that the adsorption of Sn^{2+} and Fe^{3+} on quartz increases with pH, reaching a maximum at approximately pH 5.5 and 6 respectively. Beyond these critical pH's, metal ion take-up decreases sharply. The subsequent treatment with sodium oleate results in the attachment of hydrophobic organic reagent to the quartz surface at sites covered with metal ion. The maximum pinning value is produced on surfaces containing the maximum amounts of adsorbed metal ion. A decrease in the density of metal ion adsorbed at high hydroxyl ion concentrations, results in a reduced effectiveness of the sodium oleate conditioning.

(b) When Fe^{3+}-treatment is followed by the reaction with

sodium oleate at pH 3.0, the resultant pinning behaviour of the quartz is less than that obtained by the method of simultaneous conditioning. The washing of quartz, previously conditioned in $FeCl_3$ solutions at pH's less than about 4, results in a strong desorption of the metal ion (graph 39). Hence, under these conditions oleic acid will not be readily adsorbed on the Fe^{3+}-depleted surface of the quartz. When the Fe^{3+} ions are present in solution together with the sodium oleate at pH 3.0, there is no hinderance to the adsorption of Fe^{3+} (table 22) and the consequent attachment of hydrophobic reagent.

The above observations, although not conclusive, favour the hypothesis that metal ions must adsorb on the mineral surface and serve as a link between themselves and the organic species.

9.8 Conclusions.

Cationic surface active agents are very effective in decreasing the surface conductivity of quartz and kyanite over a range of pH and above a critical reagent concentration. The decreased conductivity is attributed to (a) the hydrophobicity of the surface of the minerals and (b) the bulk insulating properties of the adsorbed matter. The latter factor is probably of minor significance.

The pinning of the minerals is slightly increased by treatment with an anionic surfactant. This is attributed

to the diminished adsorption of the fatty acid because of the like negative sign of the reagent ions and the mineral surfaces. The addition of Fe^{3+}, Sn^{2+} or Ca^{2+} to the oleate solutions markedly improves the effectiveness of the organic reagent under conditions which result in the strong adsorption of the metal ion.

The pinning behaviour of quartz after treatment with organic surface active compounds resembles the reported floatability of the mineral determined under similar circumstances.

10.0 GENERAL DISCUSSION.

1. The process of high tension separation.

Mineral particles passing through the high tension separator experience the following two major events:

(a) charging in the ionising field.

(b) discharging and inductive charging in the static field.

The charge theoretically acquired by a particle when subjected to ionic bombardment, is never attained in practice as some leakage of charge occurs. There is a simultaneous movement of ions to the surface of the particle and of others from the latter to the earthed drum. At equilibrium a steady-state charge exists which can be considerably less than the theoretical charge for conducting minerals. The factors that influence the quantity of charge acquired by the solids include:

(i) the current flow between the ionising electrode and the drum surface.

(ii) ioniser gap.

(iii) relative humidity.

All three variables control the intensity of the ionising field, while relative humidity has the added effect of lowering the steady-state charge acquired by hydrophilic insulators. The pinning of minerals (P) is related to air humidity (H) by the equation

$$P = -aH + b$$

where a and b are constants.

On leaving the influence of the ionising field, the particle loses its ionic charge to the drum and acquires a charge of opposite sign by a process of induction. The factors that increase the rates of discharging and inductive charging are:

(i) the magnitude of the ionic charge.

(ii) relative humidity.

(iii) the potential difference between the static electrode and the drum.

(iv) drum speed.

(v) the geometry of the ionising and static electrodes.

High moisture contents of the surrounding air increase the charge induced on insulators by improving the surface conductivities.

The magnitude of the induced charge (Q_n) depends primarily on the time (t) spent by the particles in the static field and the potential gradient (E) across the field, according to the equation

$$Q_n = K E e^{-K't}$$

where e = base of natural logarithms and K,K' are constants. The equation shows that voltage has a direct influence on the induced charge. Items (iv) and (v) and ioniser gap control the time, t. High values of Q_n are favoured by low drum speeds, large gaps between the ionising and static fields and large ioniser gaps. The latter factor is of minor significance as decreasing

ioniser gaps have the effects of raising the intensity of the ionic charging and widening the boundaries of the two fields.

2. Air conductivity.

Three of the more important high tension variables, viz. current, voltage and ioniser gap, are related to a single term "air conductivity". The pinning of minerals approaches a limiting value of air conductivity, the magnitude of which depends on the conductivity of the particles.

3. Correlation between pinning and surface conductivity.

The pinning behaviour of chemically-treated quartz is inversely proportional to the surface conductivity of the mineral. The relationship is represented by the equation

$$P = K/S$$

where S = surface conductivity and K = a constant.

4. Modification of the surface conductivities of quartz and kyanite.

The presence of water on the surface of quartz and kyanite decreases their insulating properties. The water may be present in various forms, viz.

(i) part of the hydrated mineral surface.

(ii) "free" molecules on the bare surface.

(iii) associated with adsorbed matter.

(iv) associated with deposited salts.

(v) adsorbed by surface films on the mineral particles.

The pinning behaviours of quartz and kyanite were modified by the following means:

(a) The adsorption of water.

The pinning of quartz is sharply decreased at low coverages of the surface with adsorbed water. This is attributed to the lateral mobility of the initially adsorbed water molecules. The rate of decrease in pinning falls off as monomolecular coverages are exceeded because the adsorbed moisture behaves as bulk water and the surface conductivity depends on the thickness of the adsorbed film. Kyanite does not respond as much as quartz to changes in relative humidity by virtue of the fact that the alumino-silicate surface has fewer silanol sites and hence its capacity to adsorb water is correspondingly less. A water-repellent quartz sample behaves very similarly to the kyanite on changes in water vapour content of the air.

(b) Metal salt treatment.

The conductivity of quartz and kyanite are modified through wide limits by treatment with metal salts. The pH and concentration of the salt solutions are important variables in determining the pinning values of the samples. The maximum adsorption of metal ions and the

maximum change in the pinning behaviours occur in the pH region of precipitation of the relevant metal hydroxides. The concentration of the solutions affects the adsorption of metal ions and the surface charge density of the mineral, both these factors determining the degree of hydration of the mineral surface.

Improved surface conductivities are ascribed to:

(i) the capacity of adsorbed layers to take-up water.

(ii) the water-avidity of deposited salts.

(iii) the increased hydration of the solid surfaces.

Decreased conductivities are attributed to:

(i) the dehydration of mineral surfaces.

(ii) the insulating properties and/or hydrophobicity of oxidised surface layers.

(c) Organic surfactant treatment.

When quartz and kyanite are rendered hydrophobic by treatment with organic reagents, their pinning values are increased. The cationic surface active agents are more effective than an anionic compound in rendering quartz insulating. The effectiveness of the anionic surfactant treatment is greatly enhanced by adding metal salts to the organic solutions and treating quartz under conditions which result in the strong adsorption of the metal ion. The suggested mechanism of metal ion activation is

as follows: Metal ions are initially adsorbed on the surface of the mineral and provide sites on to which the organic matter is attached.

The pinning behaviour of quartz after treatment with the surface active reagents, resembles the reported floatability of the mineral, the one property in common being the hydrophobicity of the mineral grains. The similarity confirms the postulation that increased pinning values can be attributed to the water-repellency of the surface of the minerals. The bulk insulating properties of the adsorbed matter appear to be of minor significance.

5. Surface conductivity increase due to the presence of surface water.

The decreased pinning of an insulator covered with surface water is attributed to:

(i) the increased conductivity of the solid-air interface.

(ii) the dissociation of the water into H^+ and OH^-.

Under the influence of the applied potential in the static field of the high tension separator, the H^+ ions migrate to the negatively-charged drum surface and there are neutralised by free electrons. The OH^- ions move in the opposite direction and concentrate on the face of the particles closest to the static electrode. The result is a further increase in the negative charge acquired by the solids at the solid-air interface by the process of

induction, thereby decreasing the pinning of the mineral grains. It is not implied that the ions behave as in solution. To do this they must acquire their full solvation energy which is only possible when the water layer is greater than 10 molecules thick[108]. However, the mobility of H^+ ions in the adsorbed water layer is the same as in bulk water and may be increased further by the dissolution of salts, alkali impurities on the mineral surface or carbon dioxide from the surrounding air.

REFERENCES.

1. Barthelemy and Mora Int. Min. Proc. Congr. (April 1960).

2. Swart U.S. Patent 959,646 (May 1910).

3. Schniewind U.S. Patent 1,153,182 (Sept.1915).

4. Kakovsky and Revnivtzev Int. Min. Proc. Congr. (April 1960).

5. Brewis D.I.C. Dissertation (1963).

6. Bikerman Surface Chemistry Theory and Application, Academic Press (1958).

7. Lapointe Cand. Dept. of Mines Research Rep. (1962).

8. Ralston Electrostatic Separation of Mixed Granular Solids, Elsevier Publishing Co. (1961).

9. Ng. Ph.D. Thesis, Univ. of London (1963).

10. Dana The System of Mineralogy, Vol.III, John Wiley & Sons,Inc. (1962).

11. Balint Ph.D. Thesis, Univ. of London (1962).

12. Ference et al Analytical Experimental Physics, Univ. of Chicago Press (1956).

13. Balint Dissertation, Royal School of Mines (1959).

14. Hudson Recent Developments in Mineral Dressing IMM (1952).

15. Fraas U.S. Patent 3,012,668 (1961).

16. Gilbert, Warren Spring Lab., Private communication.

17. Pocock Dissertation, Royal School of Mines (1960).

18. Taggart Handbook of Mineral Dressing, John Wiley Inc., N.Y. (1945).

19. Cooke Ph.D. Thesis, Univ. of London (1959).

20. Schnitzler British Intelligence Objectives Sub-Committee Final Report, No.1035 (1946).

21. Grey and Whelan Fuel, Vol.35,184 (1956).

22. Harper Powders in Industry, Soc.Chem.Ind.(1961).

23. Fahrenwald U.S. Patent 2,180,804 (Nov.1939).

24. Fraas AIME Tech. Publ. 2257 (Nov.1947).

25. Simkovich J. Phys. Chem. 67, 1001 (1963)

26. Field J. App. Phys. 17, 318 (1946).

27. Gaudin and Rizo-Patron AIMME Tech. Publ. 1453 (1942).

28. Gibbs J. App. Chem. 3, 213 (1953).

29. Iler Colloid Chemistry of Silica and Silicates Cornell Univ. Press, N.Y. (1955).

30. O'Connor and Greenberg J. Phys. Chem. 62, 1195 (1958).

31. Van Lier, De Bruyn and Overbeek J. Phys. Chem. 64, 1675 (1960).

32. Celland and Ritchie J. App. Chem. 2, 642 (1952).

33. Holt and King J. Chem. Soc. 773 (1955).

34. Parks Contact Electrification of Oxides in Humid Atmospheres Stanford Univ. California (1961).

35. McDonald J. Phys. Chem. 62, 1168 (1958).

36. Hackerman and Hall J. Phys. Chem. 62, 1212 (1958).

37. Gleniser and Rieck Z. Anorg. u Allgem. Chem. 297, 175 (1958).

38. Shapiro and Weiss J. Phys. Chem. 57, 219 (1953).

39. Hockey and Pethica Trans. Far. Soc., 2249 (1961).

40. Loeser, Harkins and Twiss J. Phys. Chem. 57, 219 (1953).

41. Zettlemoyer and Chessick J. Phys. Chem. 58, 243 (1954).

42. Shapiro and Kolthoff J. Amer. Chem. Soc. 72, 776 (1950).

43. Kurosaki J. Phys. Chem. 58, 320 (1954).

44. Gregg The Surface Chemistry of Solids, Chapman & Hall, London (1961).

45. Klassen and Mokrowsoy An Introduction to the Theory of Flotation, Butterworths, London (1963).

46. Karasev, Deryagin and Bochko Koll. Zh. 24, 467 (1962).

47. Marsh and Earp Trans. Faraday Soc., 29, 173 (1933).

48. Mukai et al Trans. Min. Metall. Alumni Assn. Kyoto Univ. Vol.14(10)558 (Dec.1962).

49. De Boer The Dynamical Character of Adsorption Clarendon Press, Oxford (1953).

50. Curtis U.S. Bureau Stds. Bull.11, 359 (1915).

51. Cook, Daniels and Hamilton J. Phys. Chem., 58, 358 (1954).

52. Glasstone An Introduction to Electrochemistry, Van Norstand Co. Inc. N.Y., (1942).

53. Sarakhov Bull. Acad. Sci. USSR Div. Chem. Sci. 2, 150 (1956).

54. Woodley, Warren Spring Lab., Private communication.

55. Jirgensons and Straumanis Colloid Chemistry, Pergamon Press, London (1954).

56. Kruyt Colloid Science, Elsevier Publ. Co. (1952).

57. Feitknecht and Schindler Solubility Constants of Metal Oxides, Metal Hydroxides and Metal Hydroxide Salts in Aqueous Solution, Butterworths, London (1963).

58. Vail Soluble Silicates Vol.1, Reinhold Publ. Cor. N.Y., (1952).

59. Anderson Second Int. Congr. Surface Activity, Butterworths, London (1957).

60. Benton and Elton Second Int. Congr. Surface Activity, Butterworths, London (1957).

61. Derjaguin and Shukakidse Trans. IMM, 70, 569 (July 1961).

62. Plaksin and Olofinsky Trans. IMM, 69, 613 (1960).

63. Sutherland and Wark Principles of Flotation Aust. IMM (1955).

64. Sun, Morgan and Wesner Trans. AIMME, 187, 369 (1950).

65. Linari-Linholm J. Chem. Soc. S. Africa, 51, 131, (1950).

66. Bogdanov et al Int. Min. Proc. Congr. Sweden (1951).

67. Ejgeles Int. Min. Proc. Congr. Sweden (1951).

68. McGlashan Fiftieth Anniversary of Froth Flotation in the U.S.A., AIMMPE (July 1961).

69. Clemmer Flotation of Iron Ores, Univ. of Minnesota (1947).

70. Gaudin et al AIME, 153, 462 (1943).

71. Taggart and Arbiter AIME, 153, 500 (1943).

72. Leja Second Int. Congr. Surface Activity, Butterworth, London (1957).

73. Gutzeit AIME, 153, 505 (1943).

74. De Bruyn and Agar Froth Flotation Fiftieth Anniversary, Vol. AIMMPE (1962).

75. O'Connor and Buchanan Trans. Faraday Soc. (1955).

76. Gaudin Flotation 2nd Ed. McGraw-Hill (1957).

77. Aplan and Fuersteneau Froth Flotation Fiftieth Anniversary Vol. AIMMPE (1962).

78. Gaudin and Rizo-Patron AIME, 153, 462 (1943).

79. Adamson Physical Chemistry of Surfaces Interscience Publ. Inc. N.Y. (1960).

80 Strathmore, Cooke and Digre AIME, 184, 299 (1949).

81. Gaudin, Spedden and Laxen AIMME, 4, 693 (1952).

82. Patrick and Barclay J. Phys. Chem. 29, 1400 (1925).

83. Bungenberg de Jong Colloid Science, Elsevier Publ. Co. N.Y. (1949).

84. Gaudin and Fuersteneau AIMME, 202, 66 (1955).

85. Rinelli Int. Min. Proc. Confer. Cannes (1963).

86. Handbook of Chemistry and Physics The Chem. Rubber Publ. Co. p.3507 (1962).

87. Johnson U.S. Patent 2,090,418 (1937).

88. Fraas and Ralston U.S. Bur. of Mines Research Invest. 3677 (1942).

89. Fraas AIMME, 183, 225 (1949).

90. De Bruyn Mining Eng. 7,291 (1955).

91. Fraas U.S. Patent 2,593,431 (1952).

92. Autenrieth et al U.S. Patent 3,073,447 (1962).

93. Halsey Ph.D. Thesis, Univ. of London (1961).

94. Tamamushi and Tamaki Second Int. Congr. Surface Activity, Butterworths, London (1957).

95. Gaudin and Morrow AIME, 199, 274 (1954).

96. Ross. W. Smith South Dakota School of Mines, Abstract in Min. Eng. 15, 56, Aug. 1963.

97. Jaycock and Ottewill Trans. IMM, 72, 497 (April 1963).

98. Soane Ph.D. Thesis, Univ. of London (1959).

99. Fuersteneau AIME, 208, 1365 (1957).

100. Gaudin and Bloecher AIMME, 187, Tech. Pub. 2813D, 499 (1950).

101. Alexander and Johnson Colloid Science, Oxford Clarendon Press (1950).

102. Wada In. Min. Proc. Congr. (1960).

103. Wasson et al U.S. Bureau of Mines Research Invest. 6199 (1963).

104. Polkin Diss. Int. Min. Proc. Congr. London (1960).

105. Tomlinson Ph.D. Thesis, Univ. of London (1963).

106. Peck and Wadsworth Froth Flotation Fiftieth Anniversary Vol. AIME N.Y. (1962).

107. Gaudin and Chang Min. Eng. 237 (Feb.1952).

108. Guerney Ions in Solution, Cambridge Univ. Press (1936).