

PHYSICO-CHEMICAL INVESTIGATIONS OF  
THE FLOTATION AND SELECTIVE FLOCCULATION  
OF MINERALS

A thesis submitted for the degree of  
Doctor of Philosophy in the University of London

by

Baki Yarar

Imperial College of Science and Technology, London. S.W.7.

October 1969.

ABSTRACT

The thesis consists of two parts. In part I, an electro-chemical investigation of the galena-diethyldithiocarbamate-oxygen flotation system is reported.

As a result of this investigation it has been established that oxygen is necessary for the flotation of galena with this collector and the formation of a saturated solution of tetraethylthiuramdisulphide is not essential for good flotation.

Also in part I the preparation of low resistance ZnS electrodes which is essential for an electrochemical investigation involving the surface oxidation of sphalerite and sphalerite-flotation collector interactions, together with a possible experimental procedure are described.

In part II, the colloidal phenomena related to mineral slimes are considered and a review of the published literature on selective flocculation is given.

Galena, quartz and calcite have been taken as representative mineral classes and the physico-chemical properties of their suspensions, one by one and in mixtures, studied. The effects of simple inorganic ions on the stabilities of these mineral suspensions are reported.

Evidence is presented in support of the dissolution mechanism of powdered quartz suspensions being by an initial breakage of the disturbed layer into fragments, which in turn dissociate into silicic acid.

The optimum conditions for flocculation by polymeric flocculants and activation of minerals by ions for flocculation are established and the related physico-chemical phenomena discussed.

The effects of mutual coagulation, polymer uptake, solids content, and nature of the flocculant on selectively flocculating one or more components from a mixture of minerals are reported.

The problem of "entrapment" and ways of overcoming it are illustrated, and it is shown that the physico-chemical principles governing selective flocculation of mineral slimes are closely related to those in the well-known froth flotation processes.

ACKNOWLEDGEMENTS

I should like to express my sincere gratitude to Dr. J. A. Kitchener for his patient guidance and encouragement over the past three years.

I am grateful to Mr E. A. Gill of B.T.I. Chemicals Limited, Bradford, for sponsoring the project on selective flocculation.

I should also like to thank my friends and colleagues in the Royal School of Mines, for their frequent assistance and useful discussions.

I am also indebted to the Department of Chemistry, the Middle East Technical University, Ankara, Turkey for providing the grant which enabled me to carry out the research forming Part I of this thesis and for leave of absence during my stay in this country.

PART I.

	<u>Page</u>
CHAPTER 1. Electrochemical Investigation of the Galena - Diethyldithiocarbamate - Oxygen System	
1.1 Introduction	10
1.2 Aim and method of investigation	11
1.3 Materials and apparatus	12
1.4 Preliminary experiments on the effect of oxygen on the flotability of galena by DEDTC	15
1.5 Effect of time and variation of galena electrode potential with oxygen and air	17
1.6 Construction of the current potential diagrams and results	19
1.7 Oxidation of DEDTC	24
1.8 The standard redox potential of the reaction $2(\text{C}_2\text{H}_5)\text{NCSS}^-_{(\text{aq})} = (\text{C}_2\text{H}_5)_4(\text{NCSS})_2 + 2\text{e}$	26
1.9 Stability of DEDTC solutions and effect of platinum	29
1.10 Discussion	30
1.11 Summary of results and conclusions	38
1.12 References	39
CHAPTER 2. Surface oxidation of zinc sulphide	
2.1 Introduction	42
2.2 Aim and method of investigation	46

CHAPTER 2 (continued)	<u>Page</u>
2.3 Materials, apparatus and procedure	46
2.4 Preparation of low resistance ZnS electrodes	47
2.5 Experiments and discussion	49
2.6 References	54

PART II .

CHAPTER 1 **Introduction**

1.1 General Concepts	58
1.2 Coagulation and flocculation processes	65
1.3 Previous work on selective flocculation	66
1.4 Aim of the present work and choice of the experimental system.	70

CHAPTER 2 **Experimental** techniques and apparatus

2.1 Measurement of the degree of flocculation	72
2.2 Method of flocculant addition	73
2.3 Electrophoretic mobility and zeta-potential measurements	74
2.4 Determination of small quantities of flocculants	80
2.5 Other experimental techniques	83

	Page
CHAPTER 3. Preliminary Experiments	
3.1 The minerals used	85
3.2 The B.T.I. flocculants	86
CHAPTER 4. Stability and flocculation of quartz suspensions.	
4.1 Introduction	90
4.2 Experiments on the stability of quartz suspensions.	93
4.3 Coagulation of quartz suspensions by divalent cations	98
4.4 Electrokinetic measurements	104
4.5 Solubility of quartz in aqueous suspensions	107
4.6 Electron microscopy of quartz suspensions	110
4.7 Discussion	115
CHAPTER 5. Stability and Coagulation of calcite suspensions	
5.1 Introduction	121
5.2 Experimental pH values of $\text{CaCO}_3$ suspensions	124
5.3 Stability of $\text{CaCO}_3$ suspensions	124
5.4 Summary	132
CHAPTER 6. Stability and coagulation of lead sulphide suspensions	
6.1 Introduction	133

CHAPTER 6. (continued)	Page
6.2 Stability of PbS suspensions and potential determining ions.	134
6.3 Summary	140
CHAPTER 7. Flocculation of calcite, galena and quartz by polymeric flocculants	
7.1 The bridging mechanism of flocculation	141
7.2 Adsorption and flocculation	145
7.3 Molecular weight and flocculation	147
7.4 Adsorption processes of flocculants	150
7.5 Optimum conditions of flocculant additions and optimum quantities	153
CHAPTER 8. Coagulation and flocculation of minerals in mixtures	
8.1 Mixture of calcite and quartz	168
8.2 The galena + quartz and galena + calcite systems	171
8.3 Effects of metal ions on the flocculation of minerals by flocculants	172
8.4 Summary	180
CHAPTER 9. Selective flocculation of PbS, CaCO <sub>3</sub> and SiO <sub>2</sub> from mixtures	
9.1 Experimental results of separations	183
9.2 The problem of entrapment	197



CHAPTER 9 (continued)	<u>Page</u>
9.3 Effect of grinding minerals together on selectivity	201
CHAPTER 10. Summary of conclusions	205
REFERENCES	210
APPENDIX A	222
" B	223
" C	224
" D	226
" E	228

PART I.

ELECTROCHEMICAL INVESTIGATION OF THE  
PbS - (C<sub>2</sub>H<sub>5</sub>)NCSS<sup>-</sup> - O<sub>2</sub> SYSTEM AND  
OXIDATION OF ZnS

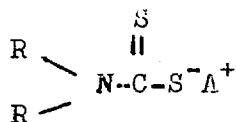
1. Electrochemical Investigation of the Galena-Diethyldithiocarbamate-Oxygen System

1.1 Introduction

Concentration of sulphide minerals by flotation with sulphohydril collectors is universally practised. This does not mean, however, that the various physico-chemical processes involved are completely understood.

In the early days, it was already recognised that the hydrophobization of the surface is preceded by the abstraction of part of the collector reagent by the mineral from the aqueous solution, and conditioning of the pulp by agitation with air led to a better recovery. Systematic research towards the understanding of the physical chemistry of flotation may be said to have started with the construction of the bubble-machine (1) and its perfection (2), together with the establishment of the conditions for the preparation of mineral surfaces free from hydrophobic contaminants as well as the establishment of the "contact angle concept" (3)(4)(5). The historical development of the flotation theory has been reviewed by a number of authors (6)(7)(8)(9) and the present day understanding of the flotation theory has been given concisely by Fleming and Kitchener (10).

Di-substituted-dithiocarbamates having the structural formula



(where  $\text{A}^{+}$  is an alkali-metal ion) have been experimentally used for the flotation of sulphide minerals (7)(11)(12)(13)(14) but not to the extent of dithiocarbonates (xanthates)

$\text{R-O-C}^{\overset{\text{S}}{\parallel}}\text{-S}^- \text{A}^+$ . Their plant application in this field seems to have been hampered by their relative cost (12). Consequently information relevant to the use of these substances in mineral processing is less abundant than that related to their use in medicine and rubber technology(14).

It was concluded by Tolun and Kitchener (15) as a result of an electrochemical investigation of the galena-ethylxanthate-oxygen flotation system that "strong bubble contact - thus good flotation - could only occur under conditions where a mixed film containing lead xanthate and dixanthogen might be expected to form". Glikov (16) has also inferred from investigations of a number of sulphide and nonsulphide mineral-collector systems that "It can be assumed that the action of dithiocarbamates.... as flotation collectors in many cases was connected with their ability to oxidize with the formation of oily substances". The oxidation of sulphohydril collectors and the importance of the resulting products in flotation is a question now receiving attention in several laboratories.

## 1.2 Aim and method of investigation

Sodium diethyldithiocarbamate was selected as a flotation collector for galena to elucidate its mode of action and see if it would behave like xanthates, leading to the possible generalization that "dithio-compounds have to oxidize to their respective disulphides before they can act as flotation collectors". Cook (45) has gone so far as to postulate this extreme hypothesis.

The electrochemical technique employed is based on the fact that a reversible electrode exhibits characteristic potentials depending on the composition of the solution it contacts with (17)(18); and electrodes have been successfully employed in corrosion studies (19)(20), in the dissolution of minerals for hydrometallurgical processes (21) and in relation to flotation

and allied phenomena (22)(23). Galena is a good electronic semi-conductor and hence can be used as an electrode in a cell (45)(18). The electrode processes are studied by either following the self-polarization of an electrode (metal or mineral) under the influence of solution composition as a function of time (19)(24a and 24b), or the electrode is deliberately polarized and a current-potential diagram constructed, which permits the related electrode phenomena to be deduced (23)(25)(26)(27).

In this study the self-polarization of the galena electrode under the influence of oxygen was used together with the polarogram construction method which was combined with bubble contact experiments as in the work of Tolun and Kitchener (15).

### 1.3 Materials and apparatus

- a. Sodium diethyldithiocarbamate (abbreviated here as DEDTC): B.D.H. "Analytical grade" DEDTC  $(C_2H_5)_2NCSSNa \cdot 3H_2O$ , was re-crystallized three times from ether solutions by the addition of acetone and the resulting white, flaky, crystals were kept in a desiccator. Solutions were prepared by dissolving weighed quantities of these crystals in double-distilled water adjusted to pH 9.2 by M/20 sodium borate. The stability of these solutions is discussed in section 1.9 below.
- b. Nitrogen: "White-spot" "Oxygen-free" nitrogen was further purified by passing it at a maximum rate of 100ml/min. over a closely packed 100 mesh copper gauze over a length of 60cm. at  $480^\circ C$  and then through a wash-bottle filled with double-distilled water prior to use.
- c. Working electrodes: A platinum electrode was made of a  $1cm^2$  foil suitably fused to the end of a ground-glass cone. It was repeatedly washed with acid and distilled water and

finally heated to redness prior to use. Galena electrodes were made of a carefully cleaved  $\frac{1}{2}$ cm diameter crystal placed in a glass holder and kept there by "Araldite" resin. Before use, galena electrodes were placed in 5% acetic acid solution for 5 minutes (to dissolve any oxidation products), then rinsed and placed in 5%  $\text{Na}_2\text{CO}_3$  solution for a few minutes and finally in approx. 5%  $\text{Na}_2\text{S}$  solution for about 10 minutes to convert the surface fully to sulphide. They were washed with buffer solution (pH 9.2) prior to introduction into the cell and rinsed with deoxygenated buffer in the cell, prior to use.

d. Apparatus: The apparatus shown in figure 1-1 was adopted for the dual purpose of polarogram construction and the oxidation of ZnS discussed in chapter 2. The part used in polarogram construction consisted of two vessels; (i) for the conditioning of solutions by nitrogen, air, or oxygen and (ii) the actual measurement cell. Both cells were provided with gas outlets connected to water traps via (T). A calomel electrode (CL) was connected to the cell via a saturated-KCl agar bridge. A capillary (CP) connected to a micrometric syringe (SY) via (FL) a flexible tubing (allowing the movement of (CP)) provided for the bubble contact experiments. The electrodes were a working electrode (WE) and a polarization electrode made of platinum (PE). Other attachments comprised a current source (CS) (AC/DC rectifier IE, type DS 50/2), a recorder (RC) (TOA Electronics Ltd., Japan, Electronic polyrecorder model EPR 2T) and a pH-meter (PYE Dynacap pH-meter-mV meter) used both for pH measurements (PM) and as a potentiometer (PO). The cell was connected to earth via a  $0.5\mu\text{F}$  condenser and a platinum wire in order to discharge any static electricity that might develop on the walls of the vessel. The condenser was merely a safety measure to prevent any high intensity current passing in case of a break-down in the rectifier used, since sometimes potentials as high as 40V were applied.

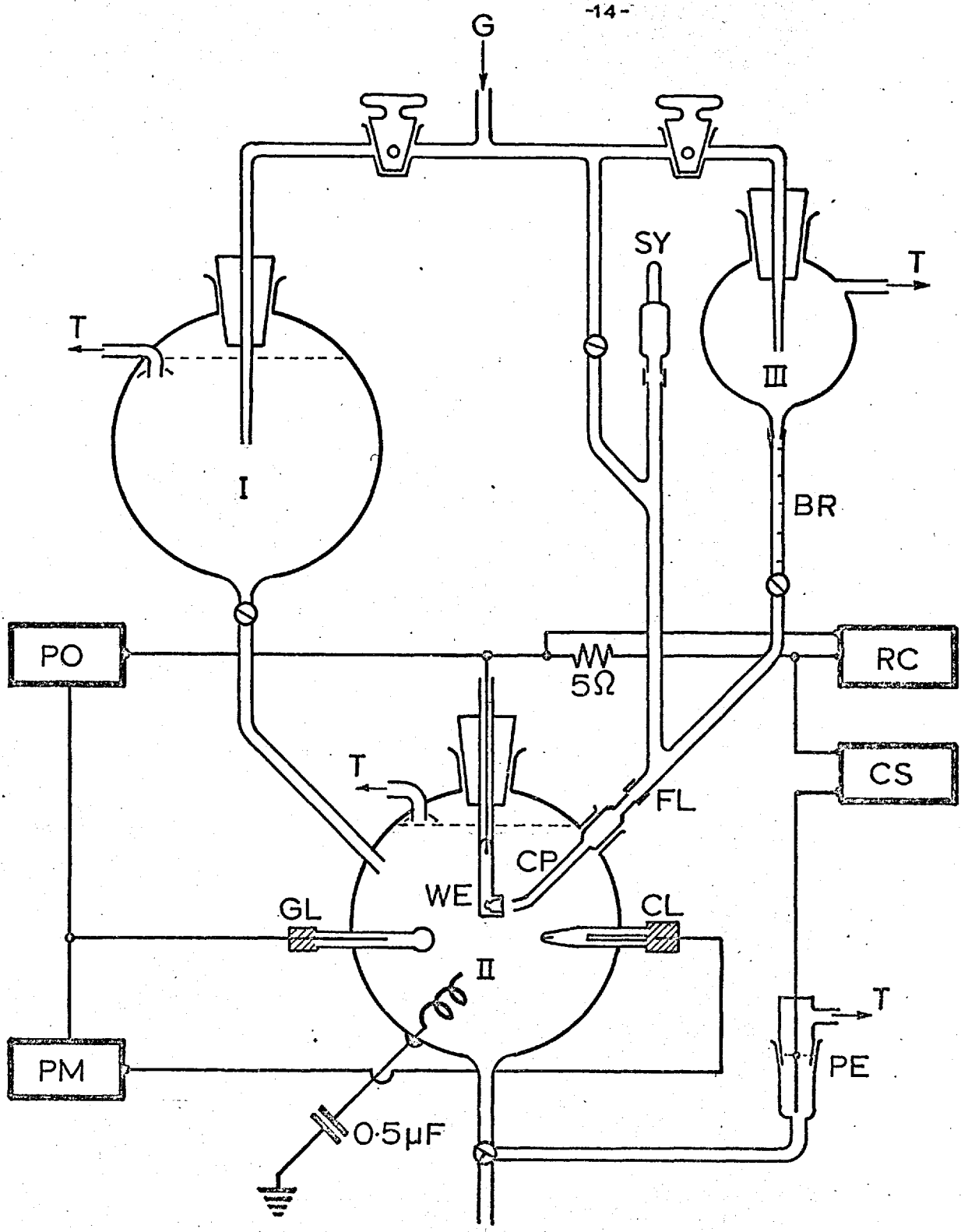
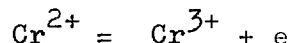


Fig. 1.1 Diagram of experimental set-up used in determining electrode potentials.

e. Reliability of the cell and calibration of the potentiometric set-up: That the nitrogen was oxygen-free and the cell gas-tight was ensured as follows:

The redox potential of a solution of chromous salt,



at initial  $\text{Cr}^{2+}$  concentration of  $1.574 \times 10^{-3} \text{M}$  prepared according to Vogel (28), assumed a constant value of  $-345 \text{mV}$  (vs SCE) with the platinum electrode dipped in it and did not change by more than  $5 \text{mV}^{\#}$  under stirring by nitrogen for 13 hours. Calculation shows that the oxygen content of the nitrogen could not have exceeded  $3 \times 10^{-5} \text{ mol per cent}$ .

The pH meter was calibrated with borate buffer of pH 9.2 and that no further calibration was necessary was deduced from the fact that the redox potential of a quinhydrone electrode at pH 4 was  $-462 \text{mV}$  vs NHE (theoretical  $-463 \text{mV}$ ).

#### 1.4 Preliminary experiments on the effect of oxygen on the flotability of galena by DEDTC

As in the case of xanthates, whether oxygen is necessary for the flotation of galena by DEDTC was checked as follows:

The set-up shown in figure 1-2 was constructed. It consisted of a deoxygenated water reservoir (A), galena attrition cell (B) adopted from an 11cm Buchner funnel placed on a mechanical flask agitator, and a flotation cell (C). This set-up allowed a conventional flotation experiment to be performed in the absence or presence of oxygen in the medium without interruption of the operations for the introduction of galena or reagents. The test was carried out as follows:

Hand picked galena crystals of about  $1 \text{cm}^3$  size were

\* This change took place within the first 30 minutes



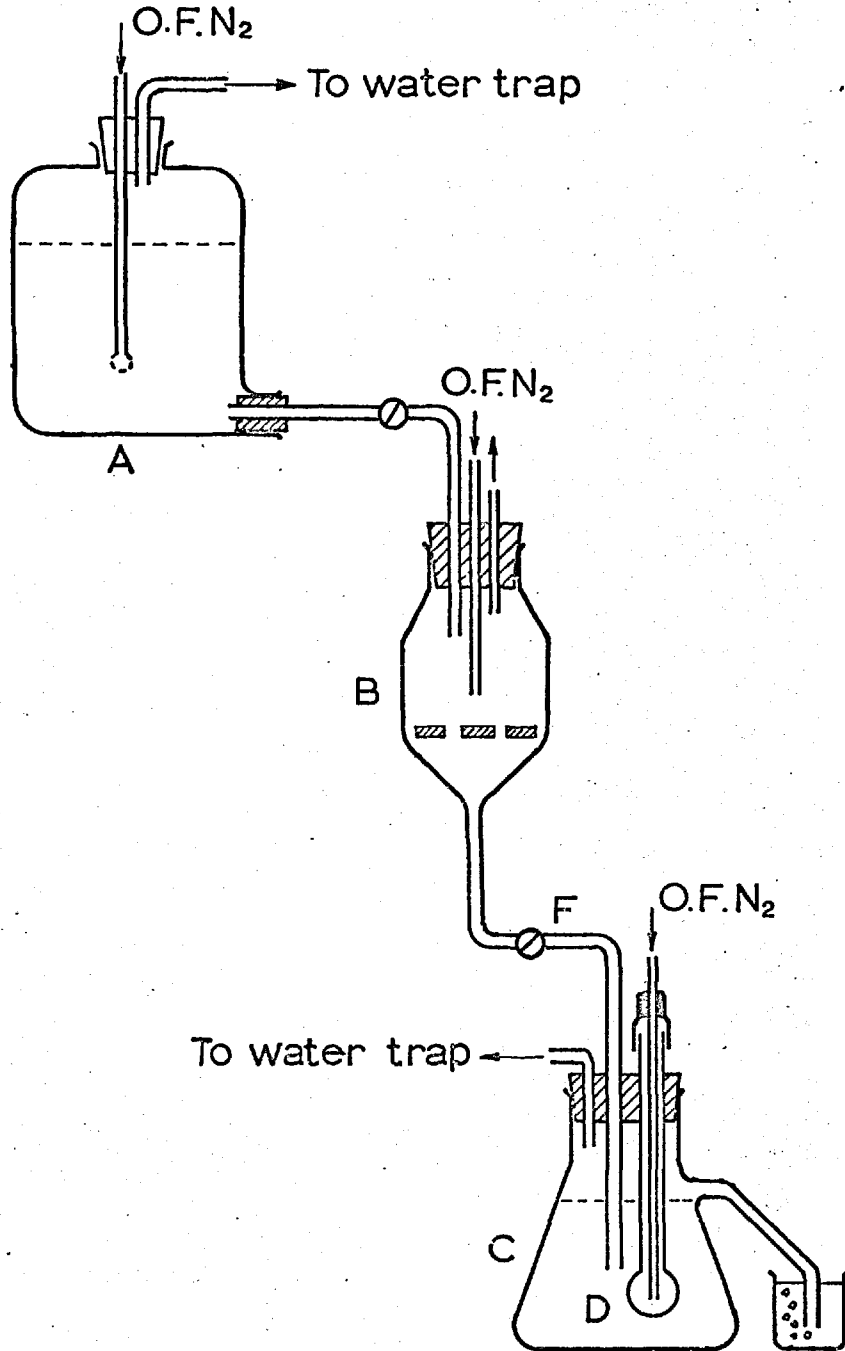


Fig.1:2 Diagram of the experimental set-up for the flotation of galena under controlled conditions.

placed in (B) with quartz of the same size to act as grinding agent under a continuous stream of oxygen-free nitrogen. The water was allowed to flow dropwise and the cell set vibrating. When galena crystals were reduced to about half their original size to remove oxidized layers, they were washed with a stream of water via (F) which is a flexible tube connected as shown in the figure, and the whole system kept under nitrogen. The attrition operation was further continued with collection of the fines in (C), which was occasionally tilted to allow any floatable galena to flow to waste. The operation was continued until the quantity of hydrophobic contaminated galena was negligible. The bulb (D) contained a quantity of DEDTC calculated to give  $10^{-3}M$  solution when introduced into the flotation cell. When the carbamate was allowed into the flotation cell by breaking (D) no galena collected in the water-gas interface after 5 minutes of agitation; on the other hand when washed air was allowed into the cell, flotation was observed in less than 1 minute and the quantity of floating galena increased as the bubbling time was extended.

Thus it was conclusively shown that air is necessary for DEDTC to act as a flotation collector on galena. This conclusion is similar to that reached for xanthate in the work of Plaksin and coworkers (8)(46)

#### 1.5 Effect of time and variation of galena electrode potential with oxygen and air

When galena was placed in a borate buffer solution at pH 9.2 it attained a steady potential of -500mV (vs. SCE) in a short time under agitation with nitrogen. When agitation was stopped, a shift of potential of about 20mV in the more negative direction was observed, as can be seen in region I of figure 1-3. In the presence of  $10^{-3}M$  DEDTC and the same

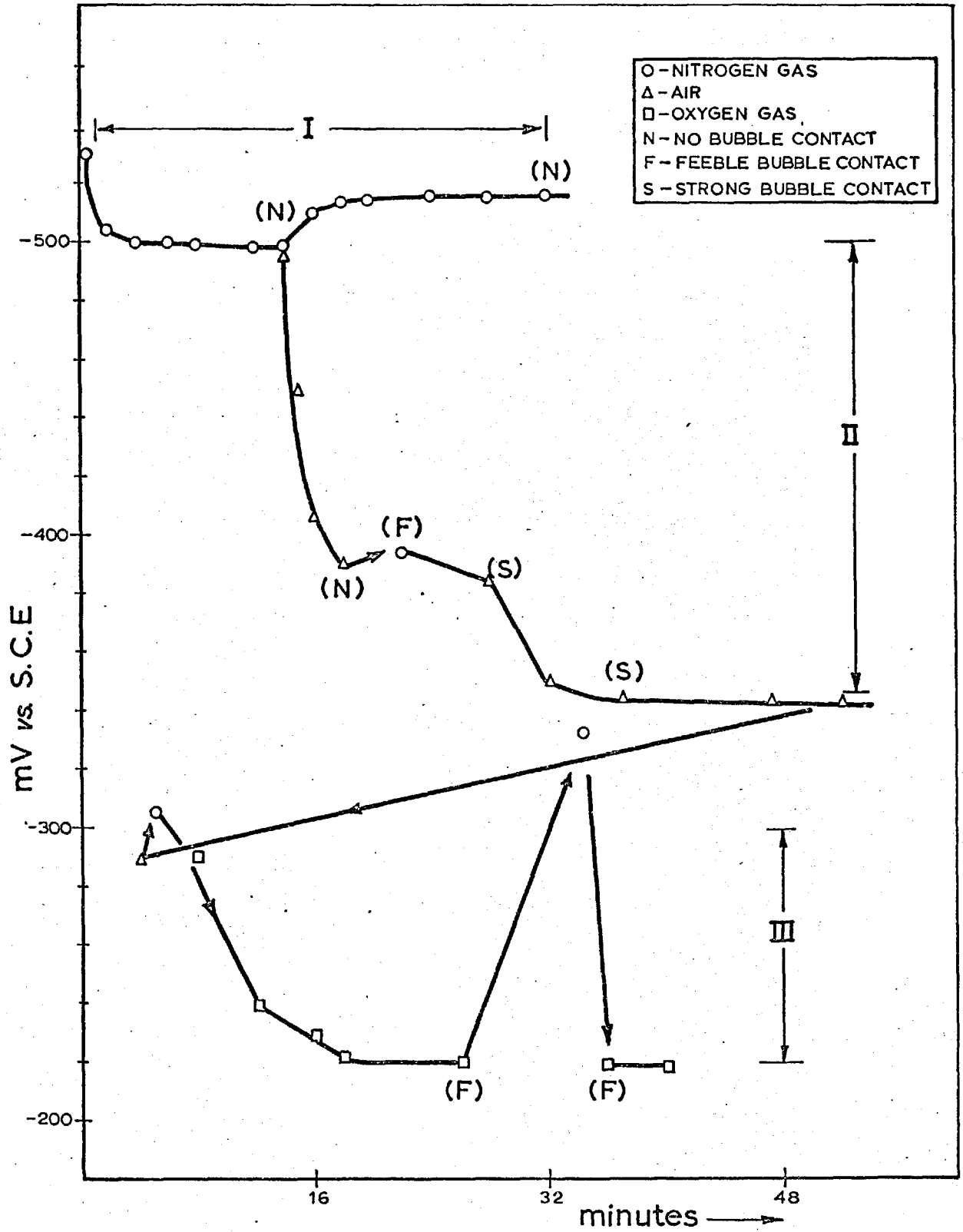


Fig. 1-3 Self polarisation of galena under oxygen, by time.

pH no change in potentials other than the above were observed until air was introduced into the system, as seen in region II of the same figure. With the introduction of air, the potential rose to  $-390\text{mV}$  in 4 minutes. Only feeble bubble contact was observed at this potential (point indicated by (F)). With the interruption of the air stream and the introduction of nitrogen for the bubble contact test the potential tended to move in the negative direction. Strong bubble contact was observed at about  $-385\text{mV}$ . The passage of more air brought the electrode potential to a steady value of  $-340\text{mV}$  which rose by only  $20\text{mV}$  after contact with air for eight hours. The introduction of oxygen gas however, brought about a further rise in the positive direction which steadied out at  $-220\text{mV}$ . When nitrogen was again passed instead of oxygen the potential shifted back to the air value. It was noted that in the presence of oxygen a white film developed slowly on the surface of the electrode and bubble contact ceased to be strong.

#### 1.6 Construction of the current-potential diagrams and results

For the construction of polarograms, the working electrode was placed in cell II in figure 1-1 and the aerated or deaerated solution ran from cell I. The equilibrium potentials or shifts in potentials were noted on the pH-mV-meter initially and the electrode polarized anodically or cathodically with a certain applied potential, the current flowing through the system being recorded continuously. Potential adjustments were made at 30 second intervals. Anodic and cathodic parts of the curves were constructed separately, each time using a fresh solution and treating the electrodes as described above in section 1-3c. Bubble contact experiments were made in a preliminary run for each region at every stage of potential increase and were finally repeated at selected potentials. Polarograms for the systems:

- a) Pt - base -  $N_2$
- b) Pt - base -  $O_2$
- c) Pt - base - DEDTC -  $N_2$
- d) Pt - base - DEDTC -  $O_2$
- e) PbS - base -  $N_2$
- f) PbS - base -  $O_2$
- g) PbS - base - DEDTC -  $N_2$
- h) PbS - base - DEDTC -  $O_2$

were constructed.

a. Platinum-base-nitrogen. The rest-potential of the platinum electrode dipping into borate buffer at pH 9.2 was -60mV to -100mV under no agitation and a shift of 50 to 100mV could be observed when nitrogen gas was bubbled through, making the potential more negative. In the cathodic range, the passage of current was less than 20 $\mu$ A before -800mV was reached whereas in the anodic range the same current was reached at +850mV. (The products of electrolysis are ofcourse,  $H_2$  on the cathodic side and  $O_2$  on the anodic).

b. Platinum-base-oxygen: The introduction of oxygen gas into the system shifted the potential to more +ve values, attaining a rest-potential of +140mV in an oxygen saturated solution under no agitation. The passage of current was not recordable before +700mV in the anodic range whereas a plateau in the cathodic interval of -70 to -750mV, which corresponds to the electrolytic reduction of oxygen on platinum, was recorded.

c. Platinum-base-DEDTC- $N_2$ : The deaerated  $10^{-3}M$  DEDTC solution gave -170mV which would be reproduced each time a clean electrode and a fresh solution were used. However, on standing, a slow drift in the negative direction set on, possibly indicating the adsorption of the carbamate on to the electrode. Adsorption was also indicated by the suppression of hydrogen evolution by about 200mV seen as difference D, between curves a and c in

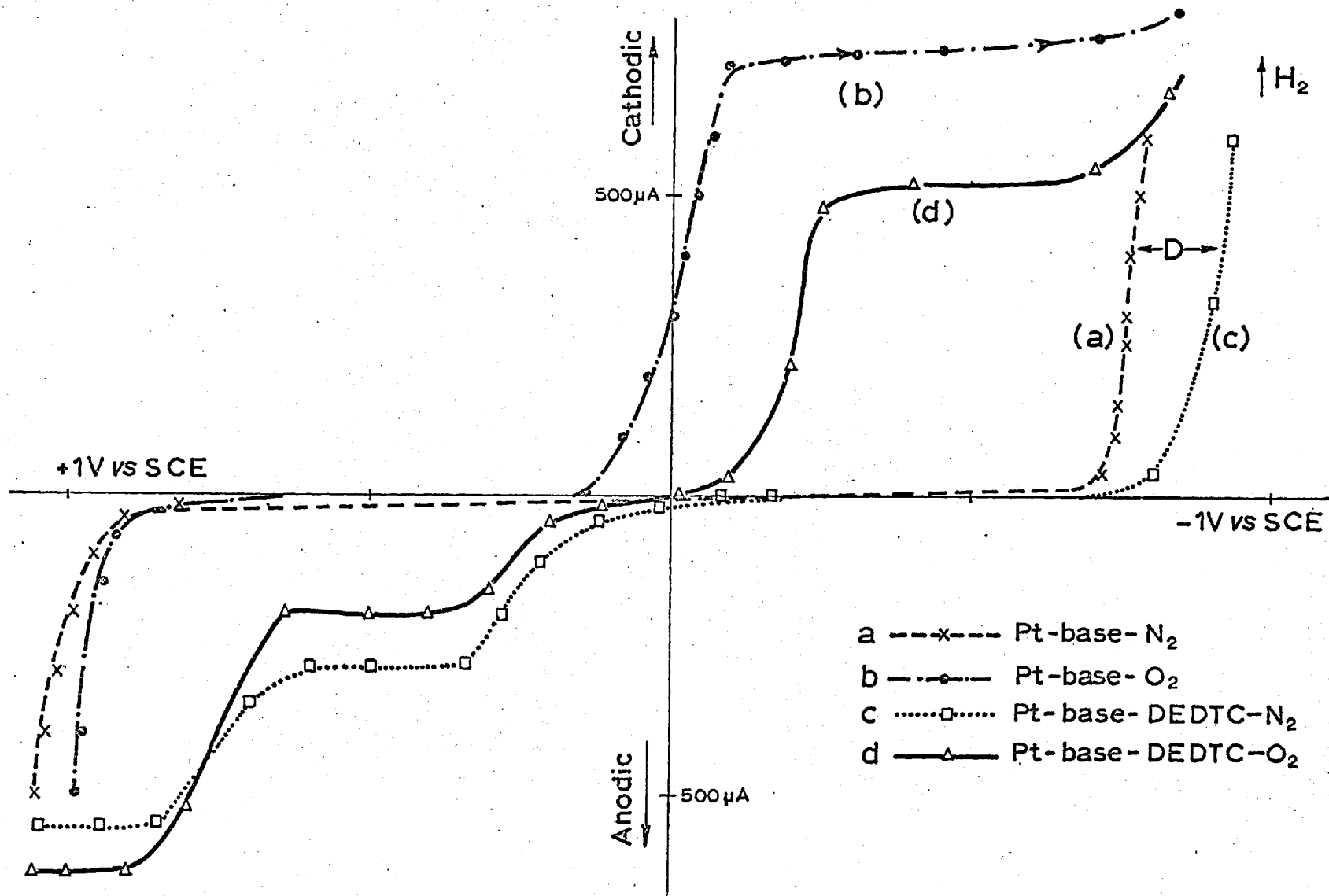


Fig.1-4 Polarograms with a Pt electrode.

figure 1-4. In line with this, the electrode became hydrophobic even during the evolution of hydrogen gas which has been reported not to occur with xanthate under the same conditions (15). It appears that DEDTC is strongly chemisorbed by platinum. The carbamate up-take by platinum was investigated separately and is given in section 1-9 below.

In the anodic range, it was possible to observe two steps in the polarogram, the first between +130 to +700mV, with a current passage of 130 to 300 $\mu$ A/cm<sup>2</sup>. At this stage a white film developed on the surface of the electrode eventually separating as a white cloud, slowly dispersing in the medium. This solid was later identified as tetra-ethylthiuram disulphide, the analogue of dixanthogen the oxidation product of xanthates. The formation of tetra-ethylthiuram disulphide is further discussed in section 1.7 below.

A second oxidation step occurred at potentials > +700mV. It was indeed noted during the titration of DEDTC solutions with iodine, that beyond the appearance of the first end point iodine was further consumed. It has also been observed by other investigators (23) that the introduction of an organic phase like petroleum ether, CCl<sub>4</sub> or CHCl<sub>3</sub> into the titrated solution gives more reliable results. This must merely mean that the first oxidation product, which is insoluble in water but in these organic phases is kept away from the reach of I<sub>2</sub> as soon as it is formed, to avoid further oxidation. The product of the second oxidation stage was not further investigated since such high potentials are never reached in ordinary flotation systems.

It was difficult to follow bubble contact while the oxidation product was being formed, but if the current was switched off to stop the propagation of electrolysis, strong bubble contact was observed.

d. Platinum-base-DEDTC-O<sub>2</sub>: In the presence of oxygen, the static potential was -15mV (in contrast to +140mV in absence of carbamate) under similar conditions, indicating strong adsorption of carbamate on platinum. The plateau in the cathodic range corresponding to the reduction of oxygen started at -250mV instead of -70mV in the absence of carbamate and the shift towards H<sub>2</sub> evolution potentials was slower with a current passage of about 500µA.

The first stage of oxidation in the anodic range started at similar potentials to those in presence of N<sub>2</sub> alone and stronger adsorption of carbamate in presence of O<sub>2</sub>, was further indicated by a lesser current passage. The reversal of the passage order of current for potentials corresponding to the second stage of oxidation as seen in figure 1-4 may probably mean that the products of this stage are less "poisoning" for platinum than tetra-ethylthiuram disulphide. Preliminary evidence to the effect that the poisoning film is electrolytically decomposed was found when a tetra-ethylthiuram disulphide suspension, made by the careful addition of I<sub>2</sub> solution to DEDTC, was electrolysed at 21°C under 2V d.c. and 500µA at pH 9.2 for 18 hours. The anode at the end of this time was covered with a yellow-brown substance not reducible by 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

e. PbS - base - N<sub>2</sub>: The static potentials of this system were fairly reproducible and gave -500mV (vs. SCE). If the electrode was polarised to potentials more negative than -700mV upon cutting off the current the potential dropped steadily towards this value and remained constant. No bubble contact was observed in the anodic or cathodic range, showing that the electrode was fully hydrophilic.

f. PbS - base - O<sub>2</sub>: Introduction of oxygen gas to the system caused an immediate shift to more positive potentials and a



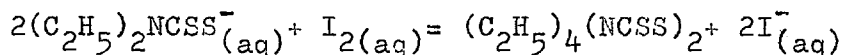
constant value of -80mV was reached in 30 minutes. This value could be reached upon longer agitation with air instead of oxygen.

g. PbS-base-DEDTC-N<sub>2</sub> : In the absence of air, the galena electrode in a solution of 10<sup>-3</sup>M DEDTC gave a rest potential closely similar to that in the absence of carbamate (i.e. ca. -500 mV) and no bubble contact was observed before anodic polarization was applied. The bubble contact was feeble initially but became stronger at potentials more positive than -350 mV. Upon cutting off the current at +100mV the potential tended to shift in the negative direction; however, strong bubble contact persisted. The plateau corresponding to the electrochemical formation of tetra-ethylthiuramdisulphide started at about +100mV and the solid fell into the medium as particles which appeared to be shooting off individual pinholes on the surface. In the presence of this solid, bubble contact was much less strong.

h. PbS-base-DEDTC-O<sub>2</sub> : The static potential for this system was -220mV. Hydrogen evolution in the cathodic range was impeded. Cathodic polarization similar to other cases involving 10<sup>-3</sup>M DEDTC was characterized by two steps but in contrast to the PbS-base-DEDTC-N<sub>2</sub> system, current passage was lower for the anodic potentials. The polarograms of the galena electrode are given in figure 1-5.

#### 1.7 Oxidation of DEDTC

If iodine is added to a carbamate solution, as mentioned earlier, a white oxidation product is formed according to the equation:



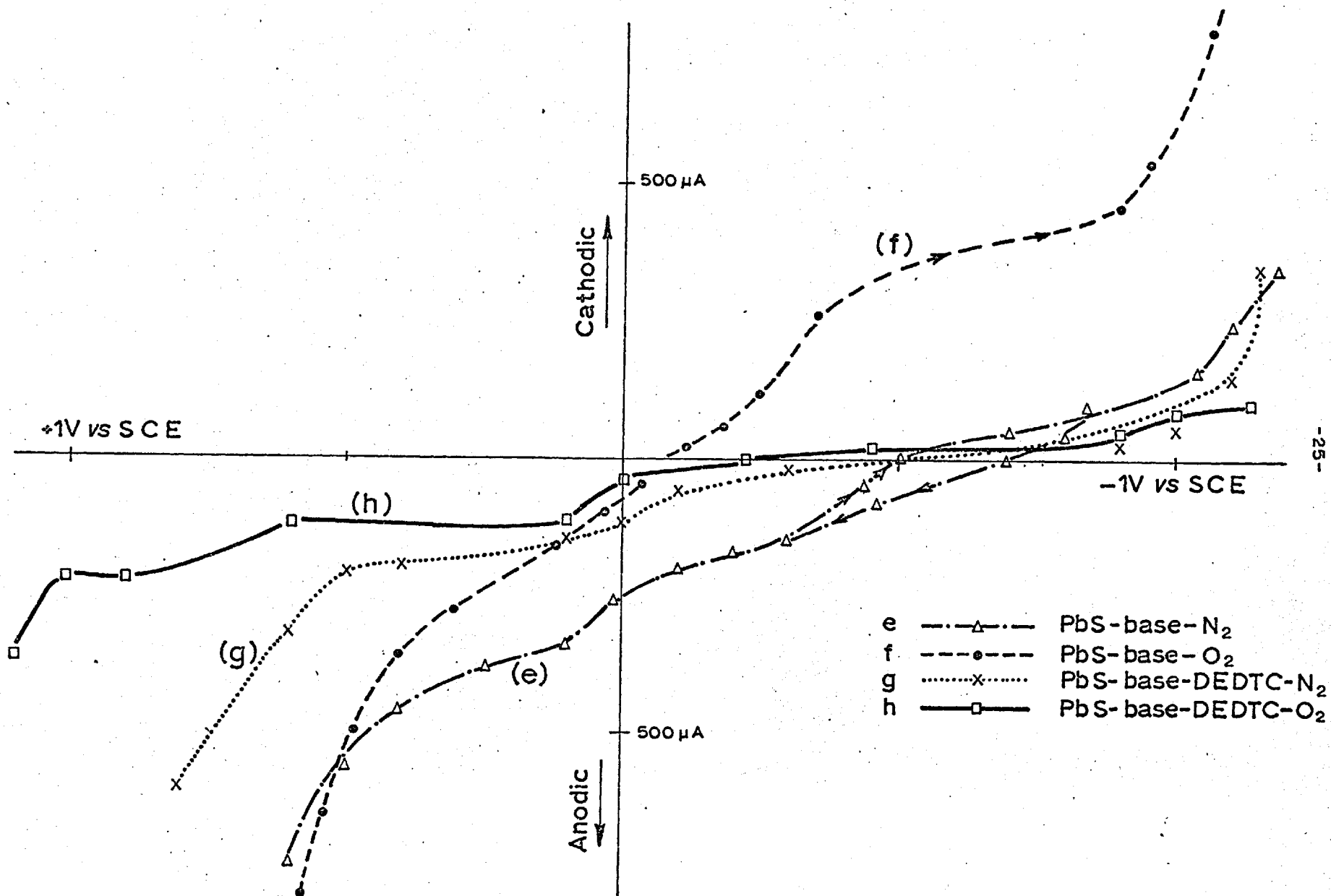
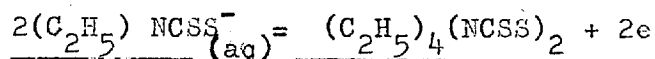


Fig. 1-5 Polarograms with a galena electrode

The solid, filtered washed and recrystallized from ethanol gave a m.p.  $70.5 \pm 0.5^\circ\text{C}$ . The white precipitate obtained by electrolyzing DEDTC solution at 0.5 V and similarly crystallized gave the same m.p. which corresponds to the melting point of tetraethylthiuram disulphide. Furthermore, a microanalysis of this solid gave the formula  $\text{C}_{10}\text{H}_{20}\text{N}_2\text{S}_4$ , confirming the identity of the substance (30).

1.8 The standard redox potential for the reaction



A clean platinum electrode was partially coated with the disulphide by electrolyzing a DEDTC solution at pH 9.2, employing another Pt electrode for cathode. The white film was visibly not adherent to the metal; however, it was possible to keep parts of it by taking the electrode out slowly and drying the solid laden droplets with the tip of a filter paper. The electrode thus prepared was immersed into deaerated solutions of DEDTC of known concentrations in which some solid was previously dispersed by ultrasonics to produce a saturated solution. The potentials were not steady and a continuous drift in the negative direction was observed. Alternatively an uncoated platinum wire was used but the situation persisted, not allowing a reversible electrode potential to be reached. This was shown to be due to the take up of DEDTC by platinum, by spectrophotometric analysis described in section 1.9.

It is known that thio-compounds do "poison" platinum which has a high catalytic activity (31), whereas gold is much less catalytically active. Therefore a gold electrode was tried for the determination of the redox potential in question. The electrode was obtained by electrolytically coating a platinum wire with gold. With this electrode it was possible to obtain fairly steady potentials. Carbamate solutions of

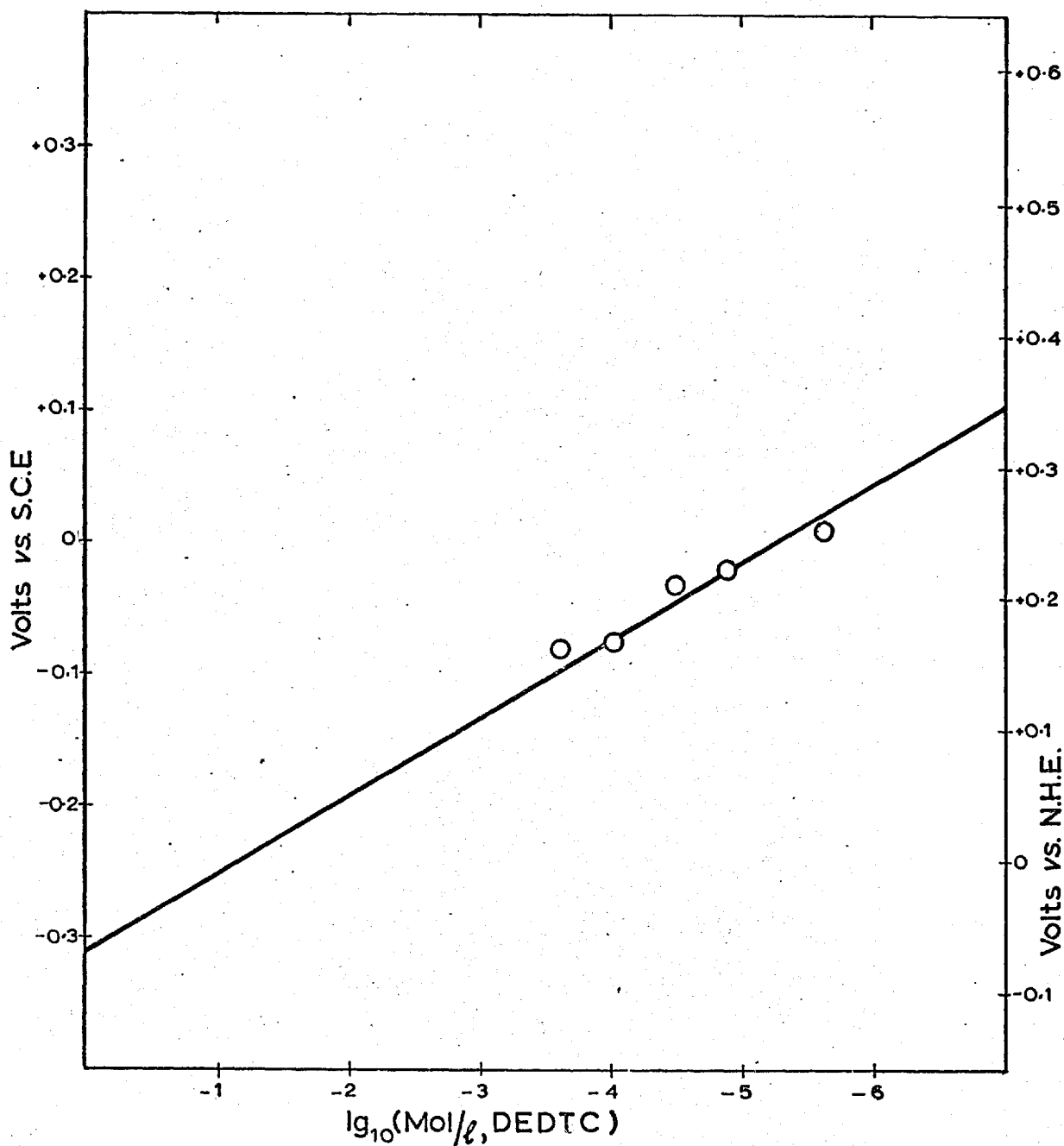


Fig. 1-6 Standard red ox potential of the reaction :-  
 $2(\text{C}_2\text{H}_5)_2\text{NCSS}^- \rightarrow (\text{C}_2\text{H}_5)_4(\text{NCSS})_2 + 2\bar{e}$

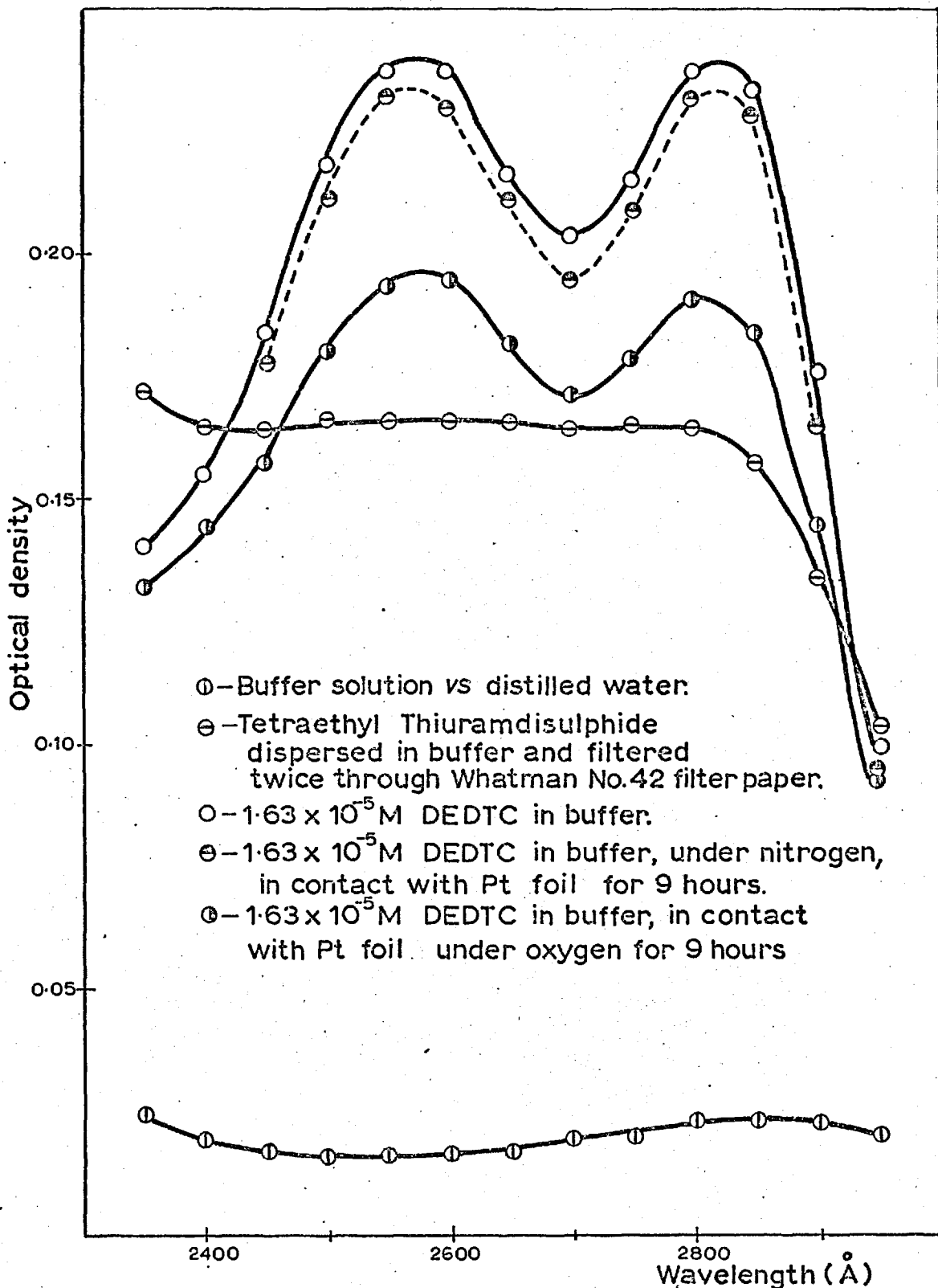
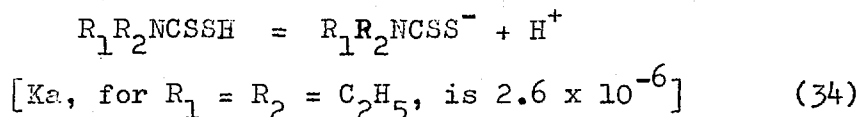


Fig. 1-7 U.V. spectrum of DEDTC.

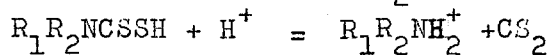
concentrations  $3 \times 10^{-4}$  to  $3 \times 10^{-6}$  M, saturated with tetraethylthiuram disulphide, gave potentials which conformed to the Nernst equation. The straight line with a slope of 0.059 gave -310 mV (vs S.C.E. or -68 mV vs NHE) when extrapolated to  $\lg C_{\text{DEDTC}} = 0$  as seen in figure 1-6. It is notable that the gold electrode ceased to give reproducible results when it was left dipped in the carbamate solution for about 8 hours, but re-gained its sensitivity upon dipping in  $\text{H}_2\text{SO}_4$  followed by rinsing with water and heating.

### 1.9 Stability of DEDTC solutions and effect of platinum

Like the xanthates, carbamates are less stable in acid than in alkaline solutions (14)(32). By analogy to the former substances (33), they may be expected to form the corresponding weak acids:



which in turn decompose further to  $\text{CS}_2$  and amine salts



with decreasing pH. (39)(35)

The U.V. absorption spectrum of DEDTC at a concentration of  $1.63 \times 10^{-5}$  M and pH 9.2 was obtained in 1cm quartz cells employing a Hilger and Watts spectrophotometer. The spectrum showed two maxima of optical density at wavelengths of 2600 and 2825 $\text{\AA}$  as is seen in figure 1-7. The optical density at these maxima depended linearly on the DEDTC concentration. The optical density values for different DEDTC concentrations at 2600 $\text{\AA}$  are given in Table 1-1 over page.

Table 1-1

Mol/l DEDTC	O.D. at $\lambda = 2600\text{A}^\circ$
$4 \times 10^{-6}$	0.06
$7 \times 10^{-6}$	0.100
$1.2 \times 10^{-5}$	0.182
$1.6 \times 10^{-5}$	0.238
$2.2 \times 10^{-5}$	0.324

The absorbance of  $1.6 \times 10^{-5}$  M DEDTC solution at pH 9.2 kept in a volumetric flask without any precaution to exclude air from the medium was measured at  $\lambda = 2600 \text{A}^\circ$  every day for one week. No change in intensity (hence concentration) was observed, indicating that the carbamate solution under the stated conditions is stable for at least one week. When a platinum foil was placed in contact with the solution a drop in concentration was detectable. 100 ml samples of  $1.6 \times 10^{-5}$  M DEDTC solutions were kept for 9 hours under the following conditions:

- a) DEDTC solution saturated with  $\text{O}_2$  gas
- b) DEDTC solution saturated with  $\text{O}_2$  gas and in contact with  $21\text{cm}^2$  Pt foil
- c) DEDTC solution deaerated and kept under  $\text{N}_2$  gas in contact with  $21\text{cm}^2$  Pt foil

The optical densities and the corresponding DEDTC concentrations at the end of this time are recorded in Table 1-2 over page.

Table 1-2

Effect of Pt on DEDTC solutions at pH 9.2

Sample	Final O.D.	% Drop in DEDTC conc.
[Initial soln.]	[0.241]	—
a	0.241	0
b	0.230	4.3
c	0.195	19.0

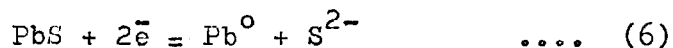
It is clearly seen that oxygen gas does not oxidise DEDTC significantly under these conditions. However, platinum metal in the absence of oxygen causes 4.3% drop in the reagent concentration and in the presence of oxygen 19% drop is caused. Thus, Pt serves as "potential mediator", providing an electron transfer path by which oxygen can react with dithiocarbamate.

### 1.10 Discussion

a) When unoxidised galena is placed in water at pH 9.2, in the absence of oxygen the subsequent equilibrium will be determined by the dissociation products; namely  $Pb^{2+}$ ,  $S^{2-}$  and  $HS^-$ , according to the solubility product of  $PbS$ , and the concentrations would be

$$[Pb^{2+}] = [S^{2-}] + [HS^-] = 8.35 \times 10^{-15} \text{ mol/l.}$$

The majority of sulphur species at this pH will be in the  $HS^-$  form. With cathodic polarization of sufficient magnitude enrichment of the  $PbS$  lattice by lead can be anticipated from the reaction



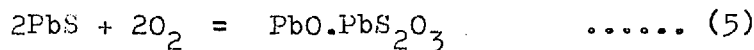
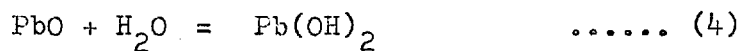
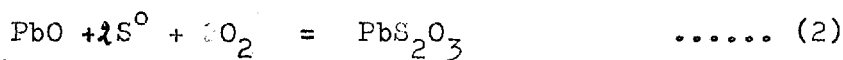
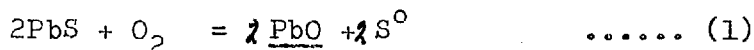


for which the redox potential expression is

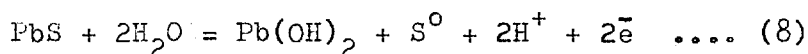
$$E = -0.957 - 0.029 \lg[S^{2-}] \quad \dots\dots(7)$$

and the redox potential at  $[S^{2-}] = 10^{-10}$  for instance, is -667mV. The difference between the rest potentials of the cathodically polarized and non-polarized electrodes seen in figure 1-5 is probably indicative of this phenomenon. With either the introduction of oxygen or anodic polarization of the electrode the reverse process is enhanced and the lattice is rendered sulphur-rich therefore more easily corrodable (i.e. oxidizable)(36). Thus, according to Plaksin and Shafeev (47) the semi-conducting properties of galena are changed from n-type (in the case of  $Pb^0$ -rich lattice to p-type in case of  $S^0$ -rich lattice, and therefore **made more readily acceptant for the** electron of the sulphohydril-collector anion. This is possibly supported by the finding that the attachment of flotation collectors on mineral surfaces is in localized regions (10) (37). Furthermore, direct measurements with a micro-probe electrode showed that the potential of the local ionic sites on galena are depressed by several hundred millivolts by the adsorption of collector ions(38).

It has been repeatedly verified (39)(40)(41) that with oxygen and in contact with an aqueous phase the oxidation of galena will take place with the resultant species indicated by the following reactions:



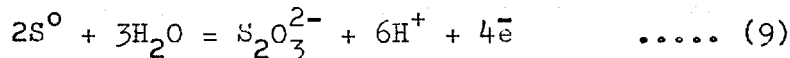
The solid reaction products are underlined. However, in a buffer solution at pH 9.2 the solubilities of these substances will not allow the formation of solid  $\text{PbS}_2\text{O}_3$ , ( $K_s = 1.5 \times 10^{-4}$  or  $\text{PbSO}_4$ , ( $K_s = 1.3 \times 10^{-8}$ ) but only  $\text{Pb(OH)}_2$  ( $K_s = 4.2 \times 10^{-15}$ ) will form, since at this pH the available  $\text{Pb}^{2+}$  concentration from  $\text{Pb(OH)}_2$  will be only  $10^{-4.6}$  M. The dissolved oxidized species of sulphur, on the other hand, will remain in their ionic forms. The first oxidation stage of galena at pH 9.2 is the overall reaction



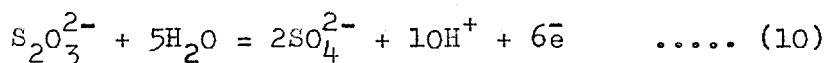
for which the electrode potential expression is

$$E = 0.765 - 0.059 \text{ pH} \dots (8a)$$

Elemental sulphur at this pH will not remain as such but will oxidise to  $\text{S}_2\text{O}_3^{2-}$  and in the final stage will be in the form of  $\text{SO}_4^{2-}$ . The reactions leading to these conversions are:



and



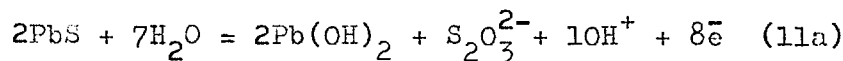
which lead to the galena electrode potential expressions

$$E = 0.580 - 0.0736 \text{ pH} + 0.007 \lg[\text{S}_2\text{O}_3^{2-}] \dots (11)$$

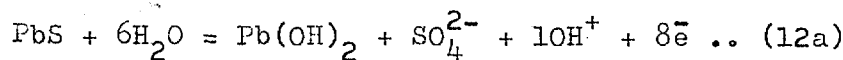
and

$$E = 0.459 - 0.0736 \text{ pH} + 0.007 \lg[\text{SO}_4^{2-}] \dots (12)$$

according to reactions

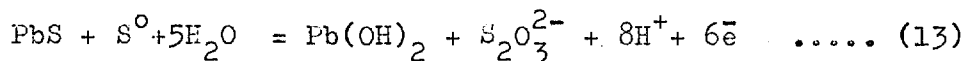


and

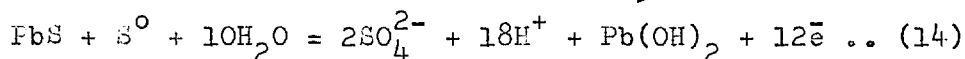


Various other combinations of reactions and products are possible in this system, and their redox potentials can be evaluated from

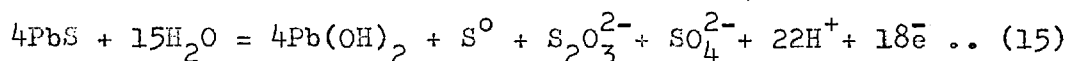
thermodynamic data; for example,



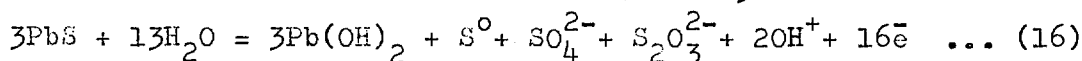
$$E = 0.580 - 0.078 \text{ pH} + 0.0098 \lg[\text{S}_2\text{O}_3^{2-}] \quad \dots (13a)$$



$$E = 0.484 - 0.0885 \text{ pH} + 0.0098 \lg[\text{SO}_4^{2-}] \quad \dots (14a)$$



$$E = 0.571 - 0.072 \text{ pH} + 0.003 \lg[\text{SO}_4^{2-}][\text{S}_2\text{O}_3^{2-}] \quad \dots (15a)$$

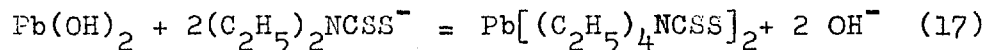


$$E = 0.547 - 0.0736 \text{ pH} + 0.0037 \lg[\text{S}_2\text{O}_3^{2-}][\text{SO}_4^{2-}] \quad \dots (16a)$$

The list could be further extended to cover various polythionates which are, however, much less stable at low concentrations so that they may be neglected.

The conventional potential - pH diagrams which are commonly employed in consideration of phase equilibria in aqueous redox reactions (42)(43), take into account only the final equilibrium states; (for example  $\text{SO}_4^{2-}$  is the only stable species in equilibrium with galena at pH 9.2) without regard to the relative rates of reactions leading to the production of intermediate species. Within the experimental times involved in the measurements reported above, however, these intermediate ions could be considered relatively stable and therefore the measured electrode potentials represent "mixed potentials" rather than potentials of single electrode reactions. A mixed potential is usually established when more than one redox reaction takes place simultaneously at the same electrode. Theoretically equilibrium should be reached; but when the reactions are sluggish the potential indicated is related to the prevalent concentrations of ionic species and these in turn to the rates of reactions.

With the introduction of  $10^{-3}M$  DEDTC at pH 9.2 in presence of oxidation products, the reaction of carbamate ion will be by displacement of the  $OH^-$  from  $Pb(OH)_2$  according to reaction 17.



It has been reported by Mellgren and Rao (13) that the pH of an unbuffered solution containing suspended galena is raised by a few pH units upon the introduction of  $10^{-2}M$  DEDTC. Such an exchange as shown in eqn., 17 can easily take place under the stated conditions since the solubility product of  $Pb[(C_2H_5)_4NCSS]_2$  is low, namely  $1.2 \times 10^{-12}$  (Mol/l)<sup>3</sup>.

The rest potentials obtained with galena and platinum under the stated conditions are summarized in column 3 of table 1-3. Considering that reactions 11a and 12a above, are taking place without the interference of others, the corresponding  $S_2O_3^{2-}$  and  $SO_4^{2-}$  concentrations necessary to produce these potentials are given in columns 8 and 9 of the same table. Similar calculations for reactions 13 and 16 showing the ion concentrations necessary to maintain the same potentials are given in columns 4 to 7. Clearly such ion concentrations are not realistic since the galena electrode under study could not produce such high ion concentrations. A common feature in all electrode potential expressions given on pages 33 and 34 is that at low concentrations of the involved oxidation products for the electrode potentials anticipated, the measured values are more positive than the calculated ones, whereas the electrode potential expression given by eqn. 8a produces a more positive value than any measured potential. In view of the fact that elemental sulphur can exist in the medium for a number of hours (40) eqn. 8a can be expressed for pH 9.2 as

$$E_{obs} = 20 - \Delta E \quad \dots\dots(18)$$

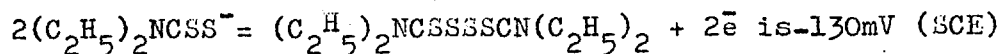
where

$E_{obs}$  = Observed electrode potential in mV vs SCE

$\Delta E$  = mV drop caused collectively by all the low concentration sulphur oxidation products, and DEDTC anion when it is present in the medium.

$\Delta E$  becomes only 2mV when galena is dipped in a fully oxygenated buffer solution, indicating that mainly reaction 8 is taking place under these conditions.

b. The formation of a saturated solution of tetra-ethylthiuram-disulphide is not necessary for the hydrophobization of galena surface since in the presence of  $10^{-3}M$  DEDTC the standard redox potential of the reaction



whereas the most positive potentials recorded in the presence of carbamate are -320mV for air and -220mV for oxygen gas. At these potentials the activities of  $[(C_2H_5)_4(NCSS)_2]$  are  $10^{-4}$  and  $3 \times 10^{-2}$  respectively, both much smaller than unity which one ought to have obtained had the solution been saturated with it.

c. Finally it should be pointed out that the electrochemical measurements show only which reactions are possible; they do not provide evidence on the actual structure of the adsorbed collector layer. This much - discussed problem remains surprisingly elusive. Infrared spectroscopy has proved that substantial amounts of lead xanthate and dixanthogen are formed in the galena-xanthate system (39). Attempts have also been made to correlate the flotation behaviour of sulphide minerals with the results of electron diffraction studies on the structure of single metal xanthate and metal carbamate crystals prepared by precipitation of these salts (48-51). But no technique has yet been discovered for the investigation of the adsorbed collector

Table 1-3. Summary of rest potentials and the corresponding ion concentrations necessary to produce them.

System	3	4	5	6	7	8	9
a Pt-base-N <sub>2</sub>	-80	-	-	-	-	-	-
b Pt-base-O <sub>2</sub>	+140	-	-	-	-	-	-
c Pt-base-10 <sup>-3</sup> M DEDTC <sup>-</sup> -N <sub>2</sub>	-170	-	-	-	-	-	-
d Pt-base-10 <sup>-3</sup> M DEDTC <sup>-</sup> -O <sub>2</sub>	-15	-	-	-	-	-	-
e PtS-base-N <sub>2</sub>	-500	+63	-12.55	-51	-35	-21.7	-5.34
f PbS-base-O <sub>2</sub>	-80	+39	+20	+46.6	+55	+21.7	+40
g PbS-base-10 <sup>-3</sup> M DEDTC <sup>-</sup> -N <sub>2</sub>	-500	+63	+12.55	-51	-35	-21.7	-5.34
h PbS-base-10 <sup>-3</sup> M DEDTC <sup>-</sup> -O <sub>2</sub>	-220	+35	+16	+34.4	+42.2	+16.3	+33
i PbS-base-10 <sup>-3</sup> M DEDTC <sup>-</sup> -Air	-320	+24.7	+5.81	+3.96	+14.6	+2.71	+19.3
j At 10 <sup>-3</sup> M redox pot of 2DEDTC <sup>-</sup> (DEDTC) <sub>2</sub> +2e <sup>-</sup>	-130	-	-	-	-	-	-

-37-

3. Rest potential (mV)

4.  $\log[\text{SO}_4^{2-}]$  from eqn. 14a

5.  $\log[\text{S}_2\text{O}_3^{2-}]$  " " 13a

6.  $\log[\text{S}_2\text{O}_3^{2-}] + \log[\text{SO}_4^{2-}]$  from eqn. 15a

7.  $\log[\text{S}_2\text{O}_3^{2-}] + \log[\text{SO}_4^{2-}]$  from eqn. 16a

8.  $\log[\text{S}_2\text{O}_3^{2-}]$  from eqn. 11a

9.  $\log[\text{SO}_4^{2-}]$  " " 12a

layer in situ.

1.11 Summary of results and conclusions

(i) Oxygen is a prerequisite for the flotation of galena with diethyldithiocarbamate.

(ii) Oxygen acts by oxidising galena to make  $Pb^{2+}$  available for the formation of  $Pb(DEDTC)_2$ , which is preceded by  $Pb(OH)_2$  in the absence of DEDTC.

(iii) In contrast to the case of xanthates for which there is some evidence that the formation of a lead xanthate-dixanthogen mixed film is necessary for better flotation, the formation of a saturated solution of tetra-ethylthiuramdisulphide is not necessary for good flotation.

(iv) On prolonged contact with air or relatively shorter contact times with oxygen gas, bubble contact is weakened due to the formation of a multilayer film of  $Pb(DEDTC)_2$  which prevents the bubble from reaching the more firmly attached lead carbamate layer on the surface.

1.12 References

1. Taggart, A.F., Taylor T.C. and Ince, C.R., Trans. Am. Inst. Min. Met. Engrs. 87 285 (1930)
2. Wark, W.I. and Cox, A.B., Ibid 112, 189, (1934)
3. Re<sup>h</sup>binder P. et al., Kolloid Z. 65, 268, (1933)
4. Siedler P. Ibid., 68, 89, (1934)
5. For Further references see for instance ref.7 p.53ff.
6. Gaudin, A.M., "Flotation", Mc Graw-Hill, New York (1957)
7. Sutherland, K.L. and Wark, I.W., "Principles of Flotation", Aust. Inst. of Min. and Met. Melbourne, (1955)
8. Klassen, V.I. and Mokrousov V.A., "An Introduction to the Theory of Flotation", Translated from Russ. by Leja T. and Poling G.W. Butterworths, London (1963)
9. Fuerstenau D.W. (Editor) "Froth Flotation 50th Anniversary Volume." Am. Inst. Min. Met. and Met. Engrs. New York (1962)
10. Fleming, M.G. and Kitchener, J.A., Endeavour XXIV, 101 (1965)
11. Steininger, J., Trans. Soc. Min. Engrs. Sept. (1967)  
p. 257
12. Schulman, J.H. and Smith, T.D. "Recent Developments in Mineral Dressing", Inst. Min. Met. London (1953) p.393
13. Mellgren, O. and Rao, S.R., Trans. I.M.M. 77(c) 65 (1968)
14. Thorn, G.D. and Ludwig, R.A., "The Dithio Carbamates and Related Compounds", Elsevier. Amsterdam (1961)
15. Tolun, R. and Kitchener, J.A., Trans. I.M.M. 73, 313, (1963)
16. Galikov, A.A., "Soviet J. of Non-Ferrous Metals " 2(11), 19, (1961)
17. Evans, N.R. and Hoar, T.P. Proc. Royal Soc. London 137, 343, (1932)



18. Mukai, S. and Wakamatsu, T., Memoirs of Fac. of Engrs. Kyoto Univ. Japan, 24 (4), 389, (1962)
19. Petrocelli, J.W., J. Electrochem. Soc., 97, 10, (1950)
20. Evans, U.R., Proc. 11th Congr. Pure, Appl. Chem., London 5, 743, (1947)
21. Tsujikawa, S. et al., Nippon Kyogo Kaishi, 83, 597, (1967)
22. Salamy, S.G. and Nixon J.C., Aust. J. Chem. 7 (2), 146, (1954)
23. Lintern P.A. and Adam N.K., Trans. Faraday. Soc. 31, 564, (1935)
24. a) Kamienski B., and Pomianowski A., Bulletin de l'Academie des Sciences, II(2), 81-92, (1954)  
b) Pomianowski, A., Proc. 2nd Int. Congr. Surf. Act. London T. III. (1957)
25. Majima H. and Peters, E., 7th Int. Min. Processing Congress. Leningrad (1968) paper E.1.
26. Kunori, S. and Ishii, F., CA. 61, 5251, f
27. Peters E. and Majima H., quoted in ref. 25. p.6
28. Vogel A.I. "A Text-Book of Quantitative Inorganic Analysis" Longmans, London 1961 pp 223 and 325
29. Sarankarayana, M.L. and Patel, C.C., Z. Anal. Chem., 179, 263, (1961)
30. Saville, B., J. Am. Chem. Soc., 81, 2749, (1959)
31. Ives, J.G. and Janz, G.J., "Reference Electrodes" Academic Press. New York (1961) pp. 288 and 489
32. Bode, H., Z. Anal. Chem., 142, 414, (1954)
33. Finkelstein, N.P., Trans. I.M.M. 76(c), 51, (1967)
34. Gregg, E.C. and Tyler, P., J. Am. Chem. Soc., 72, 4561, (1950)
35. Holloway, M., Biochim. Biophys. Acta., 36, 538, (1959)

36. Hrovath, J. and Novak M., Corrosion Science, 4, 159, (1964)
37. Plaksin I.N., Int. Min. Processing Congress London  
(1960) p.253
38. Szeglowski, Z., 3rd. Int. Surf. Act. Congress. Cologne,  
2, 110, (1960)
39. Leja, J. et al., Trans I.M.M., 72, 414, (1963)
40. Edington, P., PhD. Thesis Univ. of London (1966)
41. Reuter, B. and Stein, R., Z. Anal Chem., 61, 440, (1967)
42. Garrels, R.M. and Christ, C.L., "Solutions, Minerals and  
Equilibria" Harper and Row, London (1965)
43. Pourbaix, M., "Atlas of Electrochemical Equilibria"  
Translated by, J.A. Franklin, Pergamon Press, London (1966)
44. Wottagen, E. and Berg, I., Freiberger Forschungshefte  
437 (A), 31, (1968)
45. Ehrenberg, W. "Electric Conduction of Semiconductors and  
Metals", Oxford (1952)
46. Plaksin, I.N., Trans. A.I.M.E. 214, 319, (1959)
47. Plaksin, I.N. and Shafeev, R.Sh., Trans. I.M.M. (London)  
72, 715, (1962)
48. Hagihara, H. and Yamashita, S., Acta Cryst. 21, 350, (1966)
49. Ikeda, T. and Hagihara, H., Ibid. 21, 919, (1966)
50. Hagihara, H., Watanabe, Y., and Yamashita, S., Ibid., 24, (B),  
360, (1968)
51. Bonamica, M., et al., Ibid, 19, 898, (1965)

## 2. Surface oxidation of zinc sulphide

### 2.1 Introduction

For most fundamental work on the interaction of flotation collectors with sulphide minerals, sphalerite has been less studied than galena although both minerals bear a number of similarities as shown in table 2.1.

In contrast to the flotability of galena with flotation collectors under aeration-conditioning, sphalerite needs to be activated with heavy metal ions such as Pt, Au, Bi, Hg, Ag, Pb, Sb, As, Cu (1).

The mineral sphalerite is usually far from pure ZnS but incorporates a great number of impurities, i.e. Ag, Ge, Cd, Ga, Mn, Fe, Co ....(2)(3)(10) that lead to local galvanic actions within single grains, similar to the effects which have been established for different sulphide minerals in contact with one another (4)(5). This is said to be deliberately increased in the pressure leaching of sphalerite in presence of  $\text{Cu}^{2+}$  (32) as discussed below.

Iron is usually a substantial impurity in sphalerite and is present in solid solutions up to 45 mol % in the crystal lattice. Iron is also known to decrease its flotability, supposedly by increasing the ionic character of the bond, making its surface more hydrophilic (7)(8) or more easily oxidizable and thus more hydrophilic (9).

As mentioned above,  $\text{Cu}^{2+}$  ions are used as activators in flotation practice although other heavy metal ions could be used instead. In this connection it is interesting to note that in the pressure leaching of sphalerite (pressure  $5\text{kg}/\text{cm}^2$ ) in acid media, while the efficiency of leaching is increased by only 5-10% in the presence of  $\text{Cd}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ , the increase

Table 2-1. Some properties of ZnS and PbS

Property	PbS	ZnS	Reference
Solubility product	$7 \times 10^{-29}$	$10^{-23}$ (P)	(29)
" "	-	$1.6 \times 10^{-23}$ (W)	"
" "	-	$7 \times 10^{-26}$ (S)	"
m.p. °C	1120	1020	-
Spec. Res. ohm. cm	$10^4$	$10^{12}$	(30)(23)
Nature of cond.	Semi.	Semi	-
Nonstoichiometry	+	+	-
Me-S bond	18 ionic	22% ionic	(31)

(P) : Precipitated

(W) : Wurtzite - hexagonal ZnS -

(S) : Sphalerite - Cubic ZnS -

with the introduction of  $\text{Cu}^{2+}$  at the ratio of  $\text{CuSO}_4/\text{ZnS}$  on weight basis=0.027, is about 200%, (32) and the rate of dissolution of impure ZnS is higher than the purer species (32)(33).

It has been deduced by Romankiv and de Bruyn (33) from Pauling's electronegativity rule and from the fact that MnS is an essentially 100% ionic sulphide mineral, that the ionic character of the ZnS crystal lattice would be increased by the substitution of Fe and Mn instead of Zn into the chemical composition.

The action of  $\text{Cu}^{2+}$  in leaching has been interpreted as a catalytic one (32) where the initially generated  $\text{H}_2\text{S}$  is further oxidized to elemental sulphur with the aid of  $\text{Cu}^{2+}$  ions. On the other hand the action of  $\text{Cu}^{2+}$  in the same process has been suggested to be by the formation of CuS which in turn acts as a cathode active to oxygen (34) as it is known from studies on the effect of CuS on the corrosion of metals (35). As a counter-argument to this, the point has been made (32)(21) that the very low conductivity of a bulk ZnS crystal would eliminate such an anode-cathode interaction; but it is possible that the orientation of a colloidal CuS particle on crystal lattice defects would be such that the local galvanic action may proceed without involving highly resistive thicknesses of the mineral.

In the activation of sphalerite by  $\text{Cu}^{2+}$  for flotation,  $\text{Cu}^{2+}$  is said to form an insoluble CuS film on the mineral surface, which in turn interacts with the corresponding sulfohydryl collector by forming a Cu-collector salt which is less soluble than the corresponding Zn-collector salt. Highly oxidized sphalerite has to be initially sulphidized in order to facilitate CuS formation(1). Ionic equilibria calculations can be made to show that the observed narrow pH range of flotation (pH 8+ 1) is in accordance with the solubility product principle involving

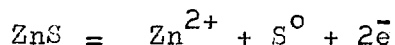
the formation of relevant metal-collector salts. Such calculations have been reproduced by Du Rietz (36).

$Zn^{2+}$  ions can be used as depressants in sphalerite flotation circuits, however, the mechanism of this process is not clear. There is evidence for both, the formation of surface  $Zn(OH)_2$  films (37), and electrostatic adsorption of colloidal  $Zn(OH)_2$  from the medium on to the mineral surface (38).

The study of the oxidation of pure  $ZnS$  and  $ZnS$  with impurities (especially iron) in various non-stoichiometric ratios, in the presence and absence of oxygen gas and with the introduction of flotation reagents would give more clues for the understanding of the observed flotation properties of this mineral.

Oxidation of sulphide minerals has been approached by various authors covering mineralogical, kinetic and analytical methods. An outline of these methods has been give by Sato(6). However, it has not been possible to reach a definite conclusion regarding the primary oxidation of  $ZnS$ .

Electrochemical studies of the oxidation of sphalerite were made as early as 1898 (28), similarly, Tamman (17) and Taggart(18) have measured the potentials of sphalerite electrodes. Other investigators have also made measurements under more controlled conditions (5)(19)(20) and have concluded that the potential of the electrode is determined by the presence of dissolved oxygen, electrolyte composition and the pH of the solution. The electrochemical approach to the dissolution of various sulphide minerals under high acid or ion content, with particular reference to the hydrometallurgical winning of their metals, has been recently outlined by Majima and Peters(21). From analogy of the oxidation of sulphide minerals other than  $ZnS$  (11-16)(21) it seems that the primary oxidation of  $ZnS$  in the acid range is probably according to the reaction:



Under oxygen further oxidation of sulphur may occur depending on the pH. Analytical results seem to support this conclusion (22) with the finding that "the S<sup>o</sup>/metal ratio in sulphide minerals decreases in the remaining bulk phase as the acidity of the aqueous medium in which it is dipped increases". Aqueous media containing sphalerite suspended alone(1) or together with other minerals (4)(5) have been shown to contain S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sub>4</sub>O<sub>6</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and of course Zn<sup>2+</sup>, but these results do not give a clue regarding the mechanism of surface oxidation of the mineral.

## 2.2 Aim and method of investigation

The electrochemical study of ZnS oxidation has not been fruitful owing to its high specific resistance. The resistances of pure synthetic ZnS crystals have been measured by Piper in the range 400-700<sup>o</sup>K (23). When the linear part of the graph of these results was extrapolated to 298<sup>o</sup>K a value of  $4.4 \times 10^{12} \Omega \cdot \text{cm}$  was obtained. Thus pure ZnS is practically an insulator.

In this investigation with the aim of possibly understanding the mechanism of the interaction of flotation collectors and the effects of inclusion elements on these processes, electrodes of relatively low resistance were prepared, and the electrochemical method applied to sulphide minerals other than ZnS by Sato (6) was adopted.

## 2.3 Material, apparatus and procedure

The apparatus shown in figure 1-1 was used for this purpose. The working electrode (WE) was placed and the solution of known composition was run from I. Further variations of

reagent concentrations or pH were effected by running known volumes of solution conditioned (i.e. aerated or deaerated) in vessel III, via the burette (BR) fitted to the system. pH alterations were made by dilute "Analar" HCl or NaOH.

The steps in Sato's electrochemical method of investigation are as follows:

a) Possible reactions of ZnS in aqueous media are written and the reversible redox potential expressions for these reactions are deduced from available thermodynamic data.

b) Variables of possible reactions i.e. pH, concentrations of assumed reaction products are changed, and the dependence of the electrode potentials on such changes recorded.

c) The measured potentials are plotted against the variables above, one by one.

d) The correlation between the calculated and measured potentials is examined, slopes of lines matched, and thus the reactions taking place deduced.

#### 2.4 Preparation of low resistance ZnS electrodes

In order to obtain electrodes with relatively low resistances, the following techniques were tried.

##### a. Natural sphalerite electrodes

Crystals of honey-coloured sphalerite were mounted on the ends of  $\frac{1}{2}$  cm diameter "Pyrex" glass tubing with "Araldite", and upon setting of the resin, the bulk of the crystal was polished just short of breaking the translucent mineral window which was about 1 mm thick.

##### b. ZnS films on Zn metal produced by tarnishing reactions

Pure zinc rods were initially polished to obtain a flat



section using carborundum paper and subsequently rubbed against one another to obtain higher smoothness. The rods were reduced by  $H_2$  gas, and sealed under nitrogen in a "Pyrex" glass tube made of two compartments joined by a thin neck of 1mm bore. In one compartment pure sulphur, and in the other the metal remained separately. The tube was then heated to  $415^\circ C$  (m.p. of Zn:  $419.5^\circ C$ , m.p. of  $S^\circ$ :  $446.6^\circ C$ ) and kept at this temperature for various lengths of time (1-30 hours). The formation of ZnS was confirmed by contact printing; however, all the films cracked, presumably because of the difference of coefficients of expansion of ZnS and  $Zn^\circ$  metal.

c. Evaporated ZnS films.

Pure zinc metal was dissolved in "Analar" HCl and ZnS precipitated at pH 4.5 by the passage of  $H_2S$  already cleaned by passing through a train of HCl,  $Ba(OH)_2$ ,  $H_2O$  (24). The resulting precipitate was filtered, washed with acetone, dried under vacuum and kept in a desiccator over silica gel and under nitrogen. Samples from this were evaporated under vacuum of  $3 \times 10^{-5}$  mm Hg on various substrates to obtain films as is the practice in optical studies (25)

c-1. Films on polished platinum sheets

$\frac{1}{4}$  mm platinum sheets were cleaned by acid, rinsed and heated to redness prior to introduction into the vacuum chamber. Films were obtained but they also cracked for the same reason as with zinc metal. Subsequent coatings on the same cracked film were also not satisfactory.

c-2. Films on glass

Films obtained similarly on optical quality glass slides also cracked on standing. One coating usually resulted with a film about  $0.3\mu$  thick as was shown by optical measurements (28). The resistance of such a film would be  $10^8$  ohm, which is not too

high for electrochemical measurements.

c-3 Films on cleaved galena

To overcome the drawback caused by differences in coefficients of expansion, a carefully cleaved galena crystal was used as substrate for deposition of ZnS films. Under these conditions no cracking was observed by microscopic examination at 40X magnification.

2.5 Experiments and discussion

a. Measurements with natural sphalerite

When the electrode was too thick (i.e. with high resistance), the electronic potentiometer having an input impedance  $>10^{12} \Omega$ , did not register any response to the variation in the electrolyte composition. The potential readings were as if the working electrode was disconnected. Further polishing of the electrodes to obtain  $10^6$ - $10^8$  ohms resistances seemed to improve the situation. In the pH range  $4 < \text{pH} < 8$  electrode potentials could be registered. However, in the range  $\text{pH} < 4$  the potentials were not steady. They fluctuated within a few hundred millivolts at times giving values  $-100 \pm 50$  mV to  $-300$  mV. At  $\text{pH} > 8$  a general increase in the negative direction was noted and equilibrium values seemed to be reached in 2-5 hours. At  $4 < \text{pH} < 8$  on the other hand, one could polarize the electrode by 100 mV in either direction and the potential reading would just remain constant ( $-275$  mV  $\pm 100$ ). The general problem was the impossibility of reproducing one potential value twice for the same electrode in a solution of the same composition. The only consistent values were obtained at  $\text{pH} > 8$ , the reproducibility being  $\pm 20$  mV.

In this case the electrode did not respond to the variations in  $Zn^{2+}$  concentration.

It is possible that the fluctuations in the range  $pH < 4$  were due to the dissolution of local sites in the lattice with the production of  $Zn^{2+}$ ,  $S^0$ ,  $H_2S$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ , known to exist in acid media containing ZnS (1)(32); in the range  $4 < pH < 8$  the film of hydroxides rendered the electrode relatively inert and at  $pH > 8$  in addition to the film of hydroxides which caused the sluggishness of the electrode, any initial concentration of  $Zn^{2+}$  was reduced to a value in accordance with the solubility products of  $Zn(OH)_2$  and  $HZnO_2^-$ .

b. ZnS films on galena

All the electrodes so prepared gave  $-80 \text{ mV} \pm 25$  in the first instance at  $pH < 4$ ; but the film was dissolved away with the resultant shift in the more negative direction which is towards the potentials of the underlying solid.

If the initial pH of the solution was  $pH \geq 5$  it was possible to obtain a steady increase in the negative direction by increasing pH for the same electrode. However, if a new electrode was introduced into the medium no two electrodes gave the same potential. Variations in either direction were 50-100 mV but the trend of increase of potential in the negative direction by increasing pH was common for them all. The possibility that the precipitated ZnS powder was oxidised to various extents is not remote, because the temperature of the tungsten filament on which the powder was placed could be greater than  $1000^\circ \text{K}$  at glowing brightness (27).

c. Redox potentials of ZnS suspensions

A number of experiments were carried out with suspensions of precipitated ZnS powder in the aqueous medium and the redox

potentials of the system measured with a platinum wire electrode. In all cases a continuous drift in the negative direction was observed, which is not surprising in view of the fact that platinum is poisoned by  $S^{2-}$  ions. At  $pH < 3$  the powder disappeared quickly by dissolution. If the pH was started at pH 4 the general tendency was again an increase of potential in the more negative direction as the pH was increased. Although this tendency prevailed in all such suspensions the responses to  $Zn^{2+}$  concentration variations were too scattered for a conclusion to be drawn. In figure 2-1 a few results, which could however, not be reliably reproduced are given to illustrate the general tendency of linear variation in potential by increasing pH. Although these results are statistically not significant, it is noticeable that at  $pH \geq 7$  their slopes are  $29 \text{ mV/pH} \pm 4$  suggesting that a potential in the form

$$E = E_0 - \frac{RT}{2F} pH$$

is developing.

In view of the irreproducibility encountered, no attempt was made to deduce any conclusions as to the reactions controlling the potentials. The exploratory experiments recorded above do, however, indicate the possibility of developing electrochemical measurements on evaporated films, with the aid of electronic potentiometers of very high input impedance. The main problem is seen to be associated with i) The preparation of continuous films perfectly free from cracks and oxidation, and ii) the setting up of cells with highly pure media and in absence of contamination. When the main electrode reaction is very sluggish or the potential change due to a reaction is too low, the presence of reactive impurities is highly deleterious.

An alternative method of electrode preparation to overcome high resistances could probably be to make electrodes by

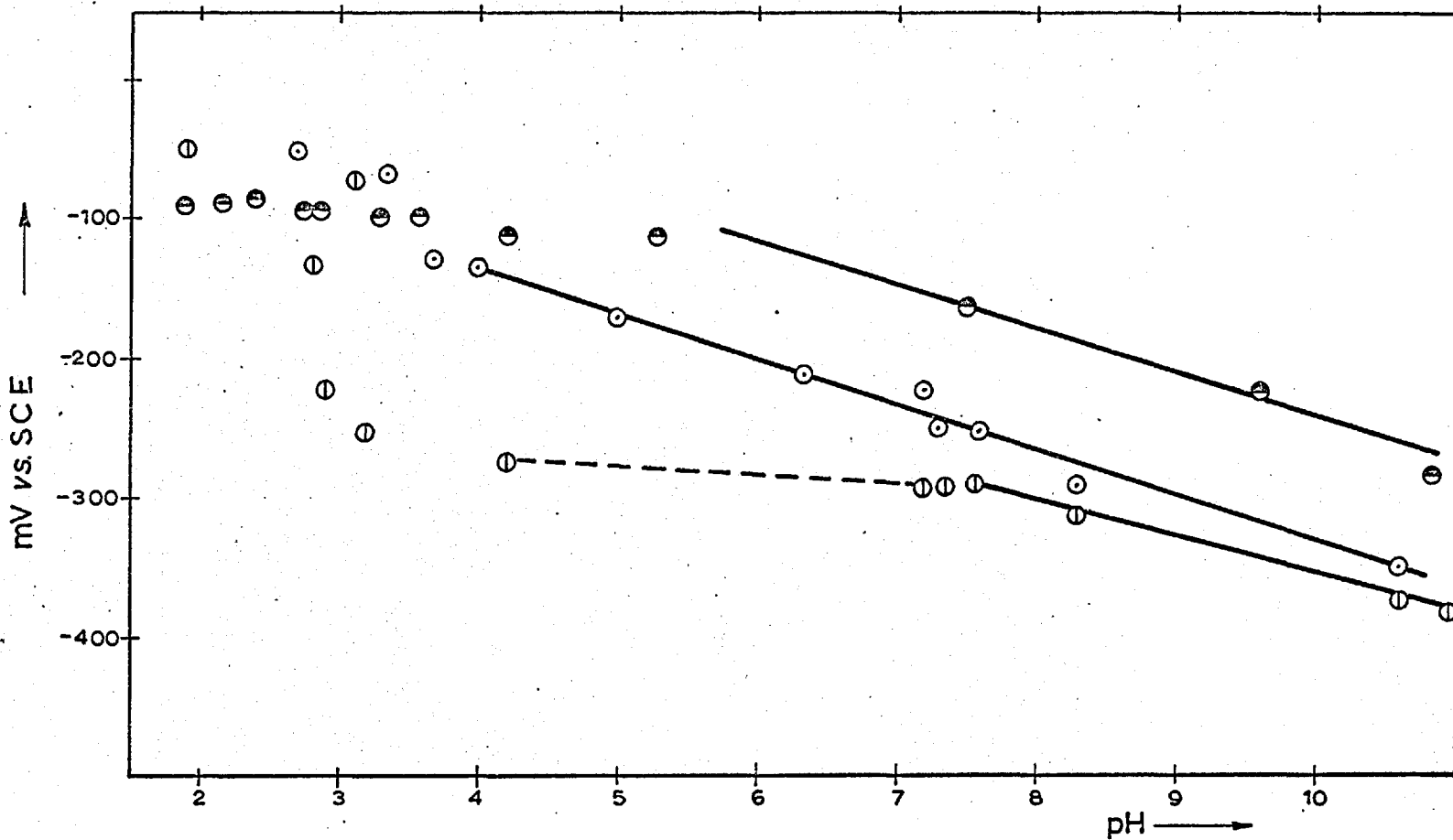


Fig. 2-1 Electrode potentials of:-  $\bullet$  - Zn S coated on galena,  $\circ$  - natural sphalerite and  $\odot$  - platinum electrode dipped in Zn S suspension.

blending ZnS powder with small quantities of graphite and press the mixture (in the presence of an inert binding agent if necessary). Thermodynamic conditions for the selective oxidation of ZnS from the mixture are favourable, and such electrodes have been used by Sawamoto and Oki (39) to obtain highly pure electrolytic zinc without oxidizing graphite.

One more method on the same lines would appear to be a solution to overcome high electrode resistances while employing thicker ZnS films coated on galena; where experiments could be conducted with a series of electrodes containing decreasing proportions of doped iron, eventually allowing an extrapolation to be made for electrode reactions at zero iron content.

2.6 References

1. Sutherland, K.L. and Wark, I.W., "Principles of Flotation"  
Aust. Inst. Min. Met. Melbourne, (1955)
2. Takabashi, T., Econ. Geol., 55, 1084, (1960)
3. Kodzhoyan, A.A., C.A., 63, 14540 d
4. Gottschalk, V.H., and Buehler, H.A., Econ. Geol., 7, 15, (1912)
5. Shvesnikov, G.B., C.A., 60, 1330 h
6. Sato, M., Econ. Geol., 55, 1202, (1960)
7. Plaksin, I.N. and Shafeev, R.S., Trans. I.M.M., 72, 715, (1963)
8. Chainikova, N.A., C.A., 62, 7425, b
9. Bogdanov, O.S., Podnek, A.K. and Semenova, E.A., C.A., 64, 9297e
10. Troshin, Yu. P., C.A., 65, 1977 e
11. Sato, M., Econ. Geol., 55, 928, (1960)
12. -----, Electrochim. Acta, 11, 361, (1966)
13. Eadington, P. and Prosser, A.P., Trans. I.M.M., 75, 125, (1966)
14. Reuter, B. and Stein, R., Z. Elektro.Chem., 61, 440, (1957)
15. Noddac, W. and Wrabetz, K., Ibid., 59, 96, (1955)
16. Noddac, W. Wrabetz, K. and Herbst, W., Ibid., p 752
17. Tamman, G., Z. Anorg. Alg. Chem., 113, 149, (1920)
18. Taggart, A.F. et. al., "A.I.M.M. Milling Methods", (1930) p 220ff
19. Sato, M. and Mooney, H.N., Geophysics, 25, 226, (1960)
20. Rachenberg, H., Neues Jahrbuch Min. Monatsh., No. 88, (1951)
21. Majima, H. and Peters, E., 7th Int. Min. Processing Congr.,  
Leningrad, (1968) preprint E1

22. Kunori, S. and Ishii, F., C.A., 61, 5251 f
23. Piper, W.W., Phys. Rev., 92 (1), 23, (1953)
24. Gmelin, "Handbuch der Anorganischen Chemie" 8th Ed.  
Verlag Chemie G.M. Weinheim-Bergstr. (1956) vol. 32 p.904
25. Wolf E., "Progress in Optics" vol. 1. North Holland, (1961)  
Publishing Co. Amsterdam (1961) p 220 ff.
26. Coutts, T.J., Lab. Practice, 16, (2), 161, (1967)
27. The Chemical Rubber Co., "Handbook of Phys. and Chem."  
Cleveland (1962) p.E-126
28. Bernfield, I., Z. Phys. Chem., 25, 46, (1898)
29. Latimer, W.M., "Oxidation Potentials" Prentice Hall,  
Englewood Cliffs (1959)
30. Plaksin, I.N., Int. Min. Process. Congress London (1960)  
Group III. Paper 13.
31. Plaksin, I.N. and Shafeev, R.S., Trans. I.M.M., 72, 715,  
(1963)
32. Fushimi, H. and Okamura, S., J. Min. Met. Inst., Japan.,  
82, 329, (1966)
33. Romankiw, L.T. and de Bruyn, P.L., in "Unit Processes in  
Hydrometallurgy, Edited by M.E. Wadsworth and F.T. Davis,  
Gordon and Beach Publisher, New York (1964) p.45
34. Hisaratsu, Y. and Masuko, N., Denki Kagaku, 31, 771, (1963)
35. Devoluy, R.P., Corrosion, 12, 33, (1956)
36. Du Rietz C. "Surface Chemistry." Edited by P. Ekwall  
et.al., Munksgaard. Copenhagen (1965) p.21
37. Malinovsky, V.A. Non-Ferr. Metals, Moscow No.1 (1967)



38. Also see Ref. 1 and "An Introduction to the Theory of Flotation" by V.I. Klassen and N.A. Mokrausov (Transl. J. Leja) Butterworths, London(1963)
39. Sawamoto, H. and Oki, T., J. Min. Met. Inst. Japan. 81, 87, (1965)

PART II.

SELECTIVE FLOCCULATION OF MINERAL SUSPENSIONS

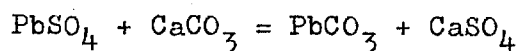
## 1. INTRODUCTION

### 1.1 General Concepts

When an ore is crushed and ground for the concentration of the valuable minerals, the degree of comminution and formation of various sizes will be mainly dependent on the physical properties of the bulk of the solid. In many cases of finely disseminated composite ores, liberation of individual mineral grains requires size reduction to an extent not suitable for froth flotation any more. It is well known that very fine minerals or slimes as they are called (1) are either lost or interfere with the actual concentration of the valuable minerals. Generally the optimum size for froth flotation is accepted as 20-100 $\mu$  (2)(3). Sometimes, it is possible to obtain reasonable recoveries down to sizes of 10 $\mu$ ; however, finer particles have to be removed by an initial desliming operation. Gaudin, Schuhmann and Schlechten (4) have shown that slimes of sizes <4 $\mu$  are harmful in galena flotation by xanthates. Other investigators have studied the phenomenon (5), and found that slimes attach themselves to bigger particles. The mechanisms of attachment proposed can be summarized as follows:

#### i. Chemical Interactions (6)(7)

Slimes interact with other solids in accordance with simple chemical reactions governed by the relative solubilities of the solids involved, and the resulting solid compounds as in the case



where  $\text{PbCO}_3$  is the solid film between the two initial solids (i.e.  $\text{PbSO}_4$  and  $\text{CaCO}_3$ ).

ii. Electrostatic forces:

Ince (7) and Sun (8), as a result of electrokinetic potential measurements, concluded that particles of opposite charge-signs are likely to stick together. Del-Guidice (6) observed that slimes are not firmly attached to the underlying solid surface but migrate over a water film. In more recent years (9)(10) attempts have been made to correlate the electric double layer effects with the density of slime coating and recovery of flotation, the conclusion is that increase of slime coating decreases recovery and increased difference in the magnitudes of zeta-potentials with opposite signs results in higher coating density.

Particles of sizes not suitable for recovery by froth flotation do not all fall in the range of nomenclature adopted for colloidal suspensions in treatises on colloid chemistry (11) since sizes ranging from 10 to 100000  $\text{A}^\circ$  (12) can be called colloidal.

When a finely ground mineral is placed in water, the particles will either remain suspended in the medium for a long time producing a "stable suspension", settle slowly and exhibit a gradation in the clarity of the aqueous phase which is highest at the top, indicating that the suspended solids are "slowly coagulating"; or it will form a clear, descending boundary, in which case the suspension is called "unstable". The various factors operative in such a system are briefly summarized below.

a. Effect of size and shape of particles. If the particles are big enough so as to be effected by gravity, depending on the particle density and diameter and the viscosity of the suspending medium at constant temperature, they will settle obeying Stokes' Law if the particles are spherical and are

falling freely (without being hindered by other particles). The particle size for sedimentation by gravity in some cases may be down to  $0.1\mu$  (13), however, an intensive Brownian movement is operative with sizes  $<0.5\mu$  (3) which is more marked at smaller sizes. Suspensions containing particles of the same size and shape are termed "monodisperse" and such suspensions can only be obtained in model colloid systems. Finely ground minerals cannot be expected to give such homogenous shapes and sizes but are "heterodisperse" or "polydisperse" and not spherical.

The sizes and shapes of particles determine the interfacial area, which is proportional to  $d^2$  (where  $d$  is the linear dimension of the particle) and the mass of the particle which is proportional to  $d^3$ ; therefore the colloidal size limit according to one definition (14) is determined by the value of  $d$  where the interfacial effect becomes significant. It is known that the surface area varies with the shape of particles particularly at small sizes (i.e.  $0 < 1.2\mu$ ) and it increases following the order

sphere < disc < cylinder.

b. Double layer effects. Solid particles suspended in an aqueous medium undergo a surface-charge re-arrangement in about  $10^{-8}$  seconds (15) with the formation of an electric double layer which is a combination of charges on the surface of the particle and charges in the aqueous space surrounding it, altogether providing an electro-neutral state in the system. The net charge on the solid particle is primarily determined by ionization, ion dissolution or ion adsorption. However, in minerals crystal lattice defects and ion substitution in the case of a semi-conductor are likely to alter the surface charge and ion adsorption properties of the solid in comparison to its model form. The stability of a suspension depends on the

properties of the double layer and the forces operating therein, namely (a) repulsive inter particle and (b) attractive forces of atomic interactions. The net interaction energy between particles is obtained by the addition of these two energies as is shown schematically in figure 1. At a certain distance of separation of two particles, depending on the magnitudes of  $E_A$  (attractive energy) and  $E_R$  (repulsive energy), the net energy of interaction reaches a maximum (M) which leads to repulsion, if the particles approaching one another have less kinetic energy than NE (the net energy of interaction). The attractive forces; apart from those of Coulombic nature, are the London-van der Waals forces originating from dipoles, induced dipole and interactions of apolar atoms (16), whereas the repulsive forces are due to double layers of similar sign as well as the Born repulsive forces which operate at the closest approach of particles.

Particles acquire their energy - if no agitation is applied - from the Brownian motion which is due to thermal energy transfer from the suspending medium to the suspended particles. The suspension is usually stable if the energy barrier to be overcome (i.e.  $E_R + E_A$ ) is  $> 20 kT$  where  $k$  is Boltzmann's constant and  $T$  is the absolute temperature.

c. Effect of solid concentration. It is to be expected that with increased crowding of particles in a suspending medium the rate of collision will be increased and, assuming that each collision leads to a permanent contact between particles, the initial rate of coagulation will be increased. According to Smoluchowski's treatment (16), where the movement of particles is controlled by diffusion and the potential energy barrier to be overcome is negligible, the number of spherical particles remaining after a coagulation time  $t$ , will be

$$N = (N_0 / 1 + 4 \pi D a N_0 t) \dots\dots\dots(1)$$

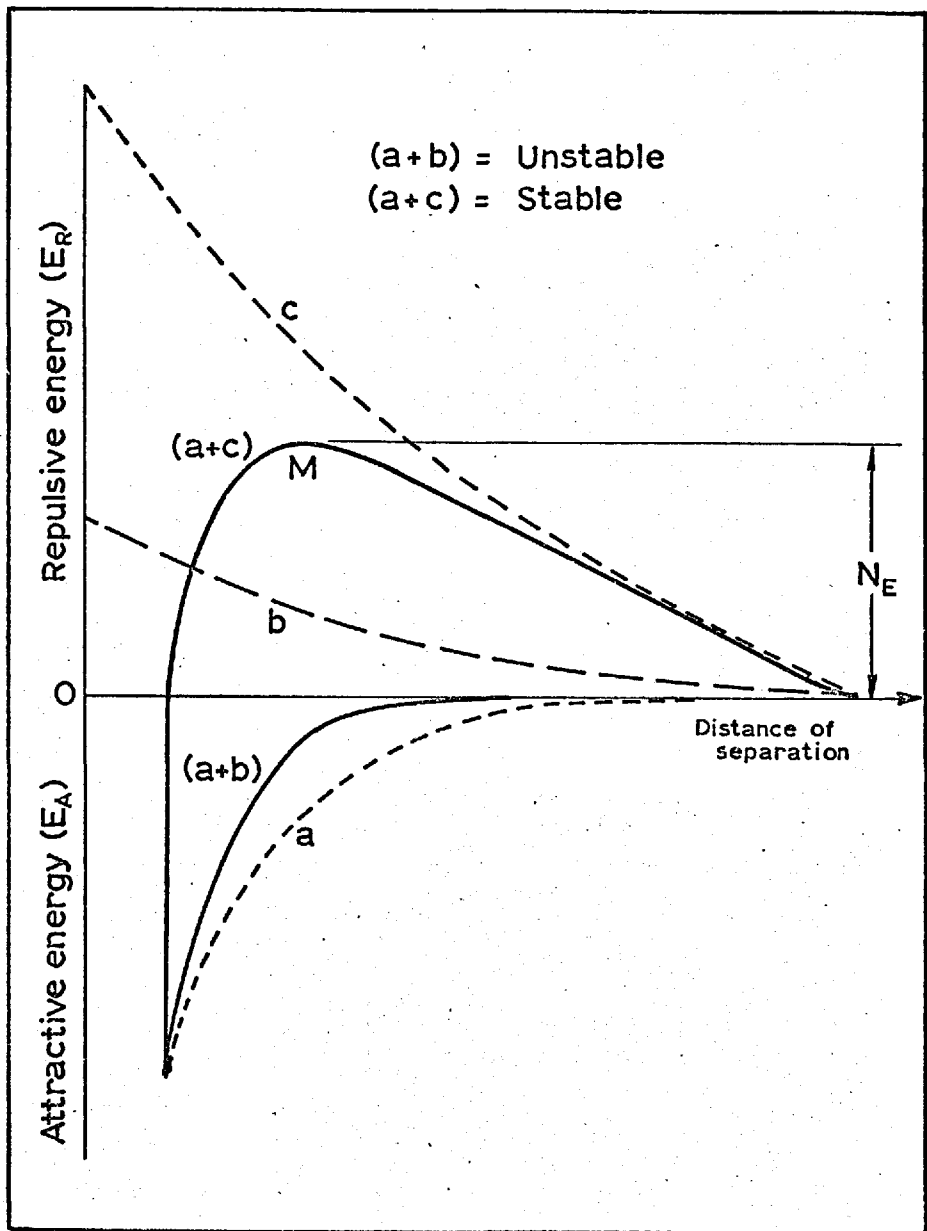


Fig. 1 Schematic representation of the interaction energies of two particles.

where  $N_0$  is the initial number of particles,  $D$  the diffusion coefficient and  $a$  the effective radius of the particles. In the presence of a repulsive energy barrier, the coagulation is slowed down by a factor  $W$  and according to an approximate theory due to Fuchs (16)  $W$  is given by

$$W \cong (2\lambda a)^{-1} \exp [V_{\max}/kT] \quad \dots\dots(2)$$

where  $\lambda/a$  is the thickness of the double layer, and  $V_{\max}$  is the potential energy maximum on the particle-particle interaction energy curve. If the source of energy is the Brownian motion only, the coagulation process is "perikinetic"; whereas if the system is slowly agitated it is "orthokinetic" coagulation. Orthokinetic coagulation is exhibited more strongly by heterodisperse systems.

Although by no means universally applied, it is probably more desirable to distinguish between "coagulation" where particle aggregation is caused by simple electrolytes and "flocculation" where particle aggregation is caused by bonding agents or polymeric flocculants which form stronger aggregates (17). The action of hydrolyzable metal ions is probably more akin to that of synthetic polymeric flocculants but it will be referred to as "coagulation".

d. Effects of solid composition and ionic content of the suspending medium. The dissolution of suspended solids and the subsequently resulting ionic equilibria determine the properties of the double layer. The primary surface charge of the solid originates from the ionization of the lattice ions or preferential adsorption of certain ions. Particularly ions present in the chemical composition of the solid or their hydrolysis products adsorb preferentially and are called "potential determining ions". Ions present in the suspending medium and <sup>which</sup> are not preferentially



adsorbed, act primarily by altering the ionic strength of the solution, and at high concentrations compress the double layer which results with coagulation. Such coagulating effects become more pronounced as the charge of the ions increases and proceed in accordance with the Schulze-Hardy rule. An ion which is specific (potential-determining) for one solid could be indifferent to another.  $H^+$  and  $OH^-$  ions for instance are potential determining for oxides (although they do not exist as such in the crystal lattice), and they are also potential determining in a sense for other minerals such as carbonates and silicates, not directly but by way of controlling the concentrations of potential determining ions. In this connection it is appropriate to mention two almost synonymously used terms. Namely "zero point of charge" (z.p.c.) or (p.z.c. from point of zero charge) and "iso-electric point" (i.e.p.). The z.p.c. indicates the pH value or the concentrations of other potential determining ions where the surface charge of the suspended particles is zero. Under these conditions the  $\zeta$ -potential of the particle is also zero; it has been suggested (156) therefore, that the conditions under which the  $\zeta$ -potential is zero should be called "zero-zeta point", however, this term does not bear any advantage to others. i.e.p. indicates the same charge condition of the surface (i.e. the +ve and -ve potential determining ions are electrically equivalent); however, Parks (212) finds it more convenient to give the name i.e.p. to z.p.c. "...if charge is established only by  $H^+$ ,  $OH^-$  and species capable of interacting with  $H^+$  or  $OH^-$  or  $H_2O$  to form species present in the solid lattice....".

The term z.p.c. will be used here without further elaboration, to indicate the conditions under which the zeta-potential is zero.

## 1.2 Coagulation and flocculation processes

Solids suspended in aqueous media in various industrial processes have to be separated at one stage for further processing of the solid or the liquid(or both). This is accomplished by sedimentation of the solid, followed by filtration or thickening or elutriation of the suspended solids while the settled ones remain unaffected. Commonly this is accomplished by the use of hydrolyzable metal salts such as alum, ferric salts etc., followed by arrangement of pH (if necessary) to form metal hydroxides which precipitate the suspended solids by bridging them together or forming a settling blanket, trapping most of the suspended solids (20)(21). An example of this process outside water treatment is the addition of  $Fe^{3+}$  ions to acid-leached zinc oxides in order to precipitate suspended silica and other contaminants prior to the preparation of the pregnant solution(22). Sometimes kieselguhr is added to a turbid solution and then the whole solids content of the medium is aggregated by hydrolyzing metal salts, thus making filtration easier (23). Extensive study in relation to effluent water clarification by the use of hydrolyzable metal ions has been reported (20)(24)(25). Various natural plant extracts (25)(26)(27) and starches (29) have also been used in the same connection.

Two other processes have been used for the purpose of aggregating solids; in one case a solid suspended in a non-aqueous medium is made to aggregate by a trace of water which apparently forms aqueous lenses between the solid particles due to the capillary action and leads to the formation of spherical aggregates with a few centimeters diameter(28)(29)(30)(31); in the other case, a clay suspension is seeded with a trace of magnetically susceptible powder (32) which leads to partial aggregation when the suspension is subjected to a magnetic field.

Aggregation is further enhanced if alum is used together with the magnetizable powder. The mechanism in this process appears to be that the magnetizable particles adhere to the suspended solid particles - or are entrapped in the metal hydroxide envelope if alum is used - and when a magnetic field is applied to the system the magnetic force overcomes the repulsive force which keeps the original particles suspended. However, these two last processes are not related to the flocculation of solids by polymers, (which forms the ~~main~~<sup>n</sup> topic of this thesis).

The use of synthetic polymeric flocculants for the aggregation of suspended solids has gained impetus in the last few decades and more than 200 such commercial products have been listed (33)(34). The published work on these products falls into three categories; (i) model systems, (ii) effluent water treatment and (iii) flocculation of mineral suspensions. Apart from the few cases listed below, most investigations have dealt with suspensions containing one solid component or the bulk flocculation of all the suspended solids, as opposed to the selective flocculation of individual components from a mixture. It has been known for several years that selective flocculation is **feasible**, but its possibilities and scope as a separation process have not been thoroughly examined.

### 1.3 Previous work on selective flocculation

i. A patent issued to Cartwright in 1910 (35) dealt with selectively flocculating one metal oxide from a mixture containing Fe, Mn, Cr, and Si oxides by using a mixture of alkali, soap and rosin grease. It appears that certain oxides were selectively stabilized by the mixture while the others remained unaffected and thus precipitated.

ii. Schwerin patented a similar process in 1912 (36) where

the use of NaOH was suggested for separating an unspecified iron ore from a mixture containing clay, and ammonia was used to separate sand from a similar clay mixture. The process, which was only vaguely understood in terms of surface charges, seems to have been operating by stabilizing the finely divided clay particles under the specified conditions and leaving the iron ore unaffected which settles by gravity due to its coarser size. Had the iron ore been as finely divided as clay, it would have been expected to have been stabilized as well. The use of what are called "non-neutral colloidal bodies" such as humic acid, silicic acid, alum, etc., has also been suggested in the same patent.

iii. A process patented by Feldheimer in 1919 (37) describes the use of  $\text{Na}_2\text{CO}_3$ , tannic acid, and  $\text{Al}_2(\text{SO}_4)_3$  for the selective stabilization of clay and coagulation of clay impurities such as fine sand, quartz, and various micas.

iv. A pre-treatment of a complex ore from which metals were to be extracted by amalgamation was described in a patent issued to Coddington (38). In this process also, silicates and clays as well as the finer parts of the ferrous minerals were made to remain longer in the suspended supernatant fraction by the use of  $\text{K}_2\text{CO}_3$  and the coagulation of other minerals (sulphides in particular) was accelerated by  $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  etc.

The selective aggregation of one mineral component during the preparation of a sulphide ore for flotation by means of sulphohydril collectors has been recognised by Gaudin and Malozemoff (39); however the possibility of leaving the suspension to let the aggregated minerals settle under gravity while the other components remained suspended was not considered by these authors.

v. A more direct application of selective coagulation-stabilization

seems to have been used in clay industry where the immediate problem does not lend itself to flotation or other conventional mineral processing practices. In a process described by Rowland (40), various plant extracts, manno-galactans, urea formaldehyde, polyphosphates, hydroxymethylcellulose, sodium salt of polyacrylonitrile and styrene-maleic acid copolymer were used to decrease the overall "viscosity" of the clay slurry and therefore allow the coarser (unspecified) clays to settle in a less hindered fashion. The settling fractions were said to flocculate.

Also, Beavers and Marshall (42) found that various clays in a mixture (i.e. illite, halloysite, kaolinite) and quartz were not affected by starch, whereas montmorillonite could be selectively flocculated from a mixture containing kaolinite and montmorillonite.

vi. Selective flocculation of colloidal phosphate ore in a real sense, from a slurry containing clays, by the use of starch, was described by Haseman (41). In this process too, the alkalinity of the pulp was increased, and the overall gain in the phosphate recovery was raised by about 10%.

vii. Another patent (43) of a similar nature was filed more recently, where the so called clay-peptizing agents (i.e. phosphates, carbonates, silicates, alkalis and their mixtures) are used to separate clay and iron and titanium-bearing minerals. The particle sizes in this process were  $90\% < 2\mu$ . An excess of the deflocculant for slurries of 10-50% solids content was used to coagulate the minor components from the clay. This is another example of selective coagulation. The separation requires a comparatively long time (i.e. coagulation sets in after  $\frac{1}{2}$ -1 hour and the stable fraction is drawn off after 24 hours). If polymeric flocculants were used, a much quicker flocculation would be obtained.

viii. Selective flocculation of silica and silicate-containing iron ores by various starches as a desliming operation has been used experimentally on a laboratory and pilot-plant scale. This makes use of the selective adsorption of starch on iron ores while <sup>of</sup> siliceous gangue in alkaline media remain suspended (because/their high zeta-potentials). This method has been used by Iwasaki et. al., (44) and by Frommer et. al. (45)(46)(47) and an upgrading of iron ore slimes by about 10% has been achieved.

ix. On an experimental basis Usoni et al. (49) studied the possibility of selective flocculation of individual minerals from their binary mixtures using 4 different flocculants and six minerals in binary mixtures. From the results of their extensive tests carried out at pH 5, 7, 9 with flocculant concentrations of  $2 \times 10^{-6}$  to  $2 \times 10^{-1}$  g/l and solids contents of 10-15% by volume it is possible in general to conclude that the problem of selective flocculation is not insurmountable although certain associated problems remain to be further investigated. These investigators seem to have overlooked the problems of "entrapment" and "activation". In many instances where perfect separation was indicated by the preliminary experiments on individual minerals, separation from mixtures was far from complete.

x. In earlier work in this Department, D.J. Collins (50) selectively flocculated calcite from mixtures containing calcite + silica by using "Seperan 2610". However, the solid contents used were extremely low ( $\approx 0.6\%$ ). Also B. Ball (51) selectively flocculated galena from a mixture of galena + quartz, employing a non-ionic polyacrylamide (which is known not to flocculate silica aged by alkaline treatment (52)). The results of this work were not satisfactorily conclusive because of the apparent mutual coagulation of the two components. Other preliminary

tests were carried out by J.P.Clark (53), but no conclusive results were arrived at.

#### 1.4 Aim of the present work and choice of the experimental system

In spite of the volume of work on bulk flocculation, the amount on selective flocculation is very limited, as has been shown above. Furthermore the number of minerals involved in these investigations is not numerous. Experimental results relevant to the stability of mineral suspensions in media containing simple inorganic ions are very few and the various physico-chemical factors involved in the flocculation of minerals remain for investigation.

This present work is intended, therefore to establish the basic principles involved in the coagulation and flocculation of minerals separately and in mixtures, and finally to investigate the possibility of separating a single component from a mixture by predicting the properties of a mineral or flocculant that may selectively interact in a given system.

Kitchener (54) has pointed out that five types of simple minerals can be distinguished according to their surface-chemical properties:

1. Sparingly-soluble ionic crystals (e.g.  $\text{CaCO}_3$ ,  $\text{CaF}_2$ ,  $\text{BaSO}_4$ ,  $\text{CaSO}_4$ , ...etc)
2. Simple oxides ( e.g.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  ...etc)
3. Sulphide minerals (e.g.  $\text{PbS}$ ,  $\text{ZnS}$ ,  $\text{FeS}_2$  ...etc)
4. Silicates and alumino silicates (e.g. clays, zeolites ...etc.)
5. Molecular crystals (e.g. native sulphur, graphite.)

Obviously further groupings can be made as the complexity of chemical composition increases and the rules applying to the surface chemical interactions of one group can be in some instances extrapolated to other minerals. Representatives of the first three groups, namely quartz, calcite and galena were chosen for experimental work, although in some instances others (i.e. ZnC, TiO, Fe<sub>2</sub>O<sub>3</sub>, CaWO<sub>4</sub>, SnO<sub>2</sub>, mica and feldspar) were also used.

For synthetic polymeric flocculants, mainly samples of polyacrylamide-based products kindly provided by B.T.I. Chemicals Ltd (Bradford) were used; but other products were also employed in some cases, as described in relevant sections below.



## 2. EXPERIMENTAL TECHNIQUES AND APPARATUS

### 2.1 Measurement of degree of flocculation

Various qualitative changes in a suspension have been used by other investigators to express the degree of particle aggregation in a given suspension: (i) In many cases good, bad or intermediate aggregation have been used to describe the state of a suspension after a certain treatment (55). (ii) For more dilute suspensions, counting the number of particles left suspended or those forming aggregates by microscopic examination has been found inconvenient (56). (iii) Measurements of light-scattering, turbidity (or light transmittance) of a suspension or supernatant liquid have often been used, both for dilute colloids and for coarser suspensions. (iv) The rate of sedimentation of the descending boundary (if it is distinct) in an unstable suspension, (v) the volume of sediment after a certain settling time, (vi) floc size, (vii) thickness of a consolidated flock bed or the thickness of a filter-cake obtained by filtration of a suspension under standard conditions have been used. (viii) A quantitative theory based on the refiltration rate of a suspension flocculated by polymers has been put forward by La Mer and Smellie (58) but its agreement with experimental data was shown by Slater and Kitchener (59) to lack significance. (ix) Conductance between electrodes placed suitably on the walls of the container holding a suspension (or a settled bed) have also been used to determine the degree of aggregation (60). (x) Another conductometric technique has been developed by Basherville and Gale (61) where the capillary movement of the suspending liquid in a filter paper, ("CST" capillary suction time) is automatically recorded and is dependent on the permeability of the flock bed. Among other possible indices of flocculation, (xi) the use of the "sedimentation balance" (62) or (xii) chemical analysis of each fraction,

particularly in the case of selective flocculation experiments, can be cited.

Correlation between the various indices above has been sought by others (59)(63)(64) but the final selection of one or more index to express the degree of flocculation remains arbitrary, depending on the particular system used for flocculation.

No theoretical treatment of orthokinetic flocculation of concentrated suspensions of heterodisperse, non-spherical particles can be hoped for, and therefore any proposed test of effectiveness of flocculation need only meet the requirements of reproducibility, sensitivity and convenience.

In this work as well as visual examination, and determination of the solids content of a fraction of a suspension by drying and weighing, measurement of thickness of the settled bed after a certain time were used for certain purposes. However, most of the test work was based on the variation of the light transmittance of a dilute mineral suspension and the measurement of the light transmittance of the supernatant liquid after a certain time, following standardized methods of addition and "conditioning". For this purpose an "EEL absorptiometer" was employed and the transmittances of liquids measured in rectangular 1 or 10 cm or a 1 cm cylindrical cell, depending on the turbidity of the liquid in the former and the heights of the flocculated bed in the latter cases. Since no difference was found in using different light filters all measurements were made without a colour filter.

## 2.2 Method of flocculant addition

The flocculants were diluted to the degree required (0.01 - 240 ppm) from a stock solution of 1000 ppm flocculant

and mixed with the agitated solid suspension in the course of 37 seconds. The optimum conditions for reagent addition and subsequent conditioning were studied separately and are given in sections 7.5

### 2.3 Electrophoretic mobility and zeta-potential measurements

Electrokinetic potential measurements on solids can be carried out by various methods such as electrophoresis, electro-osmosis, sedimentation potential and streaming potential (16) as well as moving boundary and transport methods and a new pendulum method (65) which is said to be suitable for particles of about 0.5  $\mu$ m diameter.

The double layer theory has been developed since Helmholtz (66) who considered that the double layer consists of two parallel arrays of oppositely charged ions (rather like a condenser) separated by a fixed distance; by Gouy and Chapman, Stern (67), Grahame (68) and others. Many reviews including recent developments have been published (16). When a particle moves relative to a suspending liquid (or the other way around) only part of the ionic atmosphere surrounding it moves with the particle. The potential at the shear plane (or the "slipping plane") with respect to a point in the bulk of the solution is called the zeta-potential ( $\zeta$ -potential). This is the only quantity measurable by electrokinetics (and even this treatment is subject to a number of assumptions).

The zeta-potential of a very small particle considered as a point charge which is moving with a velocity  $V_E$  under a potential gradient  $E$ , in a liquid of dielectric constant  $D$  and viscosity  $\eta$  is given by Huckel's equation, viz.

$$\zeta = \frac{6\pi\eta}{D} \frac{V_E}{E} \dots\dots(3)$$

This applies when  $\kappa a$  (the ratio of the particle diameter to the thickness of the double layer) is small. Henry's equation applies to small, medium or large particles having any value of  $\kappa a$ , viz.

$$\zeta = \frac{6\pi\eta}{D} \frac{V_E}{E} f(\kappa a) \dots\dots(4)$$

where  $f(\kappa a) = \left[ 1 + \frac{(\kappa a)^2}{16} - 5 \frac{(\kappa a)^3}{48} - \frac{(\kappa a)^4}{96} + \frac{(\kappa a)^5}{96} \right] \dots(5)$

(69). However in experiment with particles larger than  $1\mu$ , the Helmholtz-Smoluchowski equation (70) which strictly applies only for  $\kappa a \gg 1$  is commonly used

$$\zeta = \frac{4\pi\eta}{D} \frac{V_E}{E} \dots\dots (6)$$

For water as suspending medium, when  $V_E$  is expressed in  $\mu/\text{sec}$ , and  $E$  in  $V/\text{cm}$ , the factor  $4\pi\eta/D = 12.9$  at  $25^\circ\text{C}$ .

The following considerations are assumed to be true when eqn(6) is used, which is seen to be independent of the particle size and shape:

- (i) The particle is a non-conductor.
- (ii) Viscosity and dielectric constant of the solution in the double layer and in the suspending medium are the same.
- (iii) The applied field is superimposed on the electric field of the double layer.
- (iv) The liquid motion around the moving particle follows a streamline pattern.

The velocity of the particle however, is slowed down due to the relaxation effect caused by the deformation of the double layer symmetry, due to movement of the particle in one direction. The part lagging behind causes a slowing of the particle because it creates an electric field opposing the applied electric field. Corrections can be made for this effect (71) in the case of spheres, for the surface conductivity (72) and for differences between the values of  $D$  and  $\eta$  in the double

layer and in the bulk of the suspending liquid (73). These points have been frequently discussed in literature (16)(74) and are subjects of current research (75). However, the refinements can be neglected for the purposes of the present problem.

In this work the following techniques were used for the determination of the  $\zeta$ -potentials of small particles.

(a) The moving boundary method. The apparatus constructed by Saleeb (76) was adopted for the measurement of  $\zeta$ -potentials of precipitated PbS suspensions. It consisted of a "Pyrex" U-tube with taps appropriate for the formation of a boundary between the suspended solids and a clear solution with the same ionic composition as that of the suspending medium. Potential was applied from side arms without causing turbulence in the liquid system. The actual potential gradient applied was measured with platinum electrodes dipped in the solution and attached to a suitable null-meter circuit. The experimental set up is described elsewhere (76).

(b) Micro-Electrophoresis. This method was used more frequently for relatively stable mineral suspensions containing particles visible at 400X magnifications. The apparatus was that described by Bangham et.al.,(77) and manufactured by Rank Bros., Cambridge. It consisted of a cylindrical capillary tube immersed in a constant temperature bath ( $\pm 0.1^{\circ}\text{C}$ ) and fitted with platinum electrodes\*. The power supply formed an integral part of the unit. The effective distance between the electrodes was calculated by measuring the conductance of KCl solutions of known concentrations. The stationary level ( the plane where the net electro-

---

\* The manufacturers suggest the platinization of the electrodes prior to use (78) which is surprising in view of the fact that  $\text{O}_2$  and  $\text{H}_2$  over-potentials are higher on smooth platinum than on black platinum electrodes (79)

osmotic flow in the closed cylindrical cell is zero) can be determined by focussing to  $0.147r$  from the cell wall where  $r$  is the internal diameter of the cylindrical tube (80). Unfortunately the lens supplied with the cell had too short a working distance to allow the construction of a velocity profile across the cell. Half a velocity profile could be constructed horizontally and zero velocity was obtained at the calculated stationary level. (The diameter of the tube was confirmed to be 2 mm as reported by the manufacturers). A complete vertical velocity profile gave a symmetrical parabola and a plot of  $V(\text{obs})$  versus  $(Z-Z^2)$  where  $Z$  = the fraction of total depth at which  $V(\text{obs})$  (the observed velocity) is obtained gave a straight line with a slope  $d = 100$ , in accordance with equation (7) given by Moyer and Abramson (81)

$$V_{\text{obs}} = d(Z-Z^2) + e \quad \dots\dots(7)$$

Furthermore, the zeta-potential measurements made with this micro-electrophoresis apparatus agreed well with measurements made with the electro-osmosis apparatus described below (82)

(c) Gortikov's electro-osmosis apparatus: Particles with low zeta potentials (e.g. galena in distilled water) do not give stable suspensions which can be used in either of the methods described above. In such instances electro-osmosis where the movement of the equilibrium liquid with respect to a stationary bed of charged particles under the influence of an applied electric field takes place is suitable. In this case the classical electro-kinetic equation (neglecting surface conductivity) is

$$\gamma = \frac{4\pi\eta}{D} \frac{v}{E} \frac{\ell}{A} \quad \dots\dots(8)$$

where  $v$  = total volume of the liquid flowing through the porous solid bed.

$\ell$  = length of the solid bed (plug)

A = cross-sectional area of the plug

E = potential applied

which can be converted to a more convenient form by using Ohm's law for specific conductance  $\Lambda$  ; hence

$$\zeta = \frac{4\pi\eta}{\Omega} \cdot \frac{v}{i} \Lambda \quad \dots\dots(9)$$

and thus at 20°C the expression for  $\zeta$ -potential in mV becomes

$$\zeta = 2.4 \times 10^6 \frac{v}{i} \Lambda$$

if v is in ml. min<sup>-1</sup>,

i, in mA and

$\Lambda$ , in mho. cm<sup>-1</sup>

The main practical problems in using electro-osmosis for the determination of  $\zeta$ -potentials of non-conducting porous plugs, assuming the potentials are high enough to give measurable electro-osmotic flow of liquid, are in obtaining a compact bed without particle movement and in preventing gas evolution on the electrodes. These difficulties were overcome by using the so called Gortikov's apparatus (95)(96) shown in figure 2. The apparatus consisted of a centrifuge tube (A) with two 25mm glass tubes (a and b) one of which extended to the bottom. Two graduated capillary pipettes ( $p_1$  and  $p_2$ ) of 0.1 ml capacity, and two other tubes ( $t_1$  and  $t_2$ ) are joined to (a and b) as shown in the figure.  $t_1$  and  $t_2$  were filled with agar-gel saturated with KCl and current was applied through ( $B_1$  and  $B_2$ ) two beakers filled with  $H_2SO_4$ - $CuSO_4$  solution; from a d.c. power supply. The polarity of the current could be reversed by the switch (SW). Two glass stoppers (PL) could be moved up or down to arrange the positions of the menisci in  $p_1$  and  $p_2$  at the beginning of each experiment.

For the measurement of  $\zeta$ -potentials the mineral slurry was filled through (a) and centrifuged to obtain a compact bed. The tube (A) was filled with the equilibrium liquid through (b).

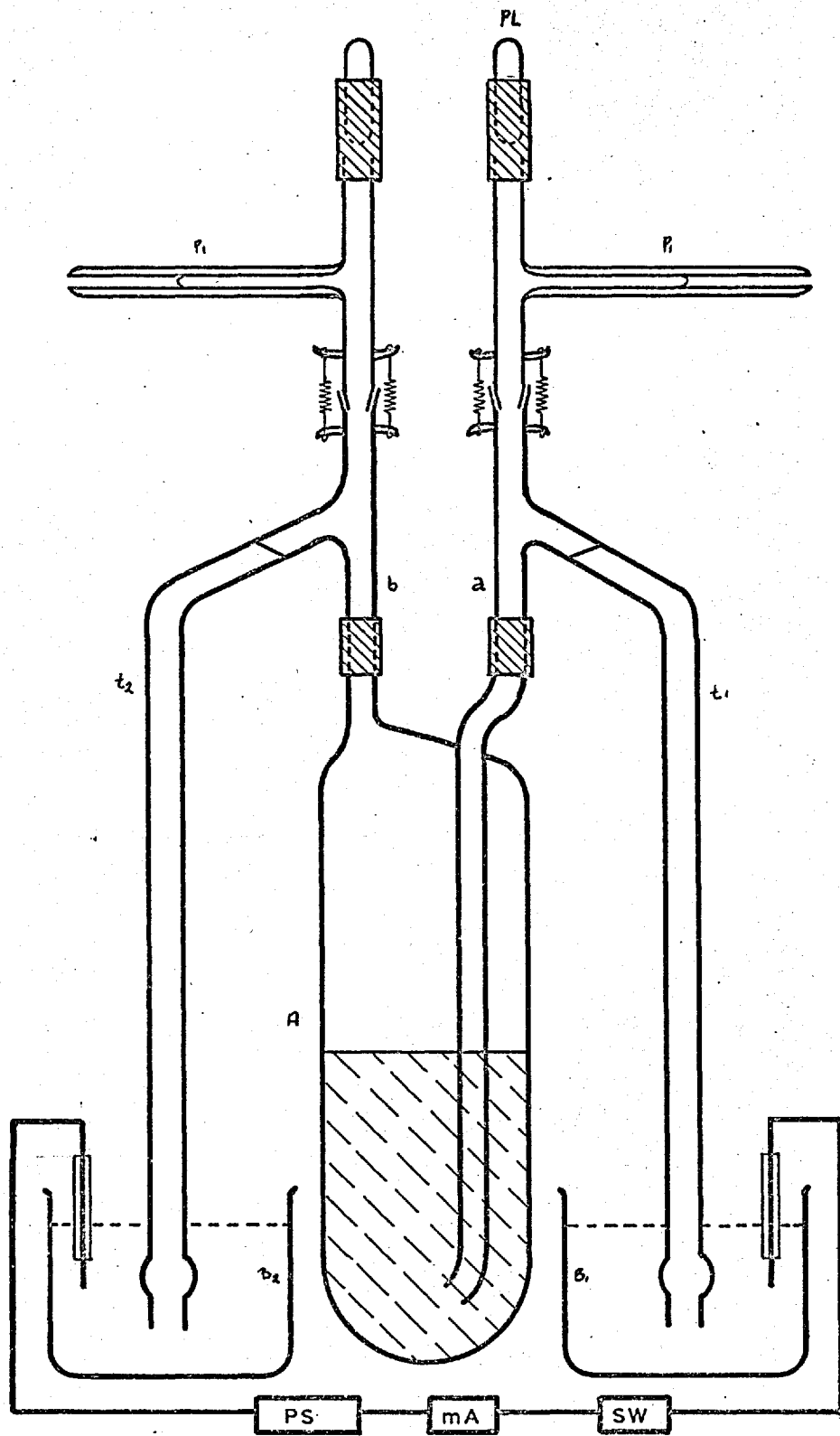


Fig. 2 Gortikov's electro-osmosis apparatus



Conductances of the equilibrium liquid were measured before and after each experiment and the average taken for the value of ( $\Delta$ ).

Various merits and disadvantages of using either of the above described methods have been discussed in a recent book by Shaw (80); similarly agreements between the values obtained by either of the methods have been discussed in various reviews (13)(83)(76). Here, it is sufficient to state that the same results were obtained by micro-electrophoresis and electro-osmosis for several systems tested on both. The differences and similarities obtained between the findings of other investigators on the minerals used in this work are discussed in the relevant chapters below.

#### 2.4 Determination of small quantities of flocculants.

The quantitative analytical determination of small quantities of flocculants is desirable particularly for the interpretation of flocculation results in terms of surface coverage and flocculant up-take. Although it is possible to determine polyacrylamide (PAM) -based flocculants in large quantities by decomposition and analysis of the chemical constituents (84)(85), i.r. or u.v. spectroscopy (86)(87) and by back titration with acid or base after treatment of the flocculant by one of these reagents for a certain time (88), very small quantities (i.e. < 2ppm) present a considerable difficulty in obtaining accurate results. The use of radioactive tracer tagging as has been done in the determination of adsorbed quantities of flotation reagents or inorganic ions (2) in the same field, has only rarely been used for flocculants (89) due to the lack of the availability of such products, a problem which is partially aggravated by the fact that the exact structural properties of many commercially available flocculants are either not reproducible or not exactly known. Turbidimetric

determinations of hydrolysed PAM (making use of the interaction of the  $\text{-COO}^-$  groups with an oppositely charged organic cation (84), where "Hyamine-1622" is added to PAM solutions under controlled conditions and the turbidity measured to obtain a Beer's Law curve) have been successfully reproduced (90) for the determination of AP-30 (hydrolyzed PAM) at quantities as low as 0.5 ppm. In some instances it is also possible to estimate small quantities of non-ionic PAM by flocculating silica with the polymer left in solution (91). This makes use of the fact that freshly ground quartz or quartz heated at temperatures  $>350^\circ\text{C}$  adsorbs PAM by hydrogen bonding. It is maintained that (92) polyacrylic acid flocculants interact with divalent metal ions (i.e.  $\text{Cu}^{2+}$ ) in accordance with the law of mass action, although agreement on this point is not universal (93). Nonetheless, there is scope for the development of an analytical technique by using divalent tracer cations which are more easily available than polymers containing  $\text{C}^{14}$ , and following the cation uptake by the polymers. Hopeful speculation could be extended for the use of paper-or thin-layer chromatography which is widely used in the study of fats, sugars, proteins etc (94), for the determination of trace quantities of flocculants. Qualitative information can be obtained about the active groups of the flocculants by adsorption of suitable dyes on the undissolved solid (97). Also the cationic or anionic properties of a flocculant can be assessed by the use of ion-exchange resins of known properties as described in appendix E. The presence of adsorbed flocculant on a substrate can also be qualitatively ascertained under suitable conditions as described below for C 110 and in section 4.5 for PEVPO.

a. Qualitative assessment of adsorption of flocculants by minerals

In some instances whether lack of flocculation is due to

lack of flocculant adsorption, excessive flocculant up-take (causing steric stabilization) or due to coiling of polymer molecules, can be checked by finding out whether the flocculant has adsorbed or not.

Two samples of solids, one <sup>treated</sup> by flocculant, and the untreated one being the <sup>reference</sup> ~~untreated~~ solid, are centrifuged if necessary and washed repeatedly and dried. It is known that limited washing does not desorb the adsorbed flocculant. A fraction of each solid is then tapped into a "Pyrex" glass tubing of fine bore of which one end is closed by heating. The glass tubing is also heated to redness prior to use, in order to remove any organic material. When the solids in the tubes are heated slowly on a flame, the one containing adsorbed flocculant chars, releasing finely divided carbon black which causes a darkening of the solid. It is noted here, that this method can only be applied to white solids which do not give colored charring products (i.e.  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , etc.)

b. Quantitative estimation of small quantities of anionic flocculants

It was found that the anionic flocculants (namely the BII-A and polyteric S-1) gave a white precipitate at  $\text{pH} < 3$  which formed an unstable suspension. It was also found that this precipitate is much more stable in the presence of polyethyl-vinyl-pyrrolidone oxide (PEVPO), for long enough time to allow measurements of turbidity. It is known for instance, that flotation collectors which are either cationic or anionic in character alone, show properties which indicate that they interact with the mineral and one another (98). The following procedure was found suitable for turbidity measurements:

Various quantities of anionic flocculants were placed in

100ml volumetric flasks with 2.5 mg of PEVPO and 25 cc of 1 N HCl and the volume completed with distilled water. The turbidity of the suspension increased in the course of 5 minutes and remained constant for 30 minutes as opposed to the decreasing of turbidity in 9 minutes (due to aggregate growth) in the absence of PEVPO. Measurements were made using an "EEL nephelometer" with a red-filter. The calibration curve obtained for BT1-A80 is given in figure 3.

### 2.5 Other experimental techniques

Other experimental techniques such as electron microscopy, viscometry, conductometric titration etc. were used as required and are given in relevant chapters below.

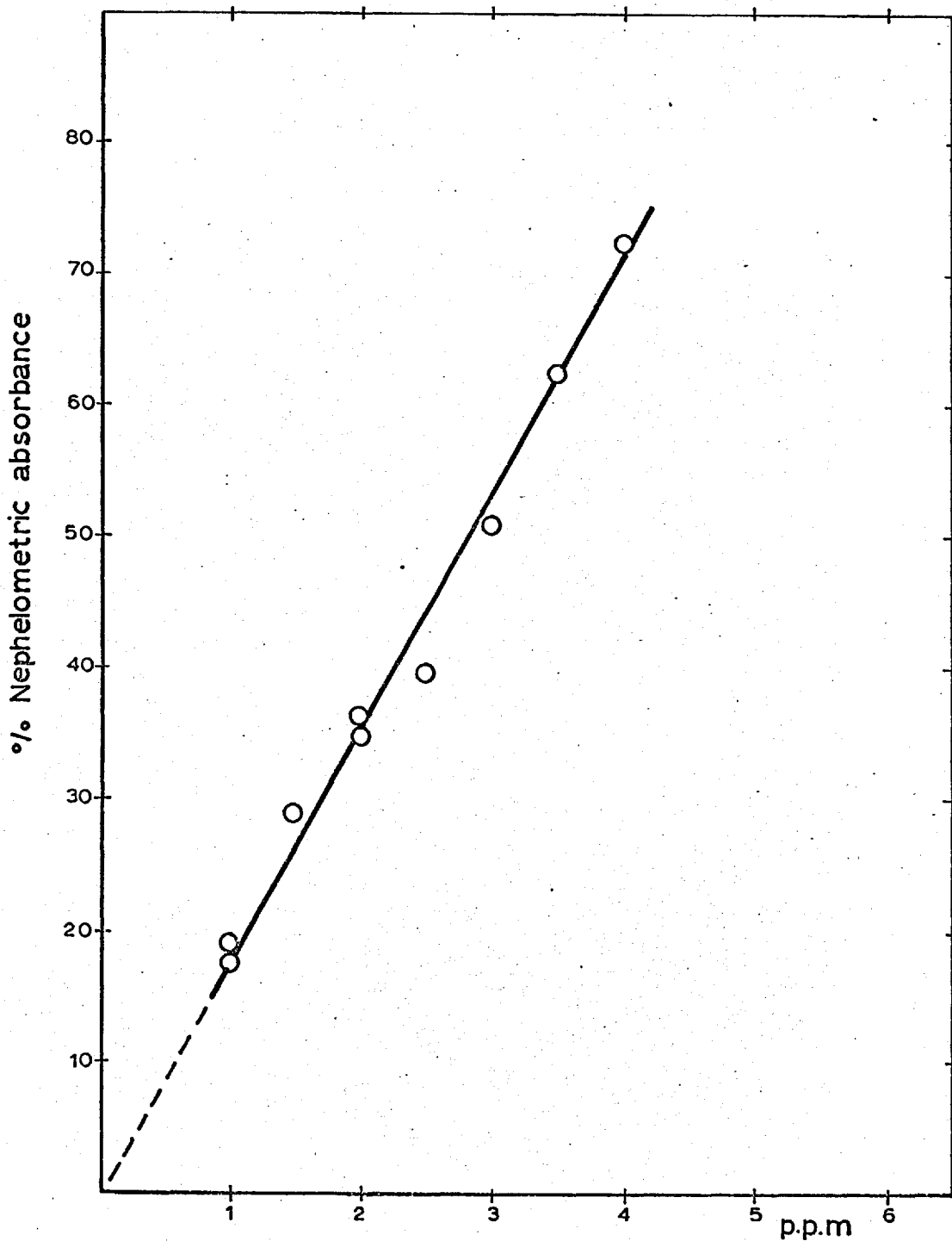


Fig. 3 Calibration curve for the nephelometric determination of BTI-A80

### 3. PRELIMINARY EXPERIMENTS

3.1 The three minerals used in this study were quartz, calcite and galena

a. Calcite was a commercially supplied powder of natural  $\text{CaCO}_3$  ("Vedar") and needed no further grinding. It has been reported by the distributors to be 99% pure  $\text{CaCO}_3$ . It was found to contain a trace quantity of iron.

b. Galena was prepared for experimentation by hand picking of natural  $\text{PbS}$  crystals after crushing to -5 mm. Grinding of the mineral was effected by placing about 100g of galena and an equal quantity of quartz of the same size in a "Pyrex" flask and agitating on a mechanical flask agitator for 1-3 days. The attrition products passing a 400 mesh ( $37\mu$ ) screen were collected and stored under water in a stoppered flask.

c. Quartz powder was prepared as follows:

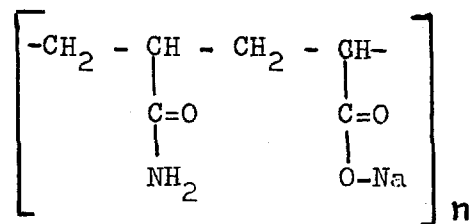
Quartz from the Isle of Man was crushed to -5 mm and inclusion-free grains selected and boiled in 10%  $\text{HCl}$ , decanting the acid and repeating the process a few times. Finally the crystals were washed with distilled water of gradually decreasing acidity, and after washing with distilled water several times they were dried at  $130^\circ\text{C}$  for one night. Grinding was affected by placing 50g batches in an all-agate vibratory mill and grinding each batch for 30 minutes. All of an average sample passed a 400 mesh screen and no contaminating ions could be detected in the powder.

Size analyses of the three mineral powders were made by micro-mesh sieves and the results are given in Table 1 over page.

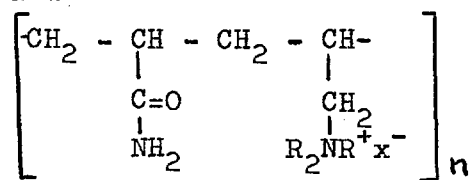
Table 1  
Size distribution of minerals

Size Range (microns)	% Weight		
	SiO <sub>2</sub>	CaCO <sub>3</sub>	PbS
-34 +22	20.74	0	0
-22 +11	19.78	0	0
-11 +5.5	27.83	40.30	67.96
-5.5	31.65	59.70	25.74

3.2 The BTI flocculants used in experiments were all water-soluble granules comprising anionic (abbreviated as A) A100, A130, A150, A70 and A80 the increasing anionic character following the above order; and cationic (abbreviated as C) C100 and C110, the latter being more cationic in character. The A products were presumably prepared by alkali hydrolysis of PAM and the C products were probably formed by the co-polymerization of acrylamide monomer with quaternary ammonium compounds, the structures being probably



and



respectively

All the polymers were reported to have essentially the same molecular weight, which is several millions. All but C100 formed viscous solutions on stirring mechanically at 400 r.p.m. for three days. However, C100 remained in lumps even after stirring for one week. On standing at dilutions of 100 p.p.m. for 1 month or more at room temperature A100, A130 and A150 developed green algae which did not visibly develop in similar solutions kept at 5°C. The same algal growth was observed in 1% solutions of AP-30, an American Cyanamide 30% hydrolyzed PAM of 3 million molecular weight.

The nephelometric method described in section 2-3b above showed that for the same quantity of flocculant (1-10 p.p.m.) the turbidity increased in the order of increasing character, namely, A100 < A130 < A150 < A70 < A80. With this method it was found that "polyteric S1" (produced by Glovers Chemicals, Leeds and of composition not disclosed) behaved like A70 although its 1% solution was much less viscous than the former.

The viscosities of the A flocculants at 100 p.p.m. were measured in 1 N NaCl solutions at pH 5 and 25°C ± 0.02 using a suitable Ostwald viscometer. The relative viscosities followed the order A150 < A100 < A130 < A70 < A80, indicating that A150 had a smaller molecular weight than all the others although its flocculating power (see table 15) for calcite was higher than that of A100 and A130.

Acid-base titration of the flocculants on the other hand gave the following results. All the anionic flocculant gave a visible turbidity at pH 2.5 ± 0.1 with an HCl consumption of approximately 10 meq HCl/lg. flocculant. However, in base titration the base consumption was greatest for A80 the order for the consumption for the others being A80 > A70 > A150 > A100. In both acid and base titrations the reagents had to be concentrated (1 N) otherwise no difference could be observed between



the titration curves. The flocculants had also to be concentrated (500 p.p.m.) for differences to be observed. In the base titration the inflection point was not clear-cut but widely stretched; however it could be estimated by extrapolation, to be at pH  $8.7 \pm 0.1$  except for A100 which was at pH  $8.3 \pm 0.1$ . The base consumption was as given below

Flocculant:	A100,	A150,	A70,	A80
NaOH meq/g:	0.3	0.4	0.9	1.1

The flocculating action of the BT1 flocculants on the three minerals were tested as follows.

Flocculants were prepared at 1000 p.p.m. concentration and samples pipetted out were diluted as required. Experiments with quartz, calcite and galena at solids contents of 0.5, 0.2 and 0.05% respectively were made. Solids suspended in distilled water (pH 4.8-5.1) were treated with quantities of flocculants that would form 5 p.p.m. on dilution in 50ml glass stoppered cylinders, first agitated vigorously and then inverted gently for about 1min. Results were noted as good flocculation (+), no flocculation (-) and partial floc formation with a haze left ( $\pm$ ), five minutes after treatment, by comparison with a reference suspension without flocculant. Galena samples were not washed before these experiments. The results are summarized in table 2 see overleaf.

Table 2

Action of BTI flocculants on minerals  
in distilled water

Flocculant	Quartz	Galena	Calcite
C100	+	+	+
C110	+	+	+
A100	-	+	+
A130	-	+	+
A150	-	+	+
A70	-	+	+
A80	-	+	+

#### 4. STABILITY AND COAGULATION OF QUARTZ SUSPENSIONS

##### 4.1 Introduction

When dry-ground silica is placed in water a negative surface charge develops with the dissociation of the solid along the broken -Si -O- bonds. The solid also dissolves in the course of a few days. There have been numerous investigations relating to the mechanism and extent of the solubility of silicas though the system is not yet fully understood. It has long been recognised that ground quartz has a surface layer which is not completely amorphous but has a somewhat looser quartz structure (99). Its thickness has been variously estimated to average 50-300Å<sup>o</sup> (100)(101)(102)(103)(104). The probability of this layer being made of two parts namely an outer completely colloidal 2 Å<sup>o</sup> thick part under which there is a less colloidal part which is more disordered than quartz has also been suggested (105). The disturbed layer can be removed by etching by HF or alkali (106)(107). A silicic acid layer is deposited on quartz when silica is equilibrated with a solution containing dissolved silicic acid (116). It appears that different methods of grinding produce disturbances of varying magnitude (109). The composition of the surrounding liquid also effects the dissolution of this layer. Okkerse (110) found that the rate of dissolution is minimal at pH 2 and the presence of NaCl in the medium at pH 4 increases the rate of dissolution. Other investigators (111) on the other hand, found that both the rate of solution and the quantity dissolved increase on increasing the NaCl concentration above 0.1 N. Findings on the same lines have been reported by Greenberg and Price (112) who observed no variation in the quantity of dissolved silica at NaCl concentrations  $10^{-4}$  -  $10^{-1}$  mol/l.

The quantity of dissolved silica also, seems to depend on the various forms of the solid but in general amorphous silica

seems to dissolve more rapidly and to a much greater extent than quartz as can be seen from table 3. The equilibrium in the silica/water system is never reached at ordinary temperatures owing to the slowness of the hydration/dehydration reactions.

The action of inorganic ions on silicas is also not completely understood. It is important, from the selective flocculation point of view, to know the effects of ions introduced into an aqueous medium in mixtures containing minerals other than quartz. It has been established, for instance, that alkali metal ions preferentially adsorb on quartz according to the

**lyotropic** series of the ions (113), the most strongly adsorbed ions being Cs, i.e.  $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ . Gaudin et al. (113) also found that the accompanying anion effects the adsorbability of a cation; for instance  $Na^+$  is more strongly adsorbed when it is in a fluoride salt and the order of the other anions is  $F^- > SO_4^{2-} > NO_3^- > Cl^-$ . French and Howard (114) found that the adsorption of a mono or polyvalent cation is accompanied by the discharge of an equivalent quantity of  $H^+$  into the solution phase. Other investigators (122) have also attributed the uptake of divalent cations to similar ion-exchange reactions. Malati (116)(117) found that the adsorbability of divalent cations increased in the order  $Ba^{2+} > Sr^{2+} > Ca^{2+}$  which is the order to be expected if hydrated ions were held by Coulombic forces, as  $Ba_{(aq)}^{2+}$  is the smallest of the three ions when in water and could therefore approach closest to a  $-SiO^-$  unit.

The mechanism of adsorption of divalent ions and their subsequent effect on the attachment of flotation collectors has received considerable attention. Fuerstenau, (118) from electrokinetic measurements concluded that the divalent cations are situated in the **Stern** plane of the double layer and are

Table 3. Solubility of silicas in water according to various authors.

Investigator(s)	Silica-Solubility mol/l	Reference
Lenher (1921)	Q. $5 \times 10^{-3}$	(200)
Hitchen (1936)	A. $2.8 \times 10^{-5}$	(201)
Paterson and Wheatley (1955)	Q. HF treated	(202)
Krauskopf (1956)	$1.8 \times 10^{-4}$	(203)
	A. $1.6 \times 10^{-3}$ to $2.3 \times 10^{-3}$	
White (1957)	- Oceans $2.5 \times 10^{-3}$ Hot springs $8.3 \times 10^{-3}$	(204)
Siever (1957)	Q. $1.2 \times 10^{-4}$	(205)
Mosebach (1957)	Q. $9 \times 10^{-3}$	(207)
Smith (1958)	Q. $1.8 \times 10^{-4}$	(206)
Fournier (1960)	Q. $6.6 \times 10^{-5}$ to $1.6 \times 10^{-4}$	(208)
Van Lier, et. al. (1960)	Q. $1.8 \times 10^{-4}$	(111)
Morey, et. al. (1963)	Q. $1 \times 10^{-4}$	(209)
Stober (1967)	various states, $2 \times 10^{-4}$ - $1.8 \times 10^{-3}$	(210)
Lindstrom (1968)	A. $1.6 \times 10^{-3}$ - $2.3 \times 10^{-3}$	(105)

held by "chemical" forces. The coagulation of silica suspensions by divalent cations has been variously assumed to be due to the formation of silicates (105)(119)(120)(121) or the formation of ionic bridges brought about by the hydrolysis products of the cations (129)(130) or the electrostatic adsorption of the colloidal hydrolysis products (124).

Because of its relevance to the present problem, an analytical attempt was made (see below) to decide whether the corresponding metal silicates can form in the presence of divalent cations involved in mixtures with quartz, calcite and galena for selective flocculation.

#### 4.2 Experiments on the stability of quartz suspensions

(a) The weight of ground quartz suspendable in water: A set of 250cc glass stoppered graduated cylinders were filled with previously boiled distilled water of pH  $6.8 \pm 0.1$  and 50g of quartz powder dispersed in each of them. They were then set in a water tank to minimize temperature variation and 1 ml samples pipetted out from the 200 ml level in each cylinder at half-hour intervals. The solids content of each sample drawn out was determined by evaporating the liquid at  $120^{\circ}\text{C}$  in a previously weighed weighing bottle. Optical transmittances of similarly taken samples were also measured in 1 cm cells, after dilution 100 times. The results are given in figure 4A and 4B respectively where it is seen that the solid suspendable under these conditions reaches a steady value of 3.5% in four hours. (This value depends of course, on the particle size distribution of the starting powder)

(b) Effect of pH (arranged by NaOH and HCl): 0.5% quartz suspensions were prepared in water of previously arranged pH values. Percent transmittances taken after 7 hours as in the above case are shown in figure 4(C). In (D) of the same figure

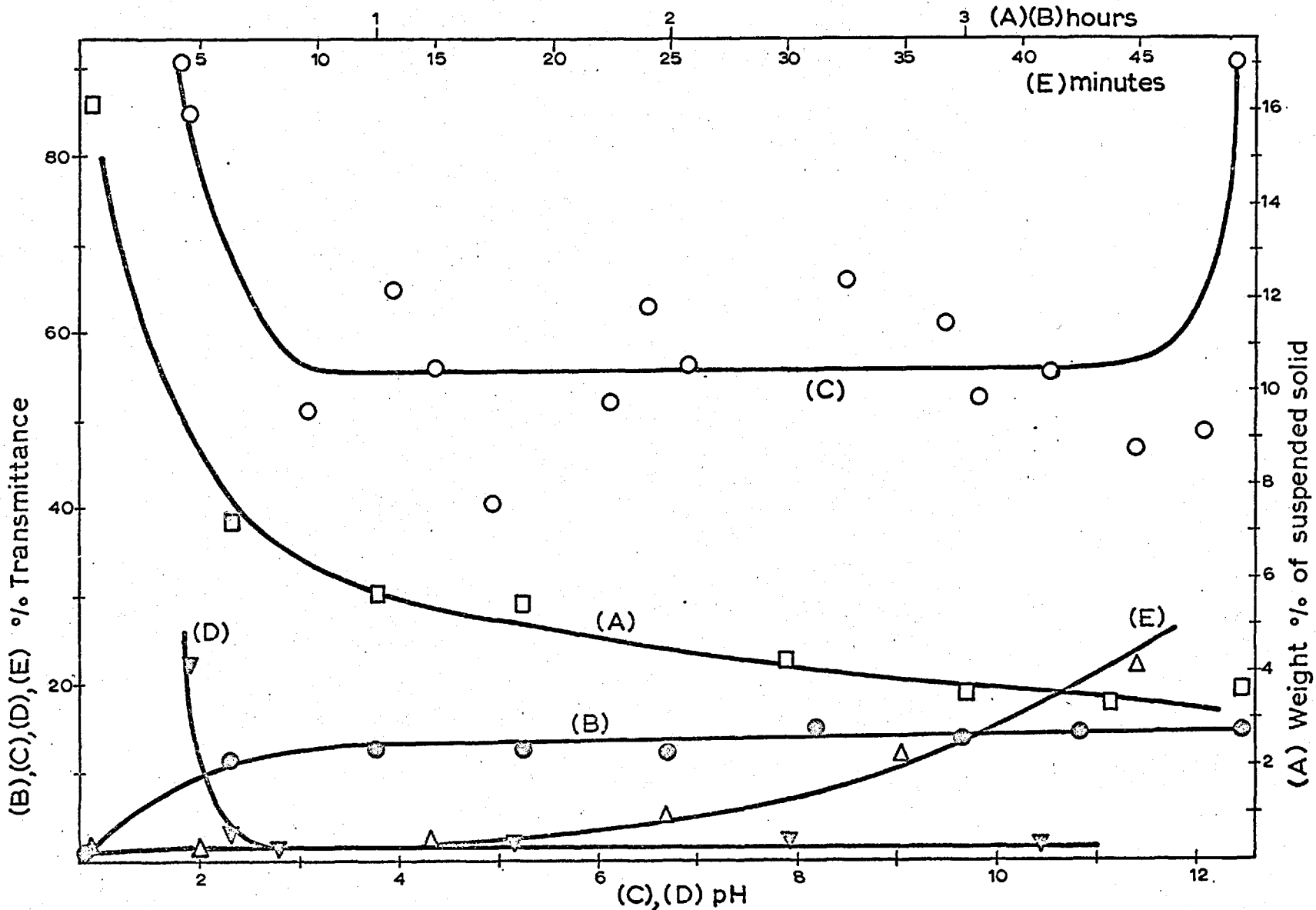


Fig. 4 Stability of quartz suspensions

transmittances measured after 45 minutes, in a medium of ionic strength of  $10^{-2}$ , and varying pH are given for a 2% quartz suspension. Figure 4(E) shows the coagulation of similar quartz suspensions at pH 1.9 for a time interval of 45 minutes.

(c) Effect of carbonates: The pH of ordinary distilled water varies from 4.5 to 6.5 depending on the quantity of dissolved  $\text{CO}_2$ . (See also section 5-1). The predominating hydrolysis species will be in the following pH ranges

pH	:	<6.7	6.7-10.3	>10.3
Species:		$\text{H}_2\text{CO}_3$	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$

Carbon dioxide was bubbled<sup>b</sup> through distilled water to obtain pH 4 and higher pH values were obtained by  $\text{Na}_2\text{CO}_3$  solution up to pH 10.5 (where the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  buffer forms). In these carbonate solutions 0.5% quartz suspensions did not show any stability properties different from those in media of which the pH was arranged by NaOH.

(d) Coagulation of quartz suspensions by NaCl: The coagulation of suspensions with electrolytes proceeds with an initial stage of slow coagulation followed by rapid coagulation with higher salt additions (16)(125). Techniques usually make use of the initial stage of coagulation in a time interval of a few minutes (126)(127). In this study, suspensions of quartz were prepared by placing a weighed quantity of quartz in NaCl solutions of known concentrations and previously arranged pH in 100 ml volumetric flasks, followed by vigorous shaking and treatment in the ultrasonic bath for 3 minutes to secure complete (or at least, reproducible) initial dispersion. Transmittances of the suspensions were then followed in a 1 cm cell for 20 minutes readings being taken at 2 minute intervals. Experiments were made with low solid contents (initial transmittance 38%) and high solid contents (0.5% solids, initial transmittance 1%).



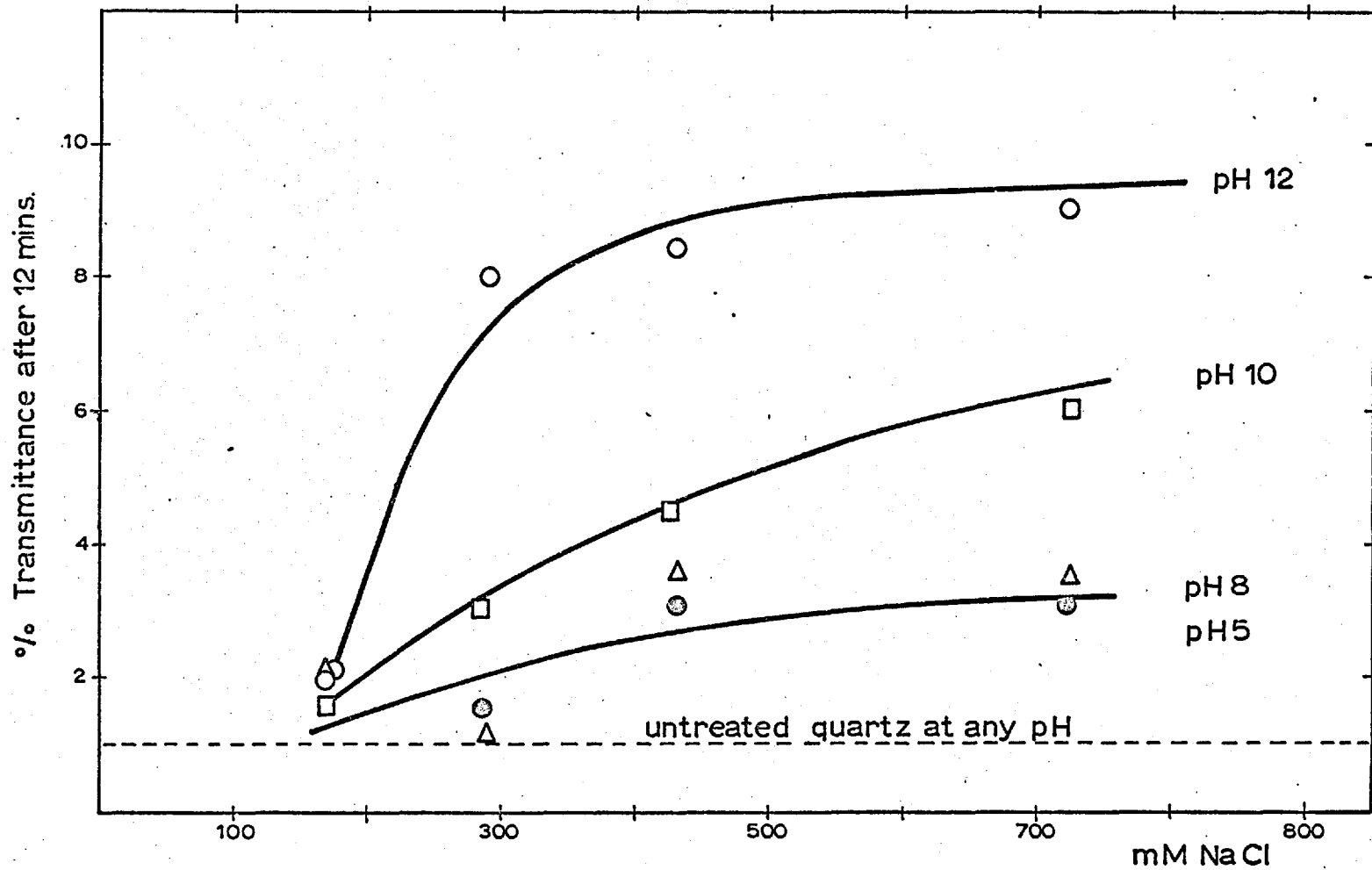


Fig. 5 Stability of dry ground fresh quartz (0.5% solids) in Na Cl solutions

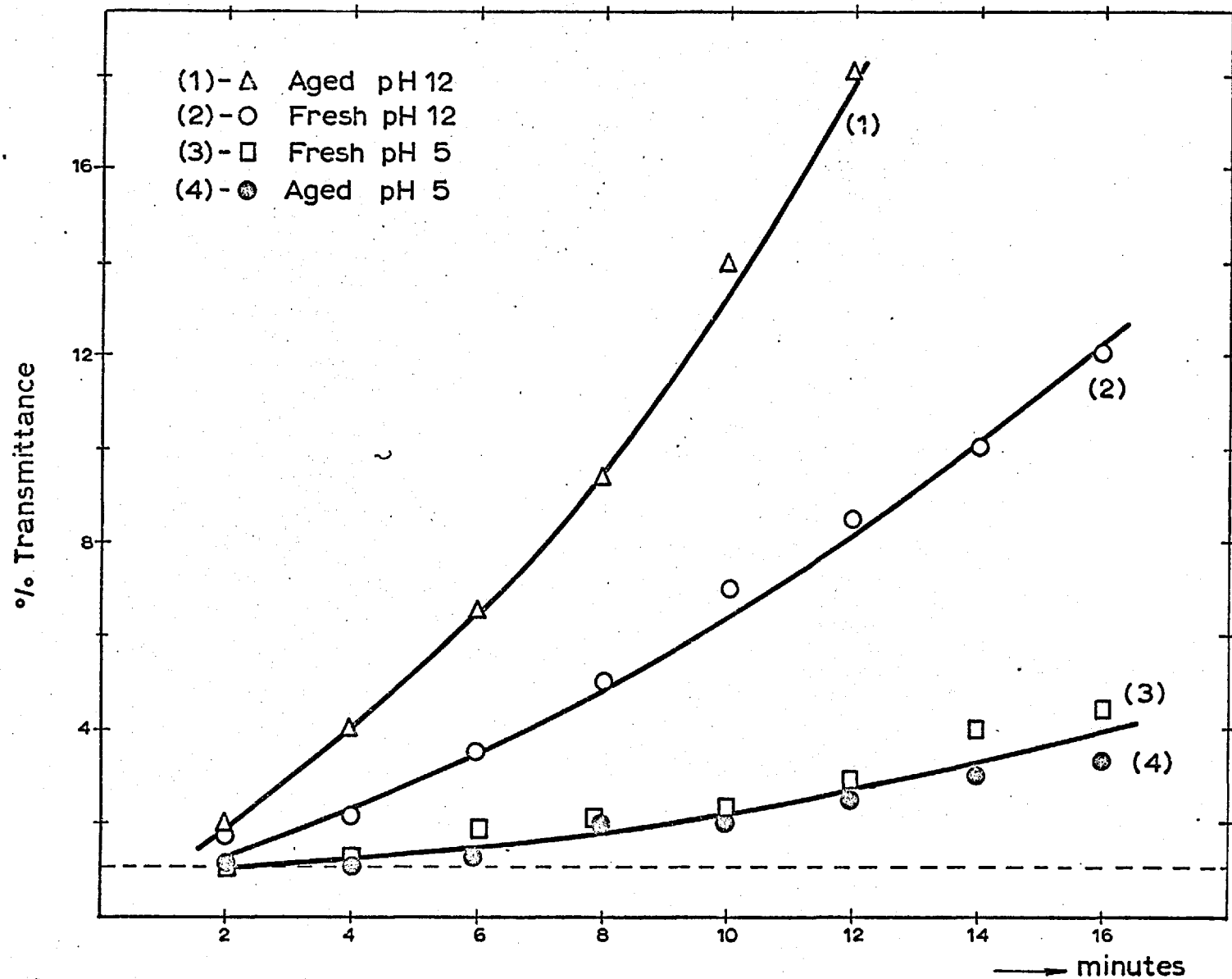


Fig. 6 Comparison of the coagulation rates of aged and fresh quartz in 426 mM Na Cl solution

In the former case the differences in coagulation rates were not satisfactorily significant whereas those of the latter case gave the results summarized below.

(i) The rate of coagulation of freshly suspended dry ground quartz is dependent on  $[\text{NaCl}]$  and  $[\text{OH}^-]$ . Coagulation is more pronounced above pH 8 than below, (as seen in figure 5).

(ii) The critical coagulation concentration (c.c.c) of NaCl for these suspensions of quartz was 172 mM at pH 12.

Similar tendencies were observed for quartz suspensions "aged" by boiling for 8 hours and kept in water for 2 months. However,

(iii) The rate of coagulation of aged quartz was higher than that of fresh quartz at similar solid, NaCl and  $\text{OH}^-$  concentrations, particularly at  $\text{pH} > 10$  as illustrated in figure 6.

(iv) The critical coagulation concentrations for these samples of aged quartz at pH 12 was 125 mM (i.e. significantly lower than for fresh quartz).

The effect of pH in these experiments is broadly in agreement with the findings of Watillon and Gerard (128) who used an essentially monodisperse silica suspension; but contrary to their statement, it is also possible to coagulate quartz at neutral pH providing the NaCl concentration is  $> 300\text{mM}$ , as seen in figure 5. In this figure, the dotted line shows the transmittance of quartz suspensions in the absence of NaCl

#### 4.3 Coagulation of quartz suspensions by divalent cations

Since a quartz suspension mixed with calcite or galena will be subjected to the possible coagulating action of the cations constituting these minerals the effects of  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  (as well as that of  $\text{Ba}^{2+}$ ) all in their  $\text{NO}_3^-$  salts were checked. For this

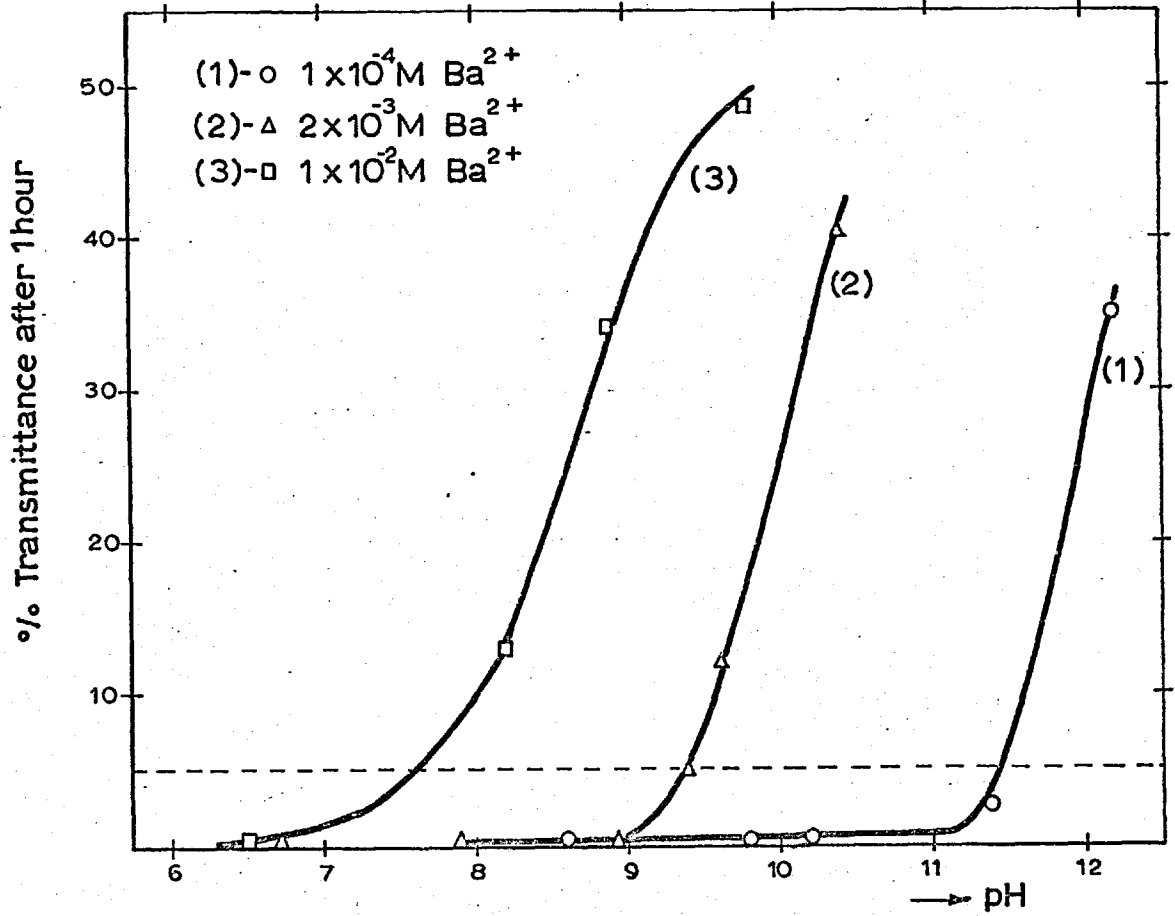


Fig. 7 Coagulation of 0.5%  $SiO_2$  by  $Ba^{2+}$

purpose quartz suspensions containing 0.5% solids were prepared in 50cc graduated cylinders at a constant pH to an appropriate level of gradation and the volume completed by a divalent cation solution of known concentration. The final  $Me^{2+}$  concentration was thus known. The cylinders were inverted gently for 1 minute and the sample placed in the 1 cm cell and the transmittance followed for 1 hour. The pH of the equilibrium solution was obtained by measuring the pH of its filtrate from a "Millipore" membrane filter of 10 $\mu$  pore size. These filters were found to contain a considerable quantity of surfactant which had to be extracted by water in a Soxhlet extractor for 1 week. The pH of the suspensions in the presence of quartz could not be measured directly because of the well known suspension effect (129)(130). Variations between measured pH values of the filtered and unfiltered suspension were more pronounced in the basic range, sometimes exceeding a difference greater than 1 pH unit.

In the cases of  $Ca^{2+}$  and  $Ba^{2+}$ , the coagulation results and the final pH values of the equilibrium solutions were reproducible irrespective of the order of addition of alkali or quartz. With  $Pb^{2+}$  solutions, however, reproducible results were obtained only if the alkali was added before  $Pb^{2+}$ . If the order of addition was reversed localized high concentrations of alkali caused the formation of silica inclusions in pockets of solid  $Pb(OH)_2$  which is not easily soluble even if the average pH of the medium is favourable for its dissolution.

Thus, for each concentration of divalent cations a set of measurements were made which gave curves similar to those illustrated in figure 7 upon arrangement. The pH corresponding to 5% transmittance after 1 hour of coagulation was taken as the critical coagulation pH for a certain concentration of  $Me^{2+}$ . The results obtained were plotted as (c.c.c) versus pH

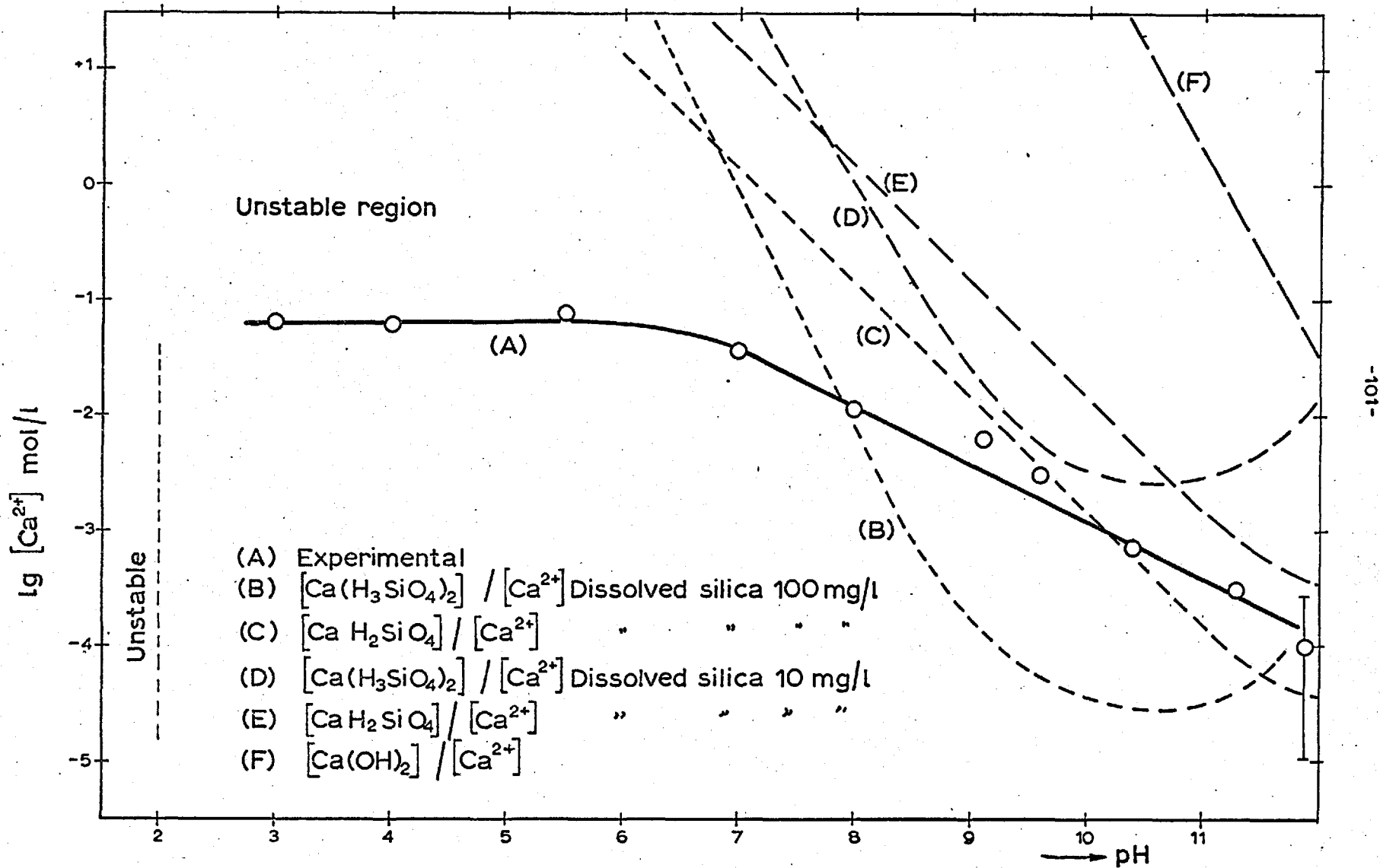


Fig. 8 Coagulation of 0.5 quartz suspensions by  $\text{Ca}^{2+}$

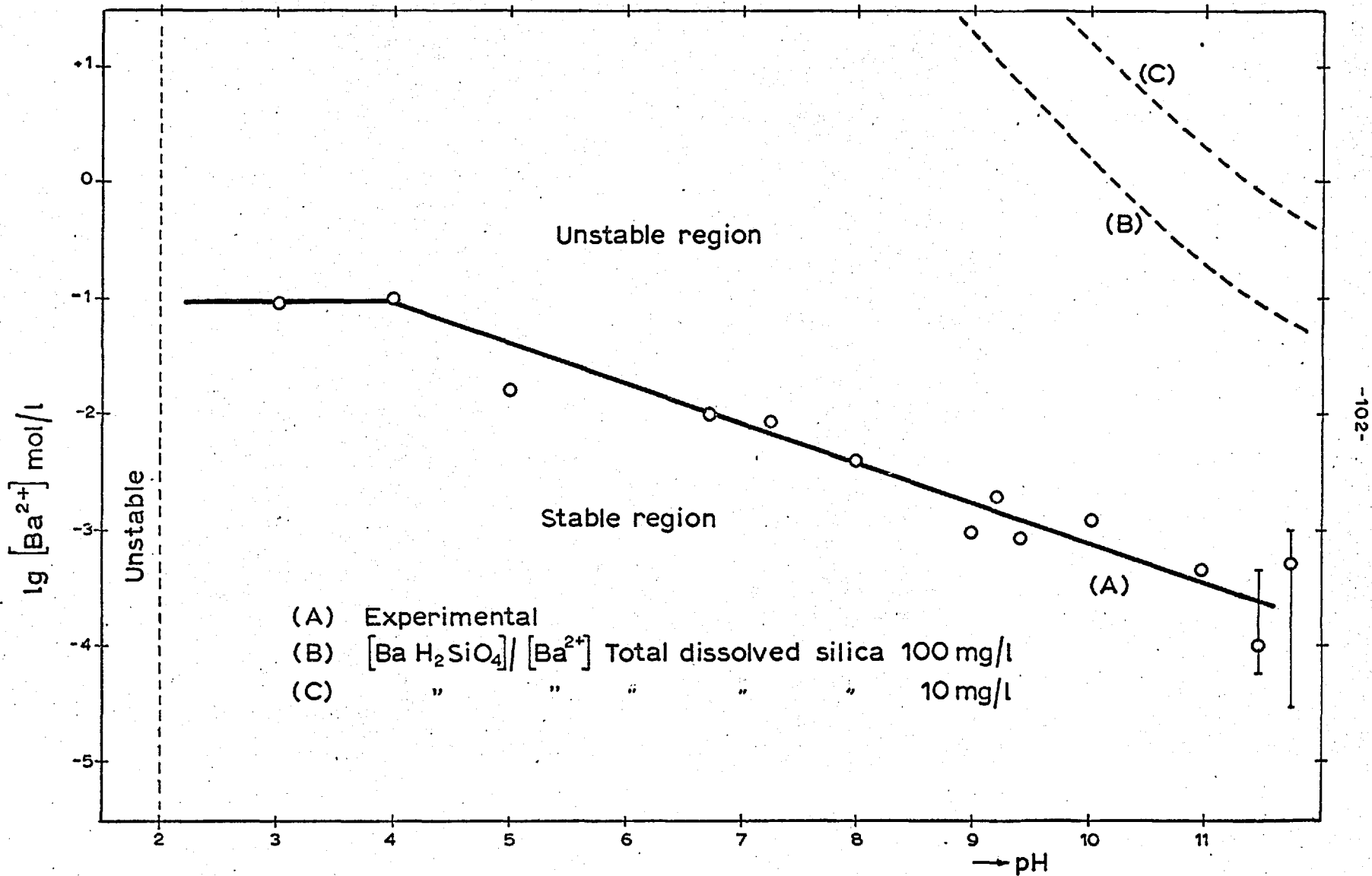


Fig. 9 Coagulation of 0.5% quartz suspensions by Ba<sup>2+</sup>

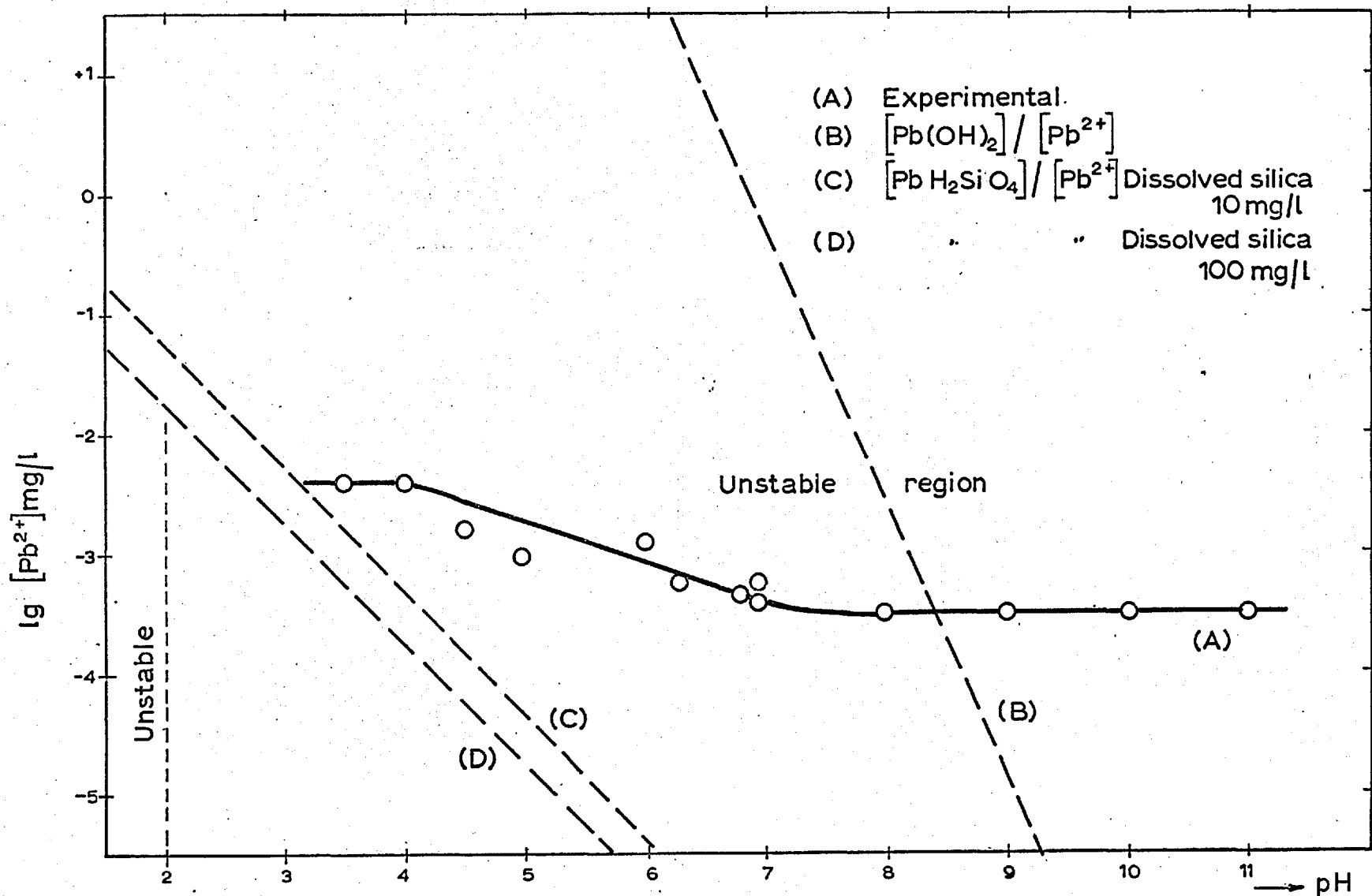


Fig. 10 Coagulation of 0.5% quartz suspensions by  $\text{Pb}^{2+}$



as shown in figures 8,9, and 10.

The following observations were recorded:

- (a) With increasing pH, particularly at  $\text{pH} > 8$  the sediment volumes increased, and at  $\text{pH} > 10$  big, fluffy aggregates, reminiscent of those obtainable by polymeric flocculants (to distinguish them from those obtainable with high concentrations of NaCl) were obtained. These aggregates, however, consolidated to a small volume on standing, and could be made much smaller by vigorous agitation.
- (b) If a coagulated suspension was washed on a filter paper it was possible to re-stabilize quartz although not completely, and it was possible to detect the presence of the coagulating ions in the filtrate.
- (c) Coagulation in the presence of  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$  took place at pH values much lower than those necessary for the formation of  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ , contrary to the unsubstantiated claims of some investigators (122), (123).
- (d) No re-stabilization with increasing pH, like those reported by other investigators for the action of trivalent cations such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  (131-134) on various silicas was observed with any of the divalent cations used.

#### 4.4 Electrokinetic measurements

(a) Effect of pH: Zeta-potential measurements on quartz suspensions were made with the cylindrical micro-electrophoresis cell described. For this purpose, quartz samples were placed in water of constant ionic strength and varying pH values arranged by NaOH or HCl and measurements made on samples pipetted out at different time intervals after vigorous agitation. All measurements were made at 25 °C.

At  $\text{pH} < 5$ , although all particles were negatively charged, fresh

quartz suspensions showed marked variations in mobilities between individual particles, sometimes the maximum mobility being twice as high as the minimum one. It was ascertained that this is not due to an incorrect setting of the apparatus. On ageing for 8 days this effect was very much diminished with the zeta potential becoming less negative in the acid and more negative in the basic pH range. Such abnormalities were also observed by Laskowski and Kitchener (82). When a sample was fully aged by boiling at pH 12, followed by repeated washing on a membrane filter, variations in mobilities disappeared and the z.p.c. was judged to be at approximately pH 2, though no reversal of sign was observed. The results of these experiments are given in figure 11.

Various authors (19)(134)(135) have reported } -potential measurements on quartz and different silicas, and it is generally recognised that the origin and previous history of the mineral play an important role in this respect. Zucker has attributed some of the discrepancies in published work on the zeta potential of quartz powders to errors arising from irreproducible electrode potentials in the streaming potential apparatus. Ahmed and Maxinov (192) after a study of a number of oxides and from inference based on the findings of other investigators concluded that the dissolved complexes which eventually saturate the solution and adsorb or precipitate on the oxide surface are the main cause for the time-dependent variation in electrokinetic potentials and the reported z.p.c. values.

(b) Effects of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Pb}^{2+}$ . Zeta-potential measurements on quartz suspensions in presence of these ions at different concentrations were made, and at c.c.c values use was made of the already mentioned fact that upon rigorous agitation the re-coagulation took longer time. At c.c.c's differences in individual particle mobilities were noticeable; however, the

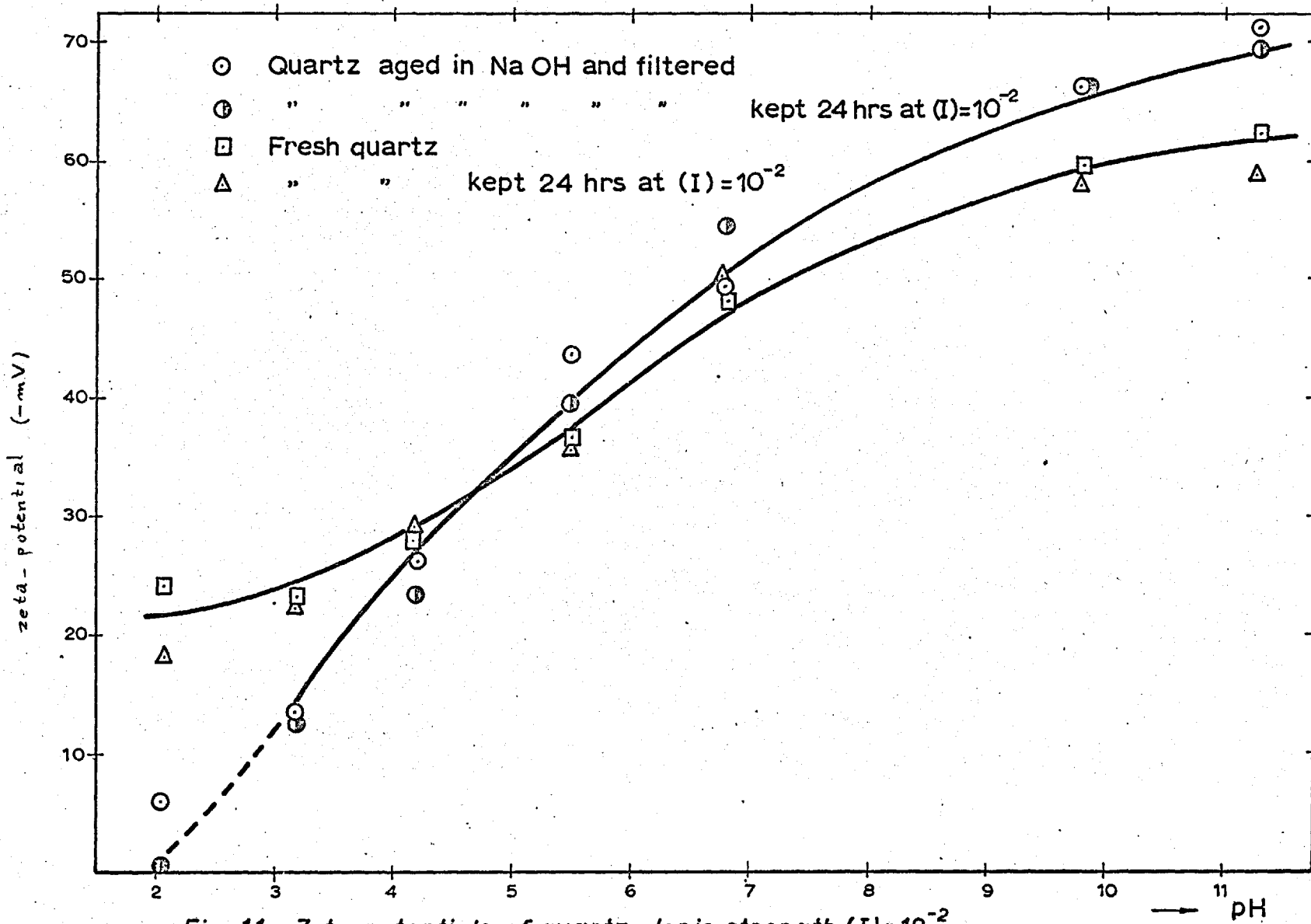


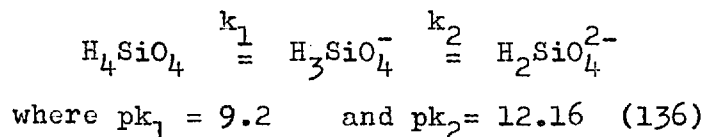
Fig. 11 Zeta-potentials of quartz. Ionic strength  $(I)=10^{-2}$

errors involved were reduced by taking the average of 20 readings for each value. The results are collected in table 4, where it is seen that at all coagulation values the  $\zeta$ -potential is near 30mV or smaller. It is usually stated that for particles of about 1 $\mu$  size this value is the minimum required for stability (16)

#### 4.5 Solubility of quartz in aqueous suspensions

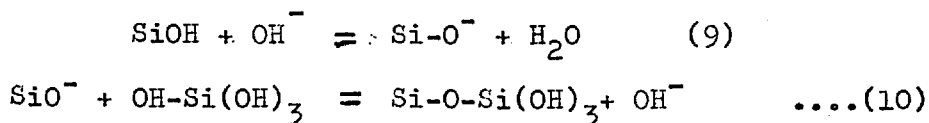
There is a great variation in the values reported for the dissolved quantity of silica in water as seen in table 3; nonetheless, the value generally quoted for the solubility of quartz is 10 $\mu$ g/l (1.8x10<sup>-4</sup> mol/l) and for colloidal silica 100mg/l (1.8x10<sup>-3</sup> mol/l) but the mechanism of dissolution is not fully understood. The disturbed layer mentioned above is accepted to enhance the initial solubility of quartz. There are two approaches to the problem.

i. The dissolution of silica is diffusion controlled; silica dissolves as monosilicic acid which in turn dissociates to the corresponding silicate species, depending on the pH of the medium as in the scheme



This explains why the solubility is little dependent on pH below pH 9, but rises steeply in more alkaline media.

ii. The condensation-decondensation mechanism; Okkerse (110) suggested that at pH>2 the quartz surface is effected as in the following scheme:



and after a certain degree of solubilization the quartz ceases to

Table 4

Critical coagulation concentration of  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Pb}^{2+}$   
and the corresponding zeta-potentials at 25°C

log [ $\text{Ba}^{2+}$ ] c.c.c.	corresponding pH	zeta- potential (mV)	log [ $\text{Ca}^{2+}$ ] c.c.c.	corresponding pH	zeta- potential (mV)	log [ $\text{Pb}^{2+}$ ] c.c.c.	corresponding pH	zeta- potential (mV)
-2	6.5	-19	-1.5	7	-15	-1.6*	3	-13
-3	9	-26	-2.5	9.3	-18	-2.6	4.2	-22
-4	11.5	-35	-3.5	11.3	-20	-3.6	7	c.40

\* This is a higher concentration than c.c.c. which is -2.4 for this pH value.

dissolve, with a dynamic condensation-decondensation reaction setting up.

It is relevant to record here a few experiments which were carried out with the water soluble polymer, poly-3-ethyl-vinyl-pyridine oxide (PEVPO) which has been suggested for the treatment of the lung disease silicosis caused by silica dust (137), and is known to flocculate polymeric silicic acid only (138). A sample of this product was kindly provided by Dr. P. F. Holt of Reading University. Conversely, the dissolved silica percentages reported in most recent literature are generally based on the reaction of monomeric silicic acid or lower molecular weight oligomers with molybdic acid to form the complex  $(\text{SiMo}_{12}\text{O}_{40})^{4-}$  (139), which was independently developed as an analytical tool by Alexander (140) and Aoki (141). By combining these two facts an attempt was made to find out *how* the primary dissolution of quartz is effected by the flocculation of polymeric silicic acid by PEVPO in situ. For this purpose 0.5g of quartz was treated by 1.8mg of this polymer at pH 3, and after  $\frac{1}{2}$  hour topped up with borax-NaOH buffer to give a final pH of 8.8 (142) and a 1% quartz suspension. A control sample was treated similarly in the absence of PEVPO. After 8 hours the dissolved silica was determined with the molybdate method, using a Hilger and Watts spectrophotometer. Prior to the determination it was ascertained that the buffer and the polymer at the concentrations involved during the determinations, did not interfere with the colorimetric determination of dissolved silica. The results showed that in the case of the control sample 65mg/l silica was released whereas in the presence of PEVPO (which flocculated polymeric silicic acid) the amount released was only 15mg/l. This result suggests that silica is firstly dispersed in a polymeric form which eventually releases monomeric silicic acid. Further confirmation

of this conclusion is provided by electron micrographs discussed below.

#### 4.6 Electron microscopy of quartz suspensions.

Various investigators have published electron micrographs of quartz and different forms of silica. The general features reported by other investigators can be summarized as follows:

The origin and method of preparation of the powder and suspension determine the appearance of the particles under the microscope (109)(136)(105)(143). In ground quartz it is usually possible to detect the disturbed layer indicated from solubility measurements, because when this layer is removed by HF etching of the powder, striations are left on the surface (105). It has also been noticed that it is not possible to prepare satisfactorily monodisperse quartz suspensions in water by elutriation owing to clustering of very fine ( $\sim 0.1\mu$ ) particles together or their sticking to the relatively bigger ones (100)(109). Thus quartz powders do not completely disperse in water, although dispersions once formed remain stable.

None of the studies found in the literature reported the state of the quartz surface at  $\text{pH} > 7$ . For the study of quartz suspensions, the electron microscopes of I.C. Chem. Eng. Dept. "J.O.E.L Jen" and "Siemens Elmicope -1" were used. Films of carbon were prepared by sputtering evaporation of carbon on optical quality glass slides at high vacuum. Alternatively, "Formvar"-films were prepared by dipping similar glass slides into ether solutions of "Formvar" and allowing the solvent to evaporate. In both cases, the films were cut to squares which were then placed on water and quartz dispersed by ultrasonic and mechanical agitation, sprayed from a dilute suspension on them. The pH of these suspensions were arranged by NaOH and  $\text{NH}_4\text{OH}$ . The e.m. observations made on the dried deposits are summarized below.



(a)

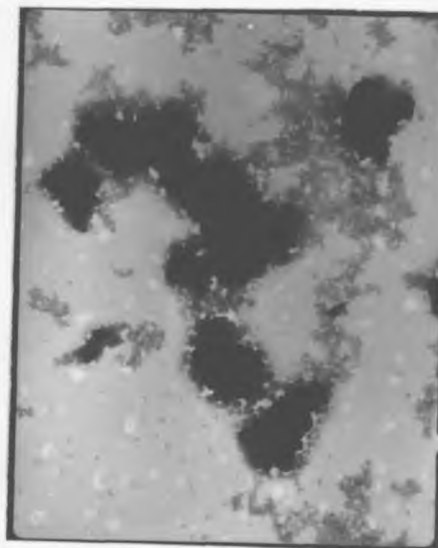


(b)

Figure 12

Electron micrographs of quartz suspensions  
pH 5.5, magnification: a=5000x, b=8000x



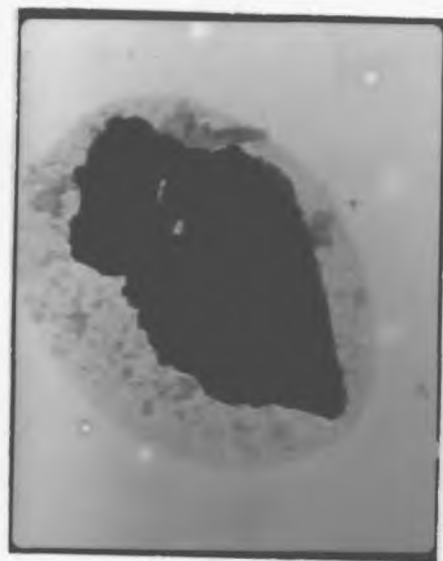
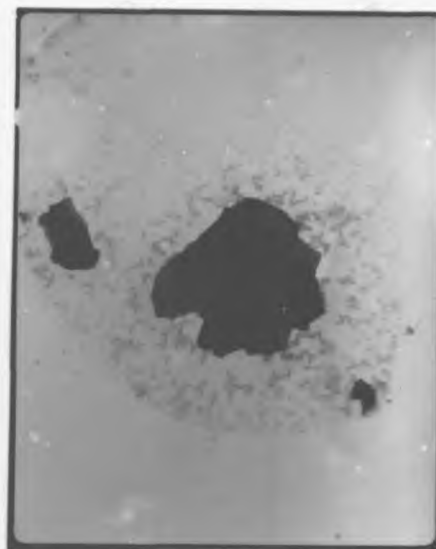


(a)

Figure 13

(b)

Electron micrographs of silica suspensions  
pH 11, magnifications: a=30000x b=5000x



(a)

Figure 14

(b)

Electron micrographs of quartz in  $\text{NH}_4\text{OH}$  solution  
pH 9.6, magnification: a=11500x, b=18000x

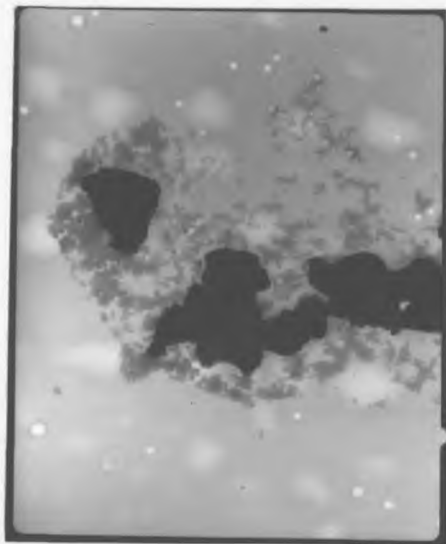


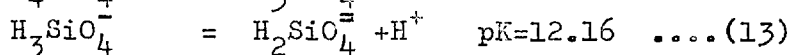
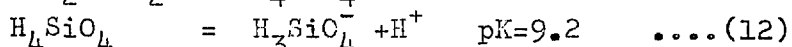
Figure 15.

Electron micrograph of quartz  
suspension in contact with 0.001M  
 $\text{Na}_2\text{SiO}_3$ . pH 9.6 ,magnification 5000 X

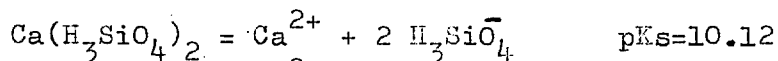
- a. At pH 5.5; quartz existed in aggregates of two or more particles. It was possible in thin particles to see distinct crystallinity through interference patterns. Particle sizes ranged from  $0.1\mu$  or less to  $5\mu$ . In many cases very fine particles were stuck to the bigger ones. See figure 12.
- b. At pH 11 arranged by NaOH; the suspension being aged for a few days, aggregation was distinctly higher than in case (a) above, and an amorphous gel layer developed around most of the particles. In many parts this layer had a fibre-like appearance and was identified as being probably a mixture of NaOH and  $\text{Na}_2\text{SiO}_3$  by comparing the electron diffraction patterns obtained, with the A.S.T.M. Standard Card Data. In many instances a number of fine globular particles appeared entrapped in the amorphous layers. See figure 13.
- c. At pH 9.6 arranged by  $\text{NH}_4\text{OH}$ ; no difference from particles suspended at pH 5.5 was observed. However, on standing of the suspension for about 2 hours, the individual particles seemed to have a circle around them, the diameter of which was comparable with that of a spray drop in which they were carried to the film. Aggregates made of particles  $<0.05\mu$  - probably colloidal silica - filled the area of this circle. See figure 14.
- d. In a solution of  $0.001\text{M Na}_2\text{SiO}_3$  at pH 9.6; the pattern observed was exactly as in (c) above, without the necessity for ageing of two hours. Compare figures 14 and 15.

#### 4.7 Discussion

The possibility of silicate formation being responsible for the voluminous aggregate formation at  $\text{pH} > 10$  in the presence of divalent cations can be considered by treating dissolved silica as a dibasic acid according to the following equilibria:



Thus at an initial concentration  $C$  of  $\text{H}_4\text{SiO}_4$ , the total dissolved silica in the medium remains constant, although the concentrations of various dissolved species will be dependent on the pH of the medium. Taking  $C = 1.8 \times 10^{-3}$  and  $1.8 \times 10^{-4}$  mol/l, the concentrations of  $\text{H}_4\text{SiO}_4$ ,  $\text{H}_3\text{SiO}_4^-$  and  $\text{H}_2\text{SiO}_4^{=}$  were calculated for the range, pH 5-13 and are given in appendices A and B. Heller and Taylor illustrated the variability of the  $\text{SiO}_2/\text{CaO}$  ratio by listing all calcium silicates known in nature (144). It is notable that most of them are formed only under hydrothermal conditions. Roller and Ervin (120) also found that in the  $\text{CaO-SiO}_2\text{-H}_2\text{O}$  system in dilute alkaline solutions the  $\text{CaO}/\text{SiO}_2$  ratio varied as 1/1, 4/5, 2/3, 1/2 ...etc.; Tsukioka(147) also found that the interaction of  $\text{Ca}^{2+}$  with  $\text{Na}_2\text{SiO}_3$  does not obey a simple stoichiometric relation which the formation of  $\text{CaSiO}_3$  would require. A complete list of thermodynamic data for metal silicates does not yet exist. Only the solubility product values given in the equations below were found in literature (120),(145),(146).



Using the concentrations of hydrolyzed silicic acid species given in appendices A and B and the equilibria given above the molar concentrations of each  $\text{Me}^{2+}$  necessary to form the corresponding silicate were obtained (see also appendices A and B) and plotted as c.c.c. versus pH as shown in

figures 8,9, and 10. The following conclusions can be derived from the comparison of the experimental c.c.c. values of divalent cations and the calculated values for the postulated formation of silicates.

- i. As can be seen from figure 8, although  $\text{CaH}_2\text{SiO}_4$  does not form in quartz suspensions at any pH, it seems possible that  $\text{Ca}(\text{H}_3\text{SiO}_4)_2$  can form in the limited pH range of  $9 < \text{pH} < 10.5$ . With silica gel, however,  $\text{CaH}_2\text{SiO}_4$  can form in the whole basic range starting from  $\text{pH} > 7.5$ . At no pH value in the range pH 1-12 can  $\text{Ca}(\text{OH})_2$  play any coagulating role with suspensions of quartz.
- ii. Because of the high solubility of silicates of barium no silicate can be expected to form in quartz suspensions, not even in supersaturated silica gel suspensions. Similarly  $\text{Ba}(\text{OH})_2$  has no coagulating role in these experiments.
- iii. In the presence of  $\text{Pb}^{2+}$  ions as can be seen from figure 10, the formation of  $\text{PbH}_2\text{SiO}_4$  at any pH in the range  $\text{pH} > 3$  for quartz seems possible because of the low solubility of this silicate. The formation of  $\text{Pb}(\text{OH})_2$  starts at  $\text{pH} > 7$ . If formation of lead silicate were solely responsible for the coagulation of quartz suspensions by lead ions at pH 8, the  $\text{Pb}^{2+}$  necessary for the silicate formation would be much less than  $10^{-6} \text{ M}$ , whereas experiments showed that coagulation occurred with only  $[\text{Pb}^{2+}] = 10^{-3.5} \text{ M} = 3.16 \times 10^{-4} \text{ mol/l}$ .

Although for each divalent cation it is possible to define the limit of silicate formation in terms of  $[\text{Me}^{2+}]$  and pH, the experimental results of coagulation with the three  $\text{Me}^{2+}$  cations used follow a more regular pattern than the silicate formation patterns.

- iv. In the coagulation ranges all the three figures (i.e. figures 8, 9, 10) present a linear part with the slopes given below:

Me <sup>2+</sup> :	Ca <sup>2+</sup>	Pb <sup>2+</sup>	Ba <sup>2+</sup>
slope:	0.59	0.36	0.33

and thus the adsorbability of these three ions decreases in the order Ba<sup>2+</sup> > Pb<sup>2+</sup> > Ca<sup>2+</sup>

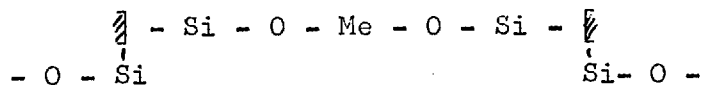
v. Irrespective of the possibility of silicate formation, the zeta-potential of quartz for each of these ions follows the same pattern namely, the coagulation is accompanied by a drop of zeta-potential to near or below 30 mV.

The dynamic condensation-decondensation mechanism for silica dissolution mentioned above, is suggested by Okkerse (110) to be due to the high surface energy of silica and the mechanism is catalyzed by H<sup>+</sup> at pH < 2 and OH<sup>-</sup> above this value, which ultimately results with particle growth. Added salts increase the rate of condensation.

Based on the results of electron microscopy, electrokinetic measurements, and the dissolution of quartz in the presence of PEVPO and its coagulation properties, its mechanism of dissolution and coagulation can be visualized as follows:

When the solid is suspended in an aqueous medium the disturbed layer on the ground quartz breaks into micro-fragments owing to its loose structure. But these micro-fragments are still not monomeric silicic acid; they rather behave as individual dispersible entities. The fall of the  $\zeta$ -potential of quartz upon ageing at pH < 5 and its increase in the alkaline range, must be related to the adsorption of H<sup>+</sup> and OH<sup>-</sup> in the two respective regions of pH.

For the action of divalent cations as coagulants, the neutralization of the -SiO<sup>-</sup> groups belonging to different particles by an "electrostatic bridging mechanism" can be visualized. The structure would be in the form:



In such a system when aggregates are broken by agitation large aggregates do not re-form although coagulation does not cease, probably because the cations undergo a rearrangement by neutralizing groups on the same particle and thus substantially reducing the bridging capacity. On the same lines the following assumptions should be correct:

(a) If not enough cations are present in the medium (i.e. the number of divalent cations is smaller than half the number of solid particles in a volume of suspension) only partial coagulation will take place with a given haze and the  $\zeta$ -potentials of individual particles might show variation.

(b) Complexes such as  $\text{Cu}(\text{NH}_3)_4^{2+}$ ,  $\text{Co}(\text{NH}_3)_6^{2+}$  should act like other divalent cations, by electrostatic action.

(c) A quantity of dissolved silica should require more coagulating ions than the same quantity of undissolved silica in the same volume of aqueous medium.

The correctness of (a) above is clear from the foregoing discussion and figures 8, 9, and 10. Also a number of experiments were conducted with the complexes of Cu and Co mentioned above and voluminous quartz residues obtained; vigorous agitation did reduce the sediment volume although coagulation was not prevented, indicating that (b) is correct. Okamoto et. al., (131) clearly showed the correctness of (c) above by the finding that "molecularly dispersed silica needs more  $\text{Al}^{3+}$  to precipitate than colloidal silica does under similar conditions".

The effect of high pH on the stability of quartz suspensions is still not entirely clear. The stability to NaCl as well as to  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$  is reduced, and the evidence presented



suggests that the formation of an insoluble metal silicate is not the cause of the peculiar type of coagulation obtained at high pH, which appears to be connected with the catalysis of the condensation/dispersion reaction. The formation of some sort of bridging material by aggregation of the previously dispersed or dissolved colloidal silica is indicated.

Nonetheless, for the purposes of the present research, the doubt about the precise mechanism of coagulation of silica at high pH is not critically important. The results establish empirically the ranges of pH and concentrations of  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Pb}^{2+}$  at which ground quartz can be considered stable for the purpose of selective flocculation.

## 5. STABILITY AND COAGULATION OF CALCITE SUSPENSIONS.

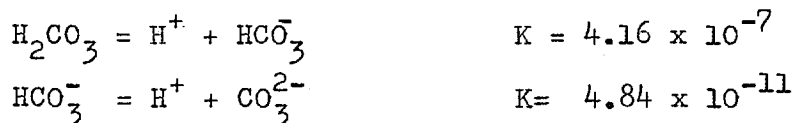
### 5.1 Introduction:

Calcium carbonate dissolves appreciably in water, dissociating into  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in accordance with the solubility product of the solid. These ions in turn give further hydrolysis products resulting in a medium containing  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CaHCO}_3^+$ , and  $\text{CaOH}^+$  the relative concentrations being dependent on the pK's of each reaction leading to the production of these species. Since in most instances no precaution is taken for the exclusion of dissolved atmospheric  $\text{CO}_2$  from water, the  $\text{CO}_2/\text{H}_2\text{O}$  system is of primary importance because of its pH determining role and the buffering action of carbonate species which in turn determine the surface-chemical conditions of calcite in its aqueous-colloidal suspensions.

The formation of carbonic acid ( $\text{H}_2\text{CO}_3$ ) as a function of the partial pressure of  $\text{CO}_2$  is given by

$$[\text{H}_2\text{CO}_3] = 3.41 \times 10^{-2} \dots(1)$$

and hence under laboratory conditions where  $P_{\text{CO}_2} = 3 \times 10^{-4}$  atm (149),  $[\text{H}_2\text{CO}_3] = 1.02 \times 10^{-5}$  mol/l. for an equilibrated solution. Using the equilibria



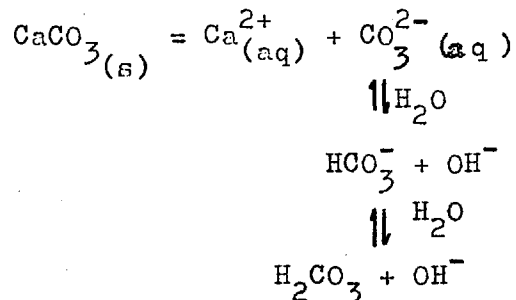
in combination with eqn 1 and considering that  $[\text{H}^+] = [\text{OH}^-]$

$$[\text{H}^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] \dots\dots (2)$$

the pH of distilled water in equilibrium with atmospheric  $\text{CO}_2$  comes out as pH 5.65 which is approximately the pH of freshly distilled water taken from a container in the laboratory. Under these conditions the total carbonate concentration i.e.

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 1.2 \times 10^{-5} \text{ mol/l}$$

The introduction of  $CaCO_3$  powder into this water to obtain a suspension would give rise to further equilibria i.e.



with a resultant rise in the pH of the aqueous medium. Calculations with some simplifying assumptions of the pH's of aqueous  $CaCO_3$  suspensions under various condition of equilibrium with  $CO_2$  have been given by Garrels and Christ (150). The case of calcite suspensions in equilibrium with atmospheric  $CO_2$  without simplification in calculations is also given by Turner (149). Under these conditions the pH of  $CaCO_3$  suspensions is 8.8 and the total ionic strength (ionic strength =  $\frac{1}{2} \sum c_i z_i^2$ , where c is the molar concentration of the i th ionic species in a solution and z is its valency) is  $10^{-3.4}$ . Carbonic acid has two buffer points at pH 6.4 and pH 10.3. Figure 16 is given to facilitate discussion. In the presence of  $CaCO_3$  a further two buffer points will be introduced into the system. They are point C in figure 16 where the total  $[HCO_3^-] = [Ca^{2+}] = 10^{-3.2} M$  at pH 8.25 and point D in the same figure where the total  $[CO_3^{2-}] = [Ca^{2+}] = 10^{-4.2} M$  at pH 8.8. Since one starts at pH < 6 it would appear that the first buffer point (C) will arrest the pH at pH 8.25; on the other hand pH 8.8 is for one order of magnitude of concentration lower; hence it is more likely that the buffer point at C will not be as stable as at D, unless one starts with an acid solution i.e. pH  $\leq 4$  thus increasing the concentration of  $HCO_3^-$  and  $Ca^{2+}$ . If  $CaCO_3$  is suspended in a solution of pH 12 no change should be expected, but if any occurs it ought to be in the direction of pH values not lower than pH 10.3.

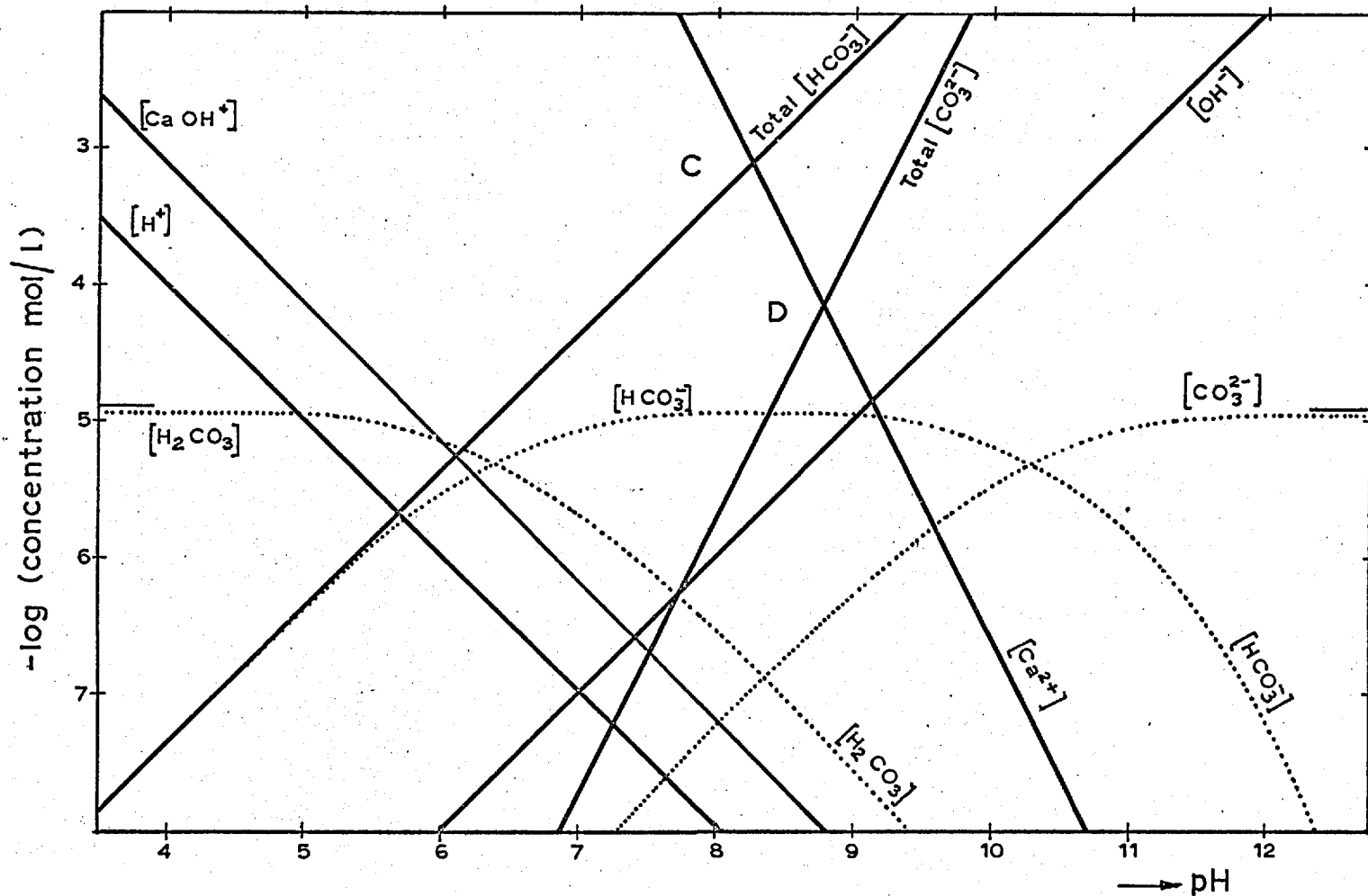


Fig. 16 Variation of ionic concentrations : ..... in distilled water at equilibrium with atmospheric  $\text{CO}_2$ ,  
 ——— in an aqueous suspension of  $\text{CaCO}_3$  under the same conditions.

### 5.2 Experimental pH values of CaCO<sub>3</sub> suspensions

The pH of distilled water was arranged to different values by HCl, Na<sub>2</sub>CO<sub>3</sub> and NaOH (NaOH used for pH 11.8 only). Then a quantity of calcite so as to form 2% suspensions was placed in these media, in glass stoppered cylinders. The mixtures were agitated and the pH values of the supernatant liquids determined after different times of standing. The results are given in table 5.

It is seen in this table, that the considerations based on figure 16, given above, are in agreement with the experimental result obtained. Namely, that if the initial pH of the suspending solution is pH < 8 the final value is 8 < pH < 9.5. With an initial pH of 10.3 + 1, the final pH remains at this HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>=</sup> buffer point, and if one starts with pH > 11.5, providing no CO<sub>2</sub> enters the system, the pH remains unchanged.

### 5.3 Stability of CaCO<sub>3</sub> suspensions and electrokinetic potentials

Electrokinetic and solubility measurements on calcite have been made by various investigators. In general it is found that natural calcite exhibits low zeta-potentials, usually below +30mV. Gortikov and Ostopinko(95) found that the mode of preparation of the CaCO<sub>3</sub> precipitates determines the sign of the  $\zeta$ -potential at equilibrium. If the precipitate is prepared in excess Na<sub>2</sub>CO<sub>3</sub> negatively charged crystals are obtained, probably due to the formation of a CaCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> double salt. Precipitates obtained in excess CaCl<sub>2</sub> solutions are positively charged. Borisov(151) found that in the pH range 2-11.5, the zeta-potential of calcite is always positive. On the other hand Reed, Müller, and Fredrickson (152) found that for natural calcite the zeta-potential varies between +10 and -10 mV. Somasundaran and Agar(153)

Table 5

Experimental pH values of  $\text{CaCO}_3$  suspensions

initial pH	after 5m	after 15h	after 40h	after 80h
2.9	8.1	-	-	-
4.0	-	8.5	8.6	8.6
4.8	8.2	-	-	-
5.1	-	8.6	8.6	8.9
6.0	8.4	-	-	-
8.1	9.5	-	-	-
9.1	9.5	-	-	-
9.3	-	9.4	9.5	9.5
11.8	11.8	11.8	11.8	11.8

obtained inconsistent  $\zeta$ -potential values varying between +25 and +5mV at all pH values except pH 11.5 where the values were -5 to -15 mV. Kuzkin and Nebera's (56) values for a calcite sample containing 0.03% Fe and 0.6% SiO<sub>2</sub> were slightly positive after grinding and screening but it became -3 to -5 mV on repeated washing with water and reached -15 mV in a 0.001 N NaOH solution (pH=11). The results of Borisov quoted above are particularly surprising in view of the questionable possibility of obtaining values at pH 2 and it is not conceivable how CaCO<sub>3</sub> can remain intact at such acid concentrations. Other investigators (154) have also made electrokinetic - potential measurements and found -10 to -40 mV in the presence of NaCl, NaOH, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, MgCl<sub>2</sub>, and PbCl<sub>2</sub> in the concentration range 0.5 - 10 mM/l. The most surprising values are given by Katasin and Kogan (155) . In their case the zeta-potential of a calcite sample which was -9 mV at pH 4 increased with rising pH reaching -62mV at pH 12.

No satisfactory z.p.c. for calcite has been given in any of the works cited above except in that of Somasundaran and Agar. When the graphs given by the above cited authors are interpolated to  $\zeta = 0$  mV the z.p.c. values obtained are as given below, which indicate that no reliable value can be deduced.

z.p.c. of CaCO <sub>3</sub> (pH) :	3	<7	8-9	9.5	12
reference :	(155),	(154),	(153),	(194),	(151), (195)

Similarly, the stability of calcite suspensions has not been mentioned in the literature except by Kuzkin and Nebera (56) who noted that calcite suspensions coagulate with a clear boundary.

(a) Effect of solid content on the stability of CaCO<sub>3</sub> suspensions:

Different quantities of solid were placed in 50 cc graduated glass stoppered cylinders and the volume completed with distilled water. Then the mixture was agitated mechanically and by

ultrasonics, and subsequently the settling of the suspensions noted. The observations are summarized in table 6 below.

Table 6.  
Stability of  $\text{CaCO}_3$  suspension in distilled water

<u>% solids</u>	<u>notes</u>	<u>pH after 15 min</u>
10-3	Descending <del>clear</del> boundary clear supernatant liquid	8.4
2	" " "	8.2
1-0.6	No boundary, <del>gradual</del> settling, supernatant liquid hazy	8.1
0.2	Stable suspension	8.1

It is seen from this table that relatively stable suspensions of calcite can be prepared only at relatively low solid concentrations (i.e. <0.5%), in contrast to quartz suspensions which are stable at concentrations 10 times this value.

(b) Zeta-potentials of  $\text{CaCO}_3$  suspensions

It appears that many of the simple inorganic salt-type minerals ( $\text{CaF}_2$ ,  $\text{BaSO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$  etc.) introduce a common problem of solubility and subsequent equilibrium as regards their electrokinetic potentials and associated surface phenomena.  $\text{CaCO}_3$  takes more than 2000 hours of agitation to reach a solubility equilibrium (156); so does  $\text{Ca}_3(\text{PO}_4)_2$  (157). Also  $\text{CaF}_2$  (90)(157) and  $\text{BaSO}_4$  (157) have to be equilibrated for long periods of time before reproducible electrokinetic potential measurements can be obtained.

Therefore the results reported for  $\zeta$ -potentials of



calcite in this work are more relevant to calcite suspensions as they are treated in mixtures of minerals for selective flocculation only. In other words, the time scale was < 1 hour and therefore the solutions must not be considered fully saturated.

i. Effect of solids content on  $\zeta$ -potential. Various solid quantities were placed in 50 cc of distilled water (pH 5.2 conductivity 5.3 $\mu$  rho) and dispersed as usual, and the zeta-potentials measured by micro-electrophoresis. At very low solid contents (i.e. <0.005%) the initially turbid suspension clarified because of dissolution of CaCO<sub>3</sub>, and with increasing solid content the measured  $\zeta$ -potentials showed a fall in general. The results are given in table 7.

Table 7

$\zeta$ -potentials of calcite suspensions  
(initial pH 5.2)

% solids	:	0.0005	0.005	0.05	0.5	1	2
Final pH	:	6.3	7.3	8.2	8.1	8.2	8.2
Zeta-potential (mV)	:	*	*	+23.5	+24.5	+20	+10.8

\* Solids dissolved

ii. Effect of pH. The pH of 0.05% CaCO<sub>3</sub> suspensions was arranged to different values by NaOH and  $\zeta$ -potential measurements made within one hour. The results are given in table 8.

Table 8

Effect of pH on the zeta-potentials of CaCO<sub>3</sub> suspensions

pH	:	8.2	9.3	9.7	10.3	10.8	11.0	11.3	12.2
Zeta-potential(mV):		+23	-3	+3	-23	-24	-23	-24	-35

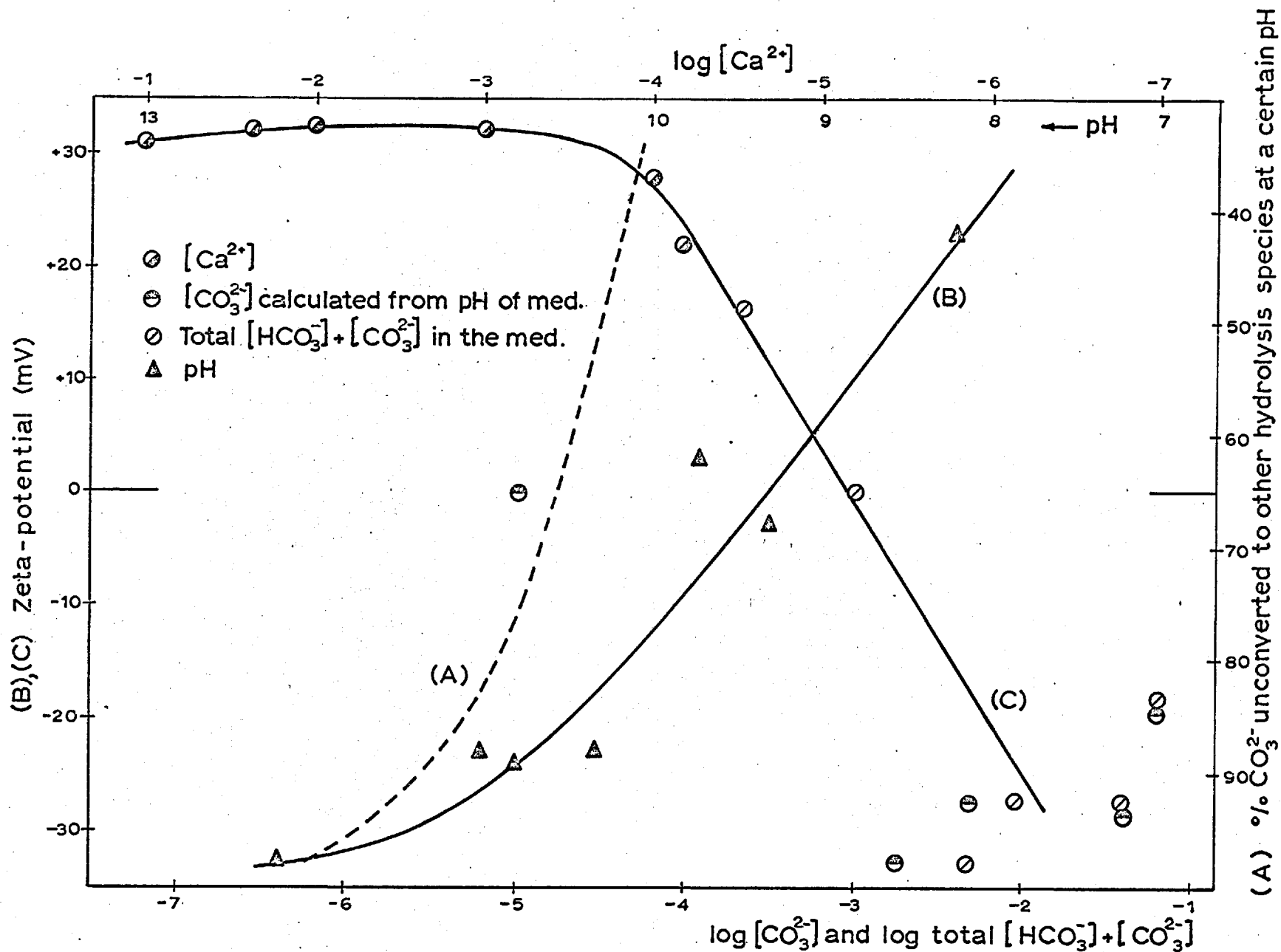


Fig.17 Variation of the zeta-potential of  $CaCO_3$  by varying ionic concentrations

iii. Effect of other ions: Zeta-potential measurements were also made in solutions of  $\text{CaCl}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{SO}_4$ . The results of measurements are given in table 9.

Table 9.  
Effects of various ions on the zeta-potential of  $\text{CaCO}_3$

concentration mol/l	$\text{Na}_2\text{CO}_3$	$\text{NaHCO}_3$	$\text{CaCl}_2$	$\text{Na}_2\text{SO}_4$
$4 \times 10^{-1}$	-	~ -3	-	~ -3
$1 \times 10^{-1}$	-19.6	~ -3	+31	~ -3
$5 \times 10^{-2}$	-29	~ -3	-	~ -3
$2.5 \times 10^{-2}$	-	-	+28	-
$1 \times 10^{-2}$	-27.5	0	+32	-
$5 \times 10^{-3}$	-33	~ -3	-	~ -3
$2.5 \times 10^{-3}$	-	-	+36	0
$1 \times 10^{-3}$	0	+20.5	+32	~ -3
$5 \times 10^{-4}$	+19.2	-	-	~ +3
$1 \times 10^{-4}$	+16.5	-	+28	0

The zeta-potentials of calcite under varying pH,  $\text{Ca}^{2+}$ , and  $\text{CO}_3^{2-}$  concentrations is given in figure 17, where also the % $\text{CO}_3^{2-}$  remaining unconverted to  $\text{HCO}_3^-$  by varying pH is given. As can be seen in this figure, the zeta-potential becomes negative at pH >9.5. (line B). The crossover from positive to negative zeta potentials (line C) in the presence of added  $\text{CO}_3^{2-}$  occurs at an added concentration of  $\text{Na}_2\text{CO}_3 = 10^{-3}\text{M}$ . (See also table 10 overleaf).

Table 10  
Variation of  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$  in  $\text{CaCO}_3$  suspensions

pH	10.9	10.8	10.3	10.	8.6	8.2
Initial $\text{Na}_2\text{CO}_3$ mol/l	0.1	0.05	0.01	0.005	0.001	0.0005
Final $[\text{CO}_3^{2-}]$ , M.	0.079	0.039	0.0048	0.0016	$1.8 \times 10^{-5}$	$3.8 \times 10^{-6}$
Final $[\text{HCO}_3^-]$ , M.	0.021	0.01	$5.1 \times 10^{-3}$	$3.3 \times 10^{-3}$	$9.8 \times 10^{-4}$	$4.9 \times 10^{-4}$
Zeta-pot. (mV)	-19.6	-29	-27.5	-33	0	+16.5

Under these conditions the  $\text{HCO}_3^-$  is predominant to the  $\text{CO}_3^{2-}$  ion. Similarly line C in figure 17 falls better on the points showing the total added  $\text{Na}_2\text{CO}_3$  than on the points obtained by calculating the  $\text{CO}_3^{2-}$  concentration in the medium. This indicates that as well as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  is also playing a potential determining role. The pH would play a role only by altering the relative concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ .

It has been maintained by some authors (153)(159) that ionic equilibria calculations can be used to predict the surface conditions of the mineral. This would, however, be true only, if the potential determining ions fortuitously adsorb equally as appears in the case with iron oxides. However this condition is not fulfilled by many solids. AgI for instance is a classic example (16) where the adsorption of  $\text{Ag}^+$  and  $\text{I}^-$  is unsymmetrical. In the case of  $\text{CaCO}_3$  the adsorption of  $\text{Ca}^{2+}$  and total carbonate

i.e.  $[\text{CO}_3^{2+}] + [\text{HCO}_3^-]$  appears to be symmetrical.

#### 5.4 Summary

From the above discussion the behaviour of  $\text{CaCO}_3$  in an aqueous medium from the point of view of selective flocculation can be summarized as follows:

- i.  $\text{Ca}^{2+}$ ,  $\text{CO}_3^{2-}$  (and  $\text{HCO}_3^-$  via pH) are potential determining ions of  $\text{CaCO}_3$ .
- ii. The pH of a calcite suspension is 8.2, and there is no point in trying to make the pH of the suspension more acid.
- iii. The z.p.c. of  $\text{CaCO}_3$  is at pH  $9.5 \pm 0.5$ .
- iv. Because of the relatively high solubility of  $\text{CaCO}_3$  and its low zeta-potentials stable suspensions with solids content more than 0.5 - 1% cannot be prepared.

## 6. STABILITY AND COAGULATION OF LEAD SULPHIDE SUSPENSIONS

### 6.1 Introduction

Galena as a sulphide mineral has received extensive attention particularly in relation to froth flotation (see Part I); however, the flocculation of the mineral does not seem to have received much attention although in their pioneering work Gaudin and Malozemof (39) recorded its flocculation in the presence of various organic collectors and wrote in their paper that "Selective flocculation of<sup>a</sup> colloidal mineral makes its flotation more complete and easier!" However, the authors were concerned with the bubble attachment mechanism rather than selectively flocculating a mineral and thus recovering it from the suspended phase as such. Flocculation in the sense of Gaudin and Malozemof has long been held a prerequisite of flotation, namely that if mineral particles are not aggregated they do not respond to froth flotation.

In analogy to other metal sulphides the lattice ions can be expected to be potential - determining for this mineral; surprisingly though, published literature treating galena from the colloid stability point of view is scarce. It is recognized that galena ground under water in a nitrogen atmosphere coagulates as soon as the particle sizes are fine enough to be affected by their surface electrical properties (39). Electrokinetic measurements also have been reported in one case and the zeta-potentials in the range pH 2.5-11 were found to be negative ( -5 to -20mV) at pH <5 and essentially no change was observed at pH >7 (~ -25mV). Freyberger and de Bruyn (161) concluded from their work on another metal sulphide ( $Ag_2S$ ) that in the range 4.7-9.2, pH has no effect on the adsorption density of the crystal lattice ions. From the point of view of selective flocculation it is essential to know the stability of galena

suspensions and the effect of ions likely to be present when PbS is mixed with other minerals. It appears that the difficulty encountered by Usoni et.al. (already mentioned in section 1-3) to separate galena from quartz when they are mixed together, is related to the "activation" of quartz by  $Pb^{2+}$  (as well as entrapment, mutual coagulation etc. discussed in relevant sections.) It was mentioned in Part I -chapter 1 that in the absence of air the dissociation products would be formed according to the solubility product of galena. However, PbS has an extremely low solubility product and in the presence of oxygen various oxidation products would be introduced into the aqueous medium in significant quantities. Unlike  $CaCO_3$ , in the case of PbS, the  $Pb^{2+}$  concentration will not be determined by the solubility product but rather by the solubilities of oxidised lead salts present, unless the pH is high enough to form an insoluble film of  $Pb(OH)_2$  on the mineral surface. Failing that, the ultimate lead salt would be  $PbSO_4$  and prior to that the alleged basic lead thiosulphate (162)(163). In reference to the results of Part 1 - chapter 1, it ought to be mentioned here that the electrode potentials reported in that chapter give no indication of the electro-kinetic potential of galena, since the electrode-potential is that potential at the solid with respect to a point far out in the bulk of the surrounding liquid, whereas the  $\zeta$ -potential is the potential at the slipping plane with respect to a point out in the bulk of the surrounding liquid. Nonetheless, the electrode potential may give an indication regarding the oxidation state of the solid which in turn can be interpreted in terms of ions available to be adsorbed on the solid.

## 6.2 Stability of PbS suspensions and potential-determining ions

Two forms of PbS were used in the following experiments  
i) precipitated PbS (discussed below) and, (ii) natural PbS

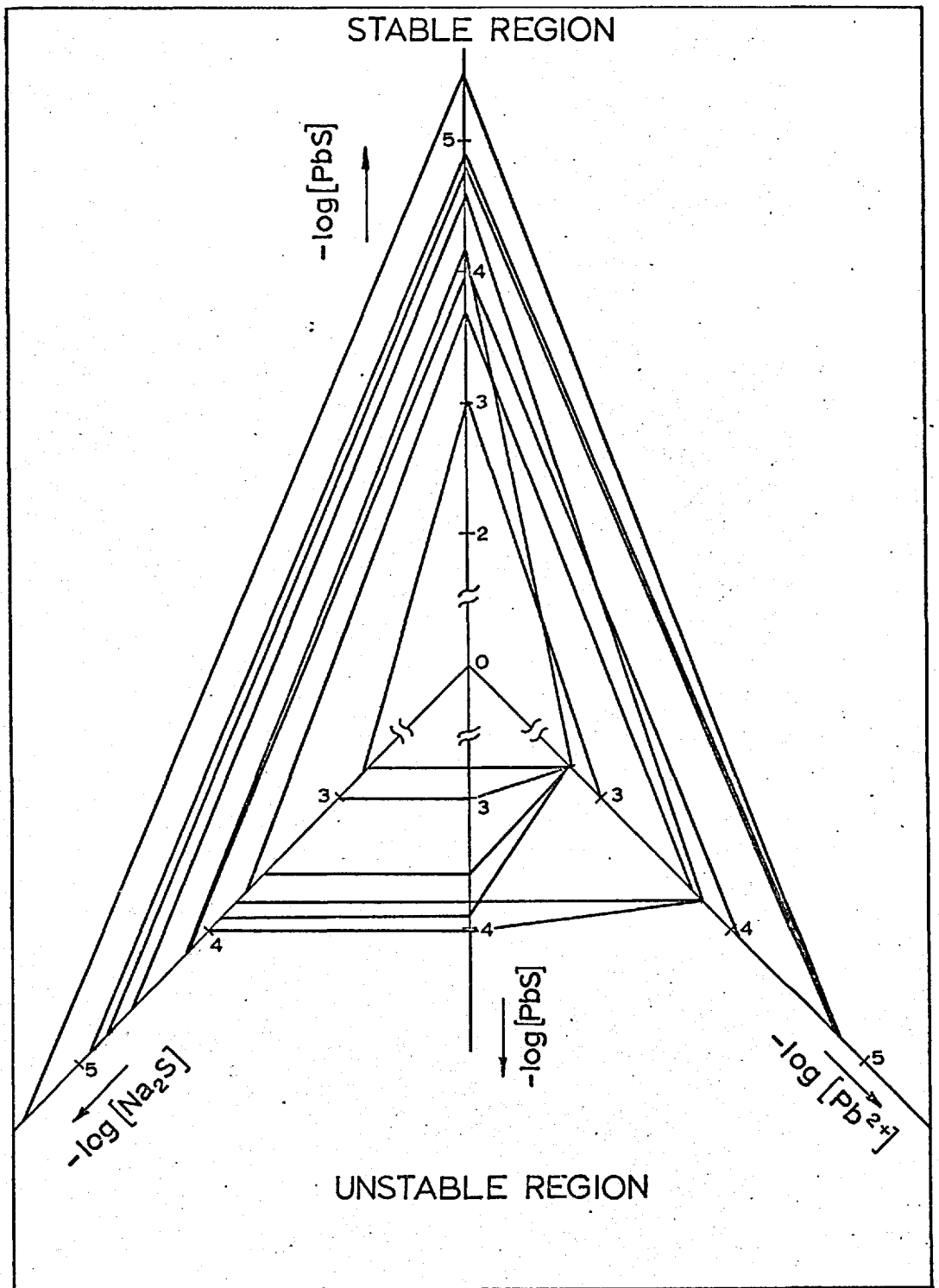


Fig.18 Stability of precipitated PbS suspensions as a function of  $[Na_2S]$ ,  $[Pb^{2+}]$  and  $[PbS]$



(galena) prepared as described in chapter 3.

i. Precipitated PbS suspensions: "Analar"  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  solutions were prepared by dissolving crystals of the salt at pH 12 and "Analar"  $\text{Pb}(\text{NO}_3)_2$  was dissolved in distilled water. PbS was precipitated in solutions containing excess  $\text{S}^{2-}$  or  $\text{Pb}^{2+}$ . For the former case, known quantities of  $\text{Pb}^{2+}$  were run from a burette into a known quantity of  $\text{Na}_2\text{S}$  solution in a 50 ml volumetric flask under continuous agitation. Where  $\text{Pb}^{2+}$  was required to be in excess, the order of titration was reversed. It is to be noted that at this alkali concentration, owing to the dissociation constant of  $\text{HS}^- = \text{H}^+ + \text{S}^{2-}$ , the ratio of  $[\text{S}^{2-}]/[\text{HS}^-] = 10^{-2}$  at pH 12. In any case the precipitation of PbS would not be hampered since the equilibrium above would shift to the right as  $\text{Pb}^{2+}$  consumes  $\text{S}^{2-}$ , in order to maintain the constant  $10^{-2}$  during precipitation. Therefore in the experiments reported below sulphide concentration is given as mol/l  $\text{Na}_2\text{S}$ .

The stability of PbS suspensions thus obtained was judged by observing the formation of aggregates which either settled down or partly collected at the liquid-air interface 15 minutes after preparation. The stabilities of these suspensions depended on the concentrations of excess  $\text{Na}_2\text{S}$ ,  $\text{Pb}^{2+}$  and PbS concentration in the medium. The results of these experiments are give in appendix C and figure 18. Figure 18 correlates the three variables. Readings on this figure are made as follows:

Initial concentrations of  $\text{Na}_2\text{S}$  and  $\text{Pb}^{2+}$  are selected on the corresponding axes, lines combining these two points leading to the stable or unstable regions. show the concentration of the resulting PbS suspension in mol/l and the difference between the two initial components indicates the concentration of the excess reagent.

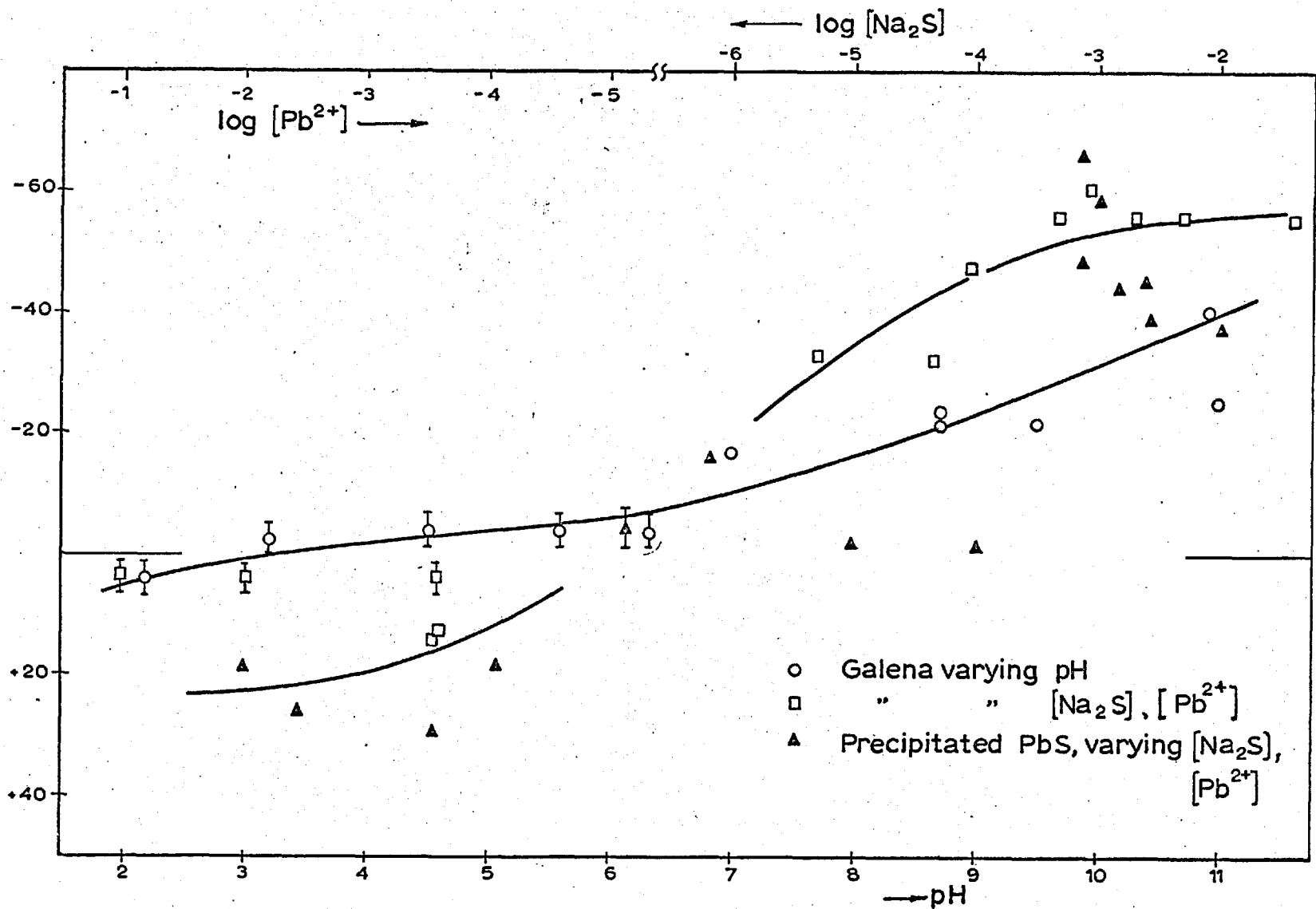


Fig. 19 Zeta-potentials of precipitated and natural PbS

Effect of pH on the stability of precipitated PbS suspensions was checked as follows:

$3.75 \times 10^{-5}$  M PbS suspensions were prepared by mixing equal quantities of  $Pb^{2+}$  and  $Na_2S$  ( $Pb^{2+}$  run into  $Na_2S$  solution) and subsequently the pH arranged by dilute  $HNO_3$  in the range pH 3.7-11.7. Suspensions at pH <6.7 formed visible aggregates in 15 minutes i.e. were unstable suspensions. Those in alkaline media remained stable, but after standing for 50 hours deposited white crystals, their quantity increasing by increased pH. It was concluded after an iodine spot test that these crystals were  $PbS_2O_3$ , formed by oxidation of finely divided PbS.

Zeta-potential measurements on precipitated PbS were made by the moving boundary apparatus described in section 2.3. For this purpose, stable suspensions of sufficiently low solid content were prepared with the help of figure 18 with varying quantities of  $Na_2S$  and  $Pb^{2+}$ . Measurements were made in 1% sucrose solutions for a better defined boundary. (It is assumed that sucrose does not significantly effect the zeta-potential (193)). When no excess lead or sulphide ions were present in the medium zeta-potentials were extremely low ( $\sim -5$  mV). In the presence of these ions, however, it was possible to make measurements, though boundary distortions in the presence of excess sulphide were less frequent than in the presence of excess lead ion. The results of these experiments are given in appendix D and figure 19.

ii. The stability of galena suspensions. Galena powder kept under water was further washed with de-oxygenated water by elutriation to remove any water - soluble oxidation products. For this purpose galena powder was placed in a flask on a magnetic stirrer. Deoxygenated water was fed to the flask with a glass tube extending from the top to about 1 cm from the bottom. The outlet glass tube was about 1m high, so that by arranging the

rate of flow of water most of the galena could be kept rising to a certain height and falling down, thus undergoing a sort of recycling operation. Magnetic stirring kept the solids in suspension and provided a rubbing action to release the oxidized layer into the continuously changing aqueous phase. 20 litres of water were run in 48 hours for each 100g of galena, and samples were syphoned out for use in experiments.

a. Effect of pH on the stability of galena suspensions:

0.5g/l samples of galena cleaned as described above were placed in water of different pH values ( $\text{HNO}_3$  and  $\text{NaOH}$  used for pH arrangement) and optical transmittance after thorough agitation followed on a fraction of the suspension as described for quartz. In general the suspensions were rather unstable; however, there was a difference between the rates of coagulation in acid and alkaline media. At  $\text{pH} < 6$  the rate of coagulation was higher than at  $6 < \text{pH} < 11.8$  although there was essentially no difference between settling rates in the alkaline pH range.

b. Effects of  $\text{Pb}^{2+}$  and  $\text{Na}_2\text{S}$  on the stability of galena were similarly tested. Owing to the oxidation of  $\text{PbS}$  which could not be prevented, the addition of  $\text{Na}_2\text{S}$  produced black  $\text{PbS}$  suspensions which did not settle with the mineral. In fact, at low concentrations of this reagent (i.e. 3-5mM or less) it acted as a coagulant, bringing galena down in big aggregates, leaving darker and darker supernatant liquids as the concentration was increased. If galena was washed with  $\text{Na}_2\text{S}$  solution of a certain concentration repeatedly, and the suspension prepared in a solution of the same concentration, stability curves could be obtained; however, they were not reproducible. Nonetheless, broadly, increased concentration of  $\text{Na}_2\text{S}$  led to increased stability of the mineral.  $\text{Pb}^{2+}$  on the other hand, had either no effect or acted as a coagulant.

c. Other ions such as  $Ba^{2+}$  and  $Ca^{2+}$  also produced no significant change in the stability of galena since the mineral was relatively unstable; but qualitatively it could be noted that  $Ba^{2+}$  and  $Ca^{2+}$  were less effective as coagulants than  $Pb^{2+}$  at similar concentrations. Sodium tripolyphosphate produced relatively stable suspensions which coagulated more slowly than the untreated samples. It was possible to obtain suspensions stable for a few hours if  $Na_2S$  (0.01M) and "Calgon" (0.1%) were used together.

iii. Zeta-potentials of galena were measured by Gortikov's electro-osmosis apparatus described in section 2.3 and also by micro-electrophoresis. In the absence of added ions, the zeta-potentials were very low but always negative. By the addition of  $Pb^{2+}$  the sign could be made positive. In media containing low concentrations of added  $Na_2S$  initial high negative potentials dropped to less negative values in half an hour's time between two consecutive measurements; however, after one night's standing the sign did not become positive. The results of zeta-potential measurements on PbS are given in appendix D and figure 19.

### 6.3 Summary

For the purpose of selective flocculation therefore, the stability of galena suspensions can be summarized as follows:

- i. Due to oxidation which cannot be prevented in ordinary flocculation work, PbS always acquires low zeta-potentials and produces unstable suspensions.
- ii.  $Pb^{2+}$  and  $S^{2-}$  are potential determining for PbS and the latter appears to adsorb more strongly.
- iii. The zeta-potential which is generally negative can be made more negative by the addition of  $Na_2S$ , or the charge could be reversed (made positive) by  $Pb^{2+}$ .
- iv. With relatively high concentrations of sodium sulphide or sodium tripolyphosphate stable suspensions of galena can be obtained.

## 7. FLOCCULATION OF CALCITE, GALENA AND QUARTZ

### BY POLYMERIC FLOCCULANTS.

Various aspects of the flocculation of solids by polymeric flocculants have been subject to numerous studies, which have been well reviewed (25)(56)(57)(90). In this chapter investigations of the action of various polymeric flocculants and stabilizing agents on the three minerals studied is presented. Reference to the works of other investigators is made in relevant sections.

#### 7.1 The bridging mechanism of flocculation

When a flocculant of high molecular weight is mixed with a relatively stable solid suspension fluffy aggregates form if the polymer adsorbs on the solid. Under gravity these flocs settle to a volume greater than that which would be occupied if the solid was to settle in the absence of the flocculant into a closely packed bed. (164) This point is also illustrated in figure 20, for the galena - Al50 system. For the construction of this figure the following procedure was followed :

Taking the specific gravity of galena as 7.5g/cc the volume to be occupied by different weights of the solid give line 1. Line 3 shows the experimentally obtained sediment volumes of different weights of galena taken after 5 minutes of sedimentation of the powder in 100cc of water. Line 2 shows the volumes for the same sediments after 12 hours of standing, while line 4 is the sediment volumes of the same galena suspensions treated with 5 ppm Al50 and taken after 5 minutes standing.

The porosity (P) of the sediment (or the empty space between particles) can be calculated from

$$\%P = \frac{V_a - V}{V_a} \times 100$$

where  $V_a$  = measured volume of sediment

$V$  = calculated volume for the same weight of solid.

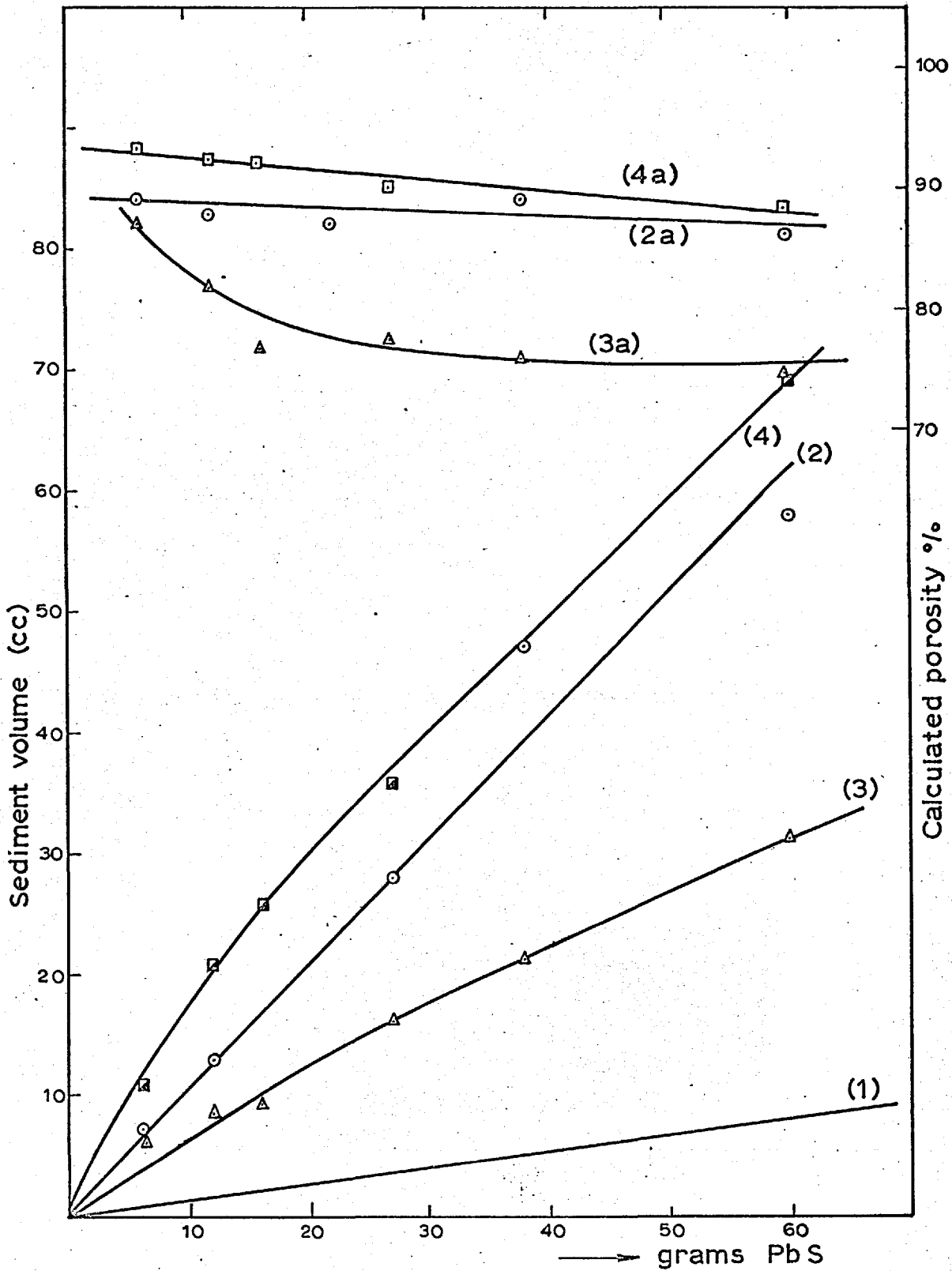


Fig. 20 Volumes and porosities of galena sediments

The measured sediment volumes and calculated porosities are given in table 11.

Table 11  
 Volumes and porosities of coagulated  
 and flocculated galena sediments

gm Pb:	Real Volume (cc)	Vol. after 5 min	% Porosity	Vol. after 12 Hours	% Porosity	5ppm Al50 added	
						Vol. after 5 min	% porosity
6	0.789	7	89	6	87	11	93.2
12	1.60	13	87.6	8.8	81.7	21	92.4
16	2.14	-	-	9	76.5	26	92.0
27	3.60	28	87.1	16	77.5	36	90.
38	5.06	47	89.1	21	76	-	-
60	8.00	58	86.2	31	74	69	88.5

The polymer, according to the current theory of the bridging mechanism of flocculation, adsorbs by either of the mechanisms given in section 7-4 on the solid particles and thus strengthening the junctions and leading to voluminous aggregates. Although attempts have been made to reveal these bridges by electron microscopy (165)(166)(167) and structures alleged to represent the polymer bridges between solid particles have indeed been observed, the experiments are not admissible because the observations were not made in situ, but the flocs were dried before introduction into the vacuum chamber of the electron microscope. It is clear that during such a treatment the movement of the meniscus of the drying liquid leads to localized concentrations of the polymer, producing structures which may look like fibres. This effect of apparent fibre structure between flocculated



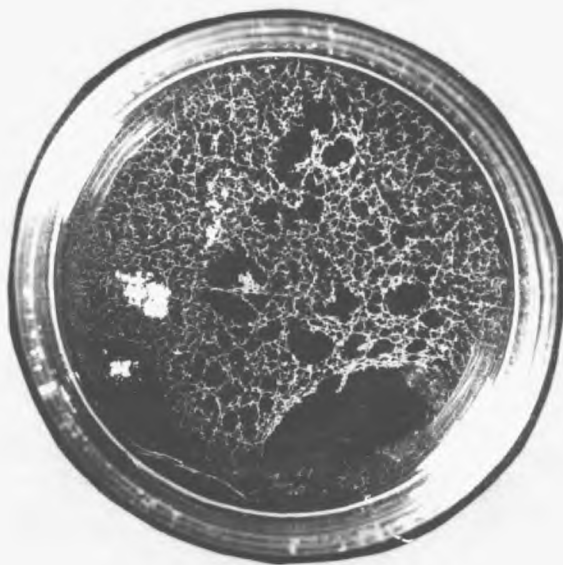


Figure 21.

$\text{CaCO}_3$  treated by an over-dose  
of A80 and subsequently treated  
by dilute acetic acid to leach  
part of the mineral in one night.

particles can be made visible without resorting to electron microscopic magnifications as can be seen from figure 21, taken at ordinary magnification. The picture shown in this figure was obtained as follows:

A calcite sample was flocculated by an "overdose" of A80 a highly anionic flocculant which was found to interact with  $\text{Ca}^{2+}$  salts giving a white precipitate probably consisting of a calcium polycarboxylate salt. The flocs obtained were placed in a petri-dish and a few drops of dilute acetic acid slowly added from one side, without greatly agitating the flocs.  $\text{CO}_2$  gas evolved slowly leaving the net-like structure shown in the photograph. With a few experiments it was seen that more solid dissolution could be effected by using more concentrated acid and conversely the acid-precipitated flocculant could be dissolved - although not completely - by making the pH more alkaline. These net-like structures are therefore a mixture of calcium polycarboxylate and salted out flocculant, nucleated around  $\text{CaCO}_3$  particles not completely dissolved by acid. Something similar must happen when flocculated suspensions are dried down for electron microscopy.

Evidence for the bridging mechanism of flocculation is rather to be deduced from flocculation experiments than from direct microscopic observation.

## 7.2 Adsorption and flocculation

It is logical to expect that flocculation is necessarily preceded by adsorption of the flocculant by the mineral; however, the opposite may or may not be true, namely that every polymer adsorption does not necessarily lead to flocculation. Griot and Kitchener (52) found that the lack of flocculation of aged silica by non-ionic PAM was due to lack of adsorption. Slater and

Kitchener (59), with another system, found that the deterioration of the flocculation of  $\text{CaF}_2$  by PAM at increased ionic strength was due to the coiling up of the polymer (which reduced its bridging capacity). Further examples illustrating the relation between flocculant adsorption and the subsequent result were found for quartz and calcite.

a. Flocculation of quartz by PEVPO described in section 4.5 was only possible at pH 3 although it remained adsorbed at pH values where no flocculation took place. That the polymer was still adsorbed at pH >3 was shown by the following experiment:

Four samples of 1% quartz suspensions were prepared in the following media :

No.	Suspension	pH
1a	quartz, no polymer	7
1b	" , +1.8mg PEVPO	7
2a	quartz, no polymer	3
2b	" , +1.8mg PEVPO	3

30 minutes after preparation, 1b and 2b were centrifuged and the residues washed with distilled water (pH 7), each time stirring the solid with a glass rod and applying ultrasonics for 3 minutes. The fifth and final washing was made by distilled water at pH 5.5. The solids were then transferred to 50 cc cylinders and dispersed in water of pH 3. Both 1b and 2b flocculated spontaneously leaving a clear supernatant liquid before long, whereas 1a and 2a were still turbid. These observations thus showed that this polymer was adsorbed at pH 3 and pH 7, although, flocculation took place only at the lower value.

The viscosity of the polymer at a concentration of 4.332g/l in a medium of ionic strength of 0.02 was measured by an Ostwald viscometer at different pH values and at 25°C. At low pH values higher viscosities were observed as seen in figure 22, indicating that the flocculation action of this polymer is a function of the degree of extension of the molecule. On the same figure the optimum dosage at pH 3 (line 4) and the variation of zeta-potential (line 3) by varying pH at the optimum dose of PEVPO are given.

b. The flocculation of calcite by A70 was found to be inhibited in a saturated borax solution. Again the question arose as to whether adsorption was prevented. A 4% calcite suspension was prepared in a saturated borax solution and 4 ppm of A70, which is a good flocculant for the mineral added. No floc formation was observed under these conditions. After one hour the supernatant liquid was sucked off and replaced by water. As the process of shaking the sediment with a renewed volume of water was repeated floc formation was clearly improved, indicating, as in case (a) above, that although the flocculant was adsorbed, because of the high ionic strength it was coiled up, not extending long enough to bridge particles together. Under these conditions the relative viscosity of the flocculant at 1% concentration was 1.22 compared with 3.6 in the absence of the salt.

### 7.3 Molecular weight and flocculation

Another requirement of the theory of polymer bridging is that increased molecular weight of a polymer should increase the efficiency of flocculation, since a longer chain would be able to bridge more effectively. Numerous investigators have reported evidence supporting this hypothesis (56)(168). Kuz'kin and Nebera (56) calculated for a series of PAM based flocculants an end to end length up to  $10^4 \text{A}^\circ$ . Spetch (169) calculated a similar end to end length for a stretched PAM chain of 1 million

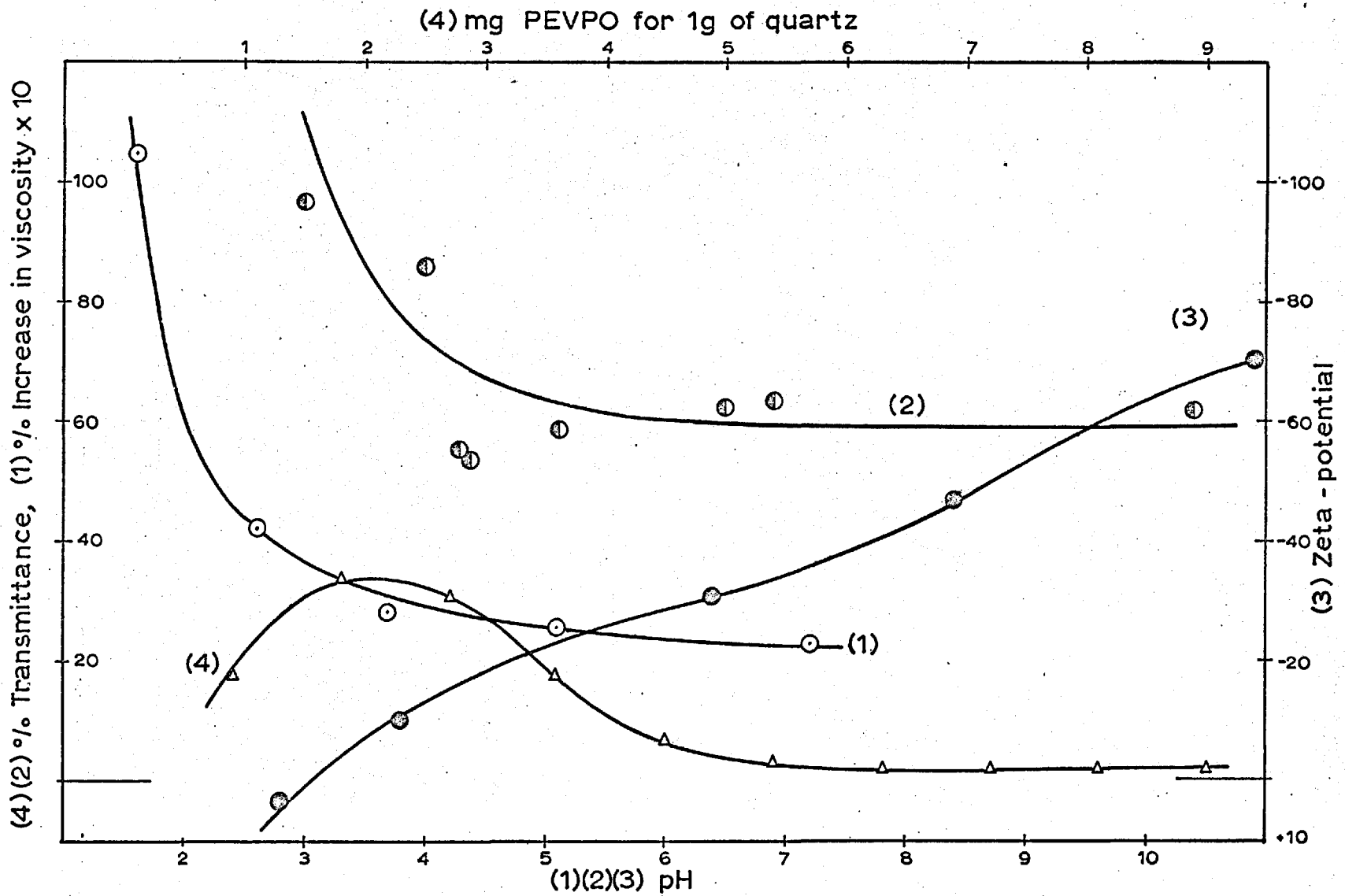


Fig. 22 Effect of pH on the properties and effectiveness of PEVPO

molecular weight. Sakaguchi and Nagase (198) also calculated an end to end length of  $10^3 A^\circ$  for a PAM flocculant of 1 million molecular weight. These authors have further calculated the distance of closest approach between particles at the secondary minimum of the potential energy to be about  $1000 A^\circ$  as well. It has to be noted that lower molecular weight polymers (i.e. mol.wt. < 1 million) can also bridge particles providing the surface charge is low enough for close approach of the particles, or if the adsorbed polymer reduces the  $\zeta$ -potential by charge neutralization, reducing repulsion between particles.

Linear polymeric chains as opposed to highly branched or cross-linked molecules (170)(167) have been found by some investigators to be more effective bridging agents, although it would be expected that more particles (if small enough) should be bridged by the branched polymer, as has been suggested by Whistler (171). A number of preliminary experiments were made with quartz of different sizes and Cl10 under optimum conditions of flocculation for this system. Quartz was classified by wet screening to size fractions starting from 150 mesh ( $104\mu$ ). Only sizes smaller than  $50\mu$  showed aggregation and as the particles became finer, more typical fluffy flocs were obtained, whereas, the coarser particles showed no stickiness and flowed freely. If a small quantity of fine particles ( $<37\mu$ ) were mixed with the coarser ones, the aggregation of the former on the latter ones could clearly be observed. The adsorption of Cl10 on the un-aggregated coarse particles was confirmed by the charring experiment described in section 2.4a.

Commercially available polymeric flocculants contain a range of molecular weights and when mixed with a solid suspension the lower molecular weights might be expected to adsorb more rapidly since they can diffuse more rapidly to the surface. Numerous examples have been quoted for and against this idea in

a review by Patat et.al.(172). More recently Droszkowski and Lambourne (173) showed by hydrodynamic measurements that the higher molecular weight acrylonitrile polymer adsorbed preferentially on  $TiO_2$ . It appears from the examples quoted by Patat et.al. that although preferential adsorption of low molecular weight chains may take place, if the adsorption is irreversible the high mol. wt. chains are not adsorbed; if it is reversible, then the high mol. wt. chains will eventually displace the smaller adsorbed ones.

In this work it was found that a high molecular weight Cl10 was a more efficient flocculant - in terms of optimum quantity required for optimum flocculation - than a lower molecular weight sample of the same product, as illustrated in figure 23.

#### 7.4 Adsorption processes of flocculants

Numerous mechanisms of polymer adsorption have been suggested by various authors and for various systems. These mechanisms can be summarized as follows.

- i. Hydrogen bonding occurs when hydrogen is attached to an electronegative element such as F,N,O,S. The interaction of fresh silica with non-ionic PAM (91) and clays (175)(176) has been claimed to be by this mechanism.
- ii. Electrostatic interactions occur if the functional groups of the polymer and the solid are oppositely charged. The attraction is non-specific and results with mutual charge neutralization or even charge reversal. The flocculating action of cationic flocculants on negatively charged suspensions is usually of this nature and it results with the decrease of the  $\zeta$ -potential of the solid at the optimum dose of flocculant.
- iii. Chemical interactions occur when the flocculant and the solid have groups that can specifically interact to form salt-like

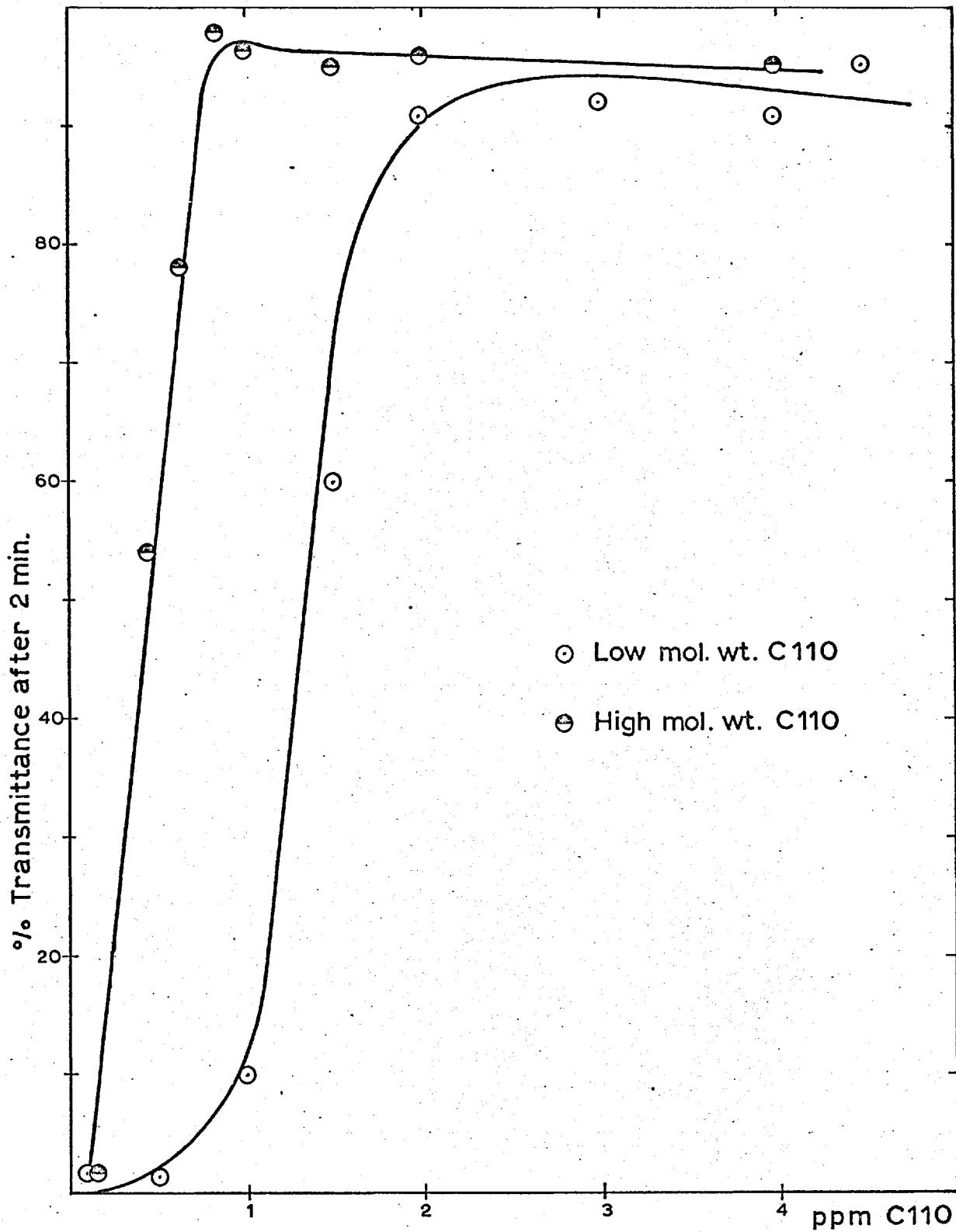


Fig. 23 Comparison of the efficiency of a polymer of different molecular weights in flocculating a 0.5% quartz suspension



structures or complexes. The interaction of modified starch with calcium phosphate (176) has been suggested to be due to a calcium salt formation. The blocking of  $\text{Ca}^{2+}$  sites on  $\text{CaSO}_4$  by the  $\text{COO}^-$  groups of P.A.A. has also been found by others (177) (178). Similarly the capability of polyethyleneimine to complex  $\text{Cu}^{2+}$  has been suggested to be operative in the flocculation of basic copper carbonate (179). Also reagents known to complex  $\text{Ag}^+$  have been shown to coagulate  $\text{AgBr}$  suspensions effectively (180). In analogy with the evidence in froth flotation of minerals the interaction of cationic sites on the solid surface with polymers containing carboxyl or sulphonate groups can be expected to be by the formation of the corresponding soaps.

iv. The flocculating action of non-ionic polymers on  $\text{CaF}_2$  has been attributed to the possible interaction of the dipoles of the amide group with the electrostatic field of the surface of the ionic crystal (57). A similar suggestion was made by Steiner (181) to account for the adsorption of tanning agents on fluorite.

Therefore, depending on the nature of the interaction energy involved between the solid and the active groups of the polymer, the nature of the chemical bond involved in the adsorption process can be expected to vary. In all cases, however, it is probable that polymers require a large number of points of attachment to cause strong adsorption. The actual number is not known for ordinary flocculants. In this connection it is worth mentioning the effects of the solvent and temperature - two less studied variables - on the flocculation process. In general in a good solvent, the polymer is more highly solvated which leads to higher extension of the polymer chains than in a poor one (11). Aqueous media are good solvents for PAM-based flocculants; however, the ionic composition of the medium plays an important role in the extension of the polymer chain as was

shown in figure 22. Water could be expected to facilitate hydrogen bonding processes by facilitating the anion exchange processes on the solid surface.

In a non-aqueous medium increased temperature was reported to lower the amount of polymer adsorbed on  $TiO_2$  (173); similarly at increased temperature the flocculation of coal (54a) was shown to be impeded. In the selective flotation of fluorite, on the other hand, increased temperature was found to lead to better recoveries (182). It would be expected that by increased temperature the interparticle and particle-polymer collisions would be enhanced. However, since adsorption processes are exothermic the observed negative effect of raised temperature could be accounted for.

#### 7.5 Optimum conditions of flocculant addition and optimum quantities

It is generally observed that for a particular suspension, flocculant has to be added under optimum conditions of agitation to obtain maximum flocculation. If polymer concentrations higher than the optimum are added, partial or complete stabilization of the solid is observed. Too slow mixing or too high a shear rate of agitation may lead to the same result. The following points need to be considered.

##### a. Steric stabilization:

i. Due to polymer "over-dose". Optimum flocculation occurs when only part of the available adsorption sites are occupied by the active functional groups of the polymer. La Mer and Healy (183) concluded that when the solid particles are half covered by polymer, optimum flocculation takes place. Fleer and Lykklema (184) have supported this value for the AgI - PVA system; however, they concluded that the mode of mixing is

equally important. Nestler (178) on the other hand in a system of  $\text{CaSO}_4$  - PAA (mol wt 21600) found that although the  $\text{COO}^-$  groups adsorbed on  $\text{Ca}^{2+}$  sites of the solid surface were 4-6% of the total, depending on the orientation of the molecule, the area rendered inactive due to shielding was 60-80%. The results given below confirm this idea namely, that at optimum flocculation the whole surface is not fully saturated by the polymer and part of the surface is still exposed. The experiments were as follows. Three samples of calcite were treated with "under-dose", "over-dose", and optimum quantities of A80. Then the flocs were placed in 50 cc cylinders and left to consolidate for about 15 minutes. Finally 5 cc of 1N HCl was added to each sample and an untreated reference sample. The mixtures were not agitated. The approximate times taken for the cessation of  $\text{CO}_2$  evolution were as follows:

Sample	Reference	under-dosed	optimum	over-dosed
$\text{CO}_2$ evolution(min):	4.5	4.5	7	18

Thus the surface was in effect protected from attack by acid.

In one case when 0.8g  $\text{CaCO}_3$  was treated with 6 times the optimum dose of A70 and subsequently centrifuged, the dissolution of the compact layer took as long as 3 hours. These experiments indicated that there were still nascent sites where  $\text{H}^+$  could attack  $\text{CaCO}_3$  and with increased flocculant content the areas shielded against an attack are increased.

An indication of limited absorbed quantity of polymer on the other hand, was provided by the  $\text{SiO}_2$  - PEVPO system, where, as already mentioned in section 7.2 at pH 3 the optimum quantity of this low molecular weight polymer is  $2 \pm 0.2$  p.p.m. beyond which a complete re-stabilization of the solid takes place. The zeta-potential also follows a Langmuir type isotherm pattern as illustrated in figure 24, probably indicating that above 5 mg/g

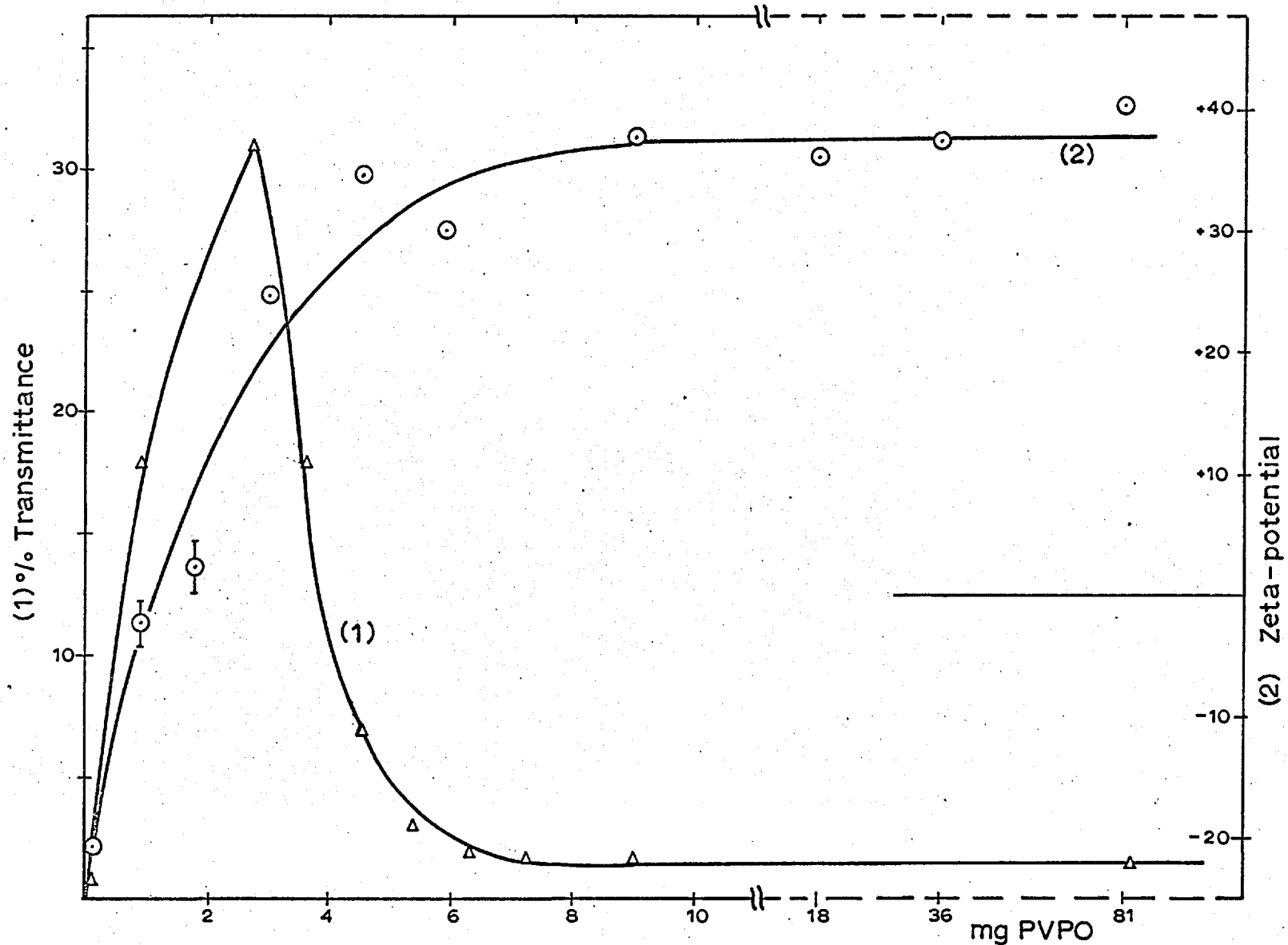


Fig. 29 Effect of PEVPO on the zeta-potential and flocculation of quartz at pH 3

no more of the polymer is adsorbed since the zeta-potential remains essentially constant. It is clear, however, that at the optimum, the adsorption has not reached saturation.

ii. Due to polymer wrapping. The polymer is initially adsorbed via a few active groups on one particle the rest of the molecule extending into the solution, and eventually adsorbing onto another particle upon colliding with it. Failing this, the polymer adsorbs on other available sites of the original particle thus reducing the possibility of polymer bridging. It is known for many systems that the quantity of adsorbed polymer increases with time (185)(186)(157); however there are exceptions to this (183). The adsorption is irreversible (183)(184), but indications of polymer rearrangement taking place in the  $\text{CaCO}_3$  - A80 system upon ageing of the flocs was observed as illustrated in figure 25, which was obtained as follows:

Three 0.5% calcite suspensions were flocculated with an under-dose ( $\frac{1}{5}$  the optimum), optimum dose and over-dose ( 5 times the optimum) of A80. Part of the clear supernatant liquid of each sample was decanted and the flocs transferred together with the remaining part of the supernatant liquid to a cylindrical cell suitable for turbidity measurement with the "EEL absorptiometer". The clarification rate of the supernatant liquid was followed after gently inverting the tube twice. The measurements were made just after flocculation and after 24 hours' standing of the flocs in the tube. It is seen that the over-dosed system did not undergo a great change in 24 hours and the optimum system became similar to the over-dosed one by the end of this time; this combined with the fact that the under-dosed system was also partially stabilized indicates that the energy of individual particles due to thermal motion is comparable with the energy of the  $-\text{COO}^- - (\frac{1}{2}\text{Ca}^{2+})$  bond and the polymer - new particle bond formation in this system (under thermal agitation

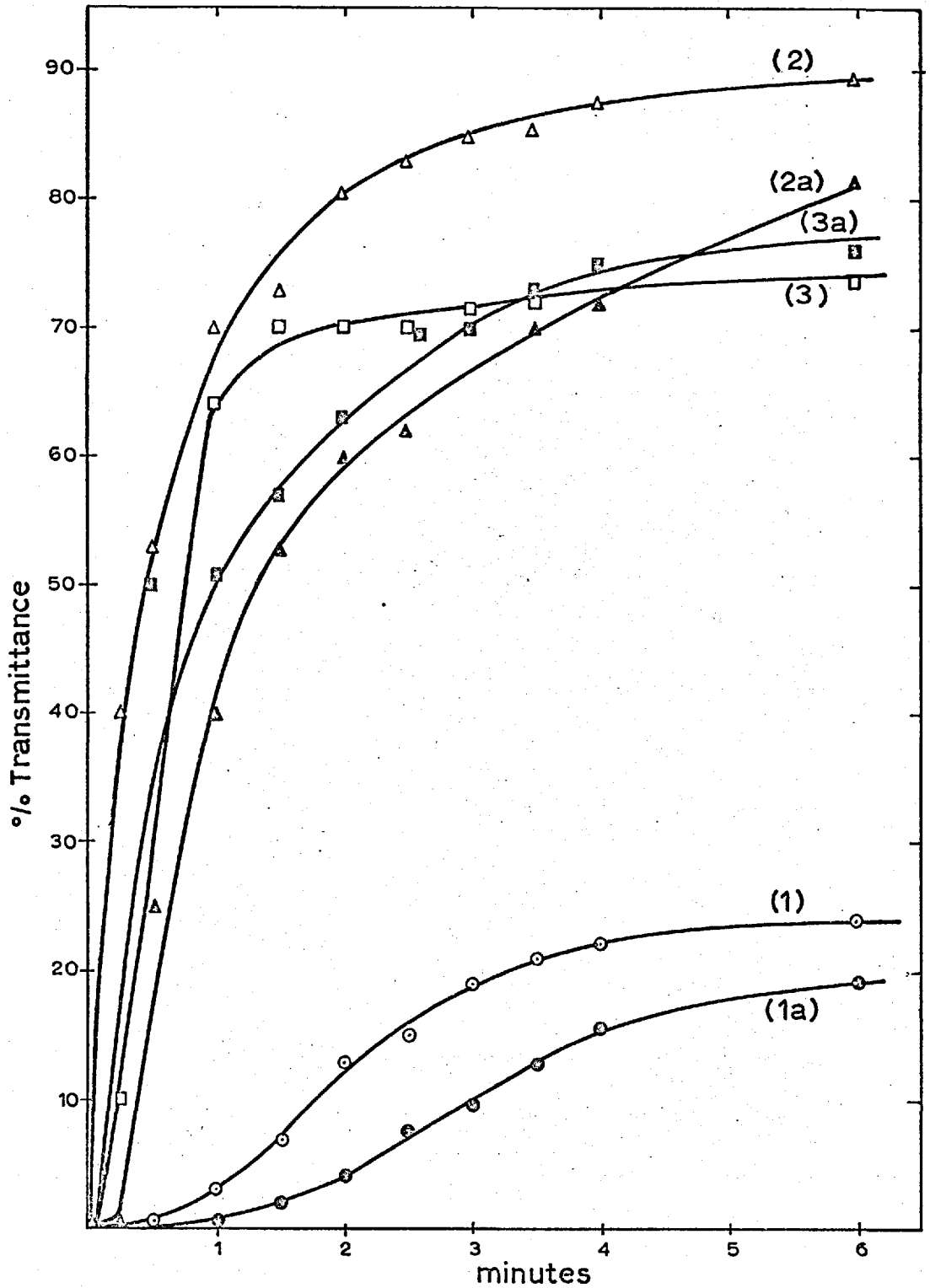


Fig. 25 Effect of 24 hrs. ageing on the clarification rates of A 80 treated  $\text{CaCO}_3$  suspensions. 1, under-dosed; 2, optimum; 3, over-dosed (a) indicates 24 hrs. ageing

only) is less probable than the formation of polymer - original particle bond.

The re-stabilization due to polymer wrapping in this sense is more pronounced if the mechanism of polymer adsorption is not electrostatic and the molecular weight of the polymer is high. If the adsorption mechanism is electrostatic as in the case of cationic polymers, the result will be a reduction of the  $\zeta$ -potential of the particles which in any case de-stabilizes them and thus polymer wrapping can not be easily deduced from turbidity measurements, unless the molecular weight is too low where charge reversal of the solid occurs leading to reversal of the zeta-potential in the opposite direction to the original.

Experiments with high molecular weight polymers were carried out to test whether interruption of the flocculant addition in a dilute solid suspension, where the particle collision is less frequent, would lead to polymer wrapping around the original particles before bridging occurs. The experiments were carried out for two flocculant-mineral systems, one negatively charged solid with a cationic flocculant (i.e.  $\text{SiO}_2 + \text{Cl10}$ ) and the other a positively charged solid with anionic flocculant. (i.e.  $\text{CaCO}_3 + \text{Al30}$ ). For this purpose, the two minerals were previously size classified as much as possible, by repeated decantation and intermittent ultrasonic agitation and equilibrated with the suspending medium for 24 hours. Solids concentrations suitable for turbidity measurements in a 1cm cell were found by trial and error. The agitation intensity (600 r.p.m.) and total time (6 min) of agitation were kept constant in all experiments; however, flocculant addition regimes were varied.

The results for the  $\text{SiO}_2 - \text{Cl10}$  system are given in table 12 and figure 26a and those for the  $\text{CaCO}_3 - \text{Al30}$  system are given in table 13 and figure 26b, where it is seen that under

Table 12

Effect of Cl10 addition regime on the flocculation of quartz suspension. 0.135g solids, 600rpm, agitation time 6 minutes.

<u>No.</u>	<u>p.p.m.</u>	<u>Flocculant addition regime</u>	<u>% Trans.</u>	<u>Shown in Fig. 26a as:</u>
i.	0.3	Added in 2 lots. i.e.: 1/2 in. 15 sec - 15 sec. more agitation stop 10 min: repeat the process: Agitate for further 5 min.	91	△
ii.	0.2	As above	88	△
iii	0.3	All added in 35 sec: 15 sec. more agitation: stop 10 min: agitate for further 5 minutes	91	○
iv	0.3	Added in 6 fractions, i.e.: addition time for each fraction completed to 30 sec: stop 2 min. between additions: etc: finally agitate for 3 minutes.	89	▽
v	0.3	Flocculant added to half the solids in 35 sec: 15 sec. more agitation: stop 10 min: add other half of solids: agitate 10 sec: stop 10 min: Finally agitate 5 min.	85	x
vi		Agitation of (v) continued for 5 more minutes.	89	-



Table 13

Effect of Al<sub>3</sub>O addition regimes on the flocculation of calcite 0.025g CaCO<sub>3</sub>, Agitation at 600 rpm for 6 minutes.

No.	p.p.m.	Flocculant addition regime	% Trans.	Shown in Fig.26b as:
i.	0.04	Added in 10 fractions i.e.: 1 fraction in 37 sec: continue to complete 1 min: stop 2 min: Add next fraction, etc.	85	▽
ii.	0.04	Added in 2 lots, i.e.: half in 15 sec: agitate 15 more sec: stop 10 min: repeat the process: stop 10 min: finally agitate for 5 min.	74	△
iii.	0.04	All in 37 sec: complete 60 sec. agitation: stop 10 min: finally agitate for 5 more minutes.	75	○
iv.	0.02	Added in 2 lots as in ii	74	△
v.	0.06	" " " " " " "	80	△
vi.	0.04	Solid added in 2 fractions i.e.: 1 fraction treated with all flocculant in 35 sec: continue agitation for 25 more sec: stop 10 min: add rest of solid, complete agitation time to 6 minutes	73	X

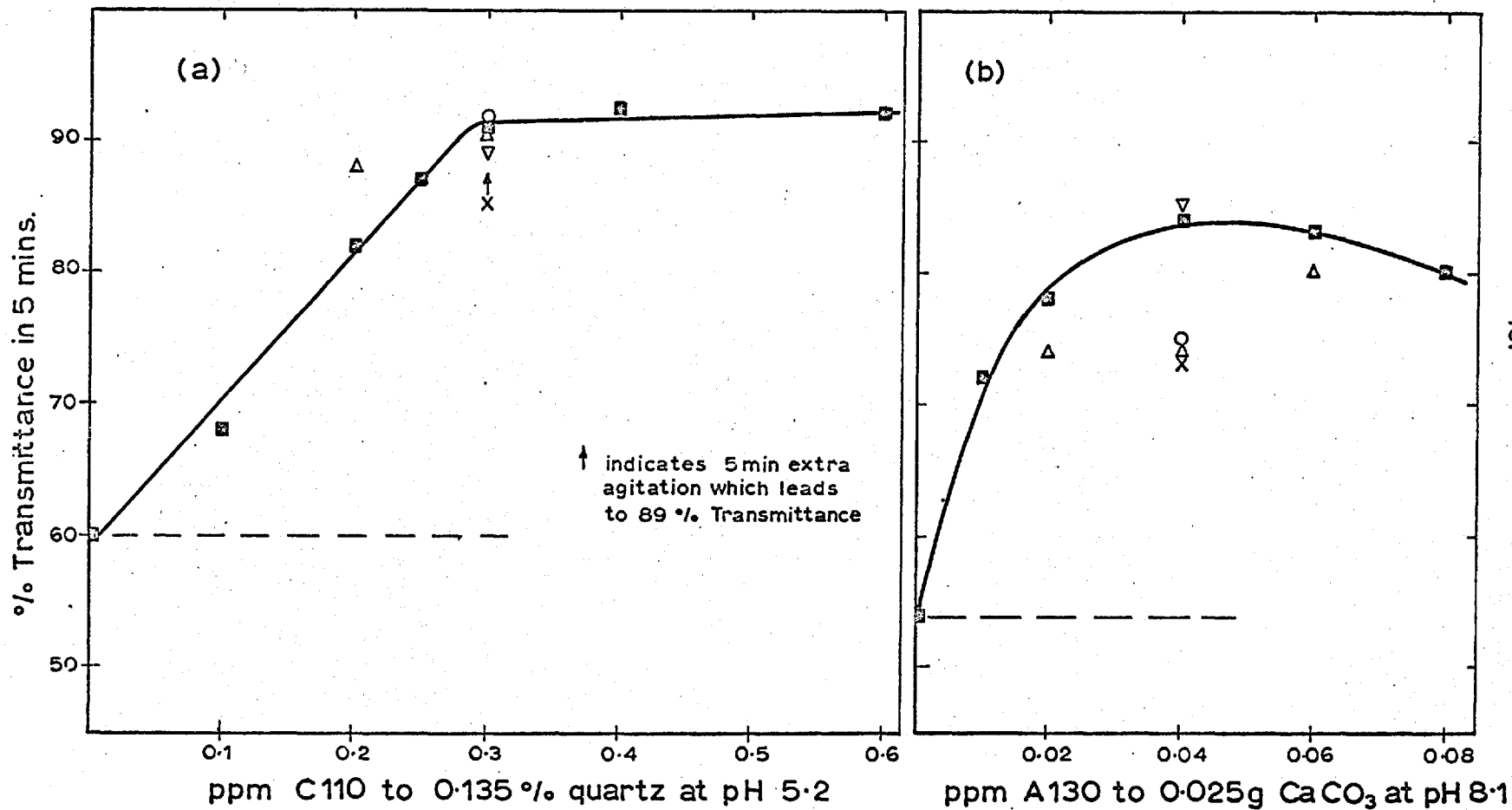


Fig. 26 Effect of flocculant addition regime on flocculation

such shear rates, ~~short~~ times of interruption (i.e. 2 min) of agitation has little effect but if the interruption is 10 minutes re-stabilization takes place. Under no agitation the process takes even longer time (i.e. 24 hours) for the same re-arrangement of polymer to occur as was shown in figure 25. In the cationic high molecular weight polymer [C110 - quartz system], (expectedly) no such re-stabilization is observed since the polymer adsorption mechanism is by charge neutralization. Even at 6 times the optimum concentration of flocculant no stabilization is observed.

iii. Due to inhomogenous distribution of flocculant

Under varying conditions of shear in a flocculation system the rate of polymer adsorption varies, it is also recognised that under too low or too high an intensity of agitation only partial flocculation takes place, the apparent reasons being inhomogenous distribution of flocculant in the former and breakage of flocs in the latter case into smaller fragments. In either case the more stable fractions have either not taken up flocculant or carry an excessive quantity of flocculant (199). Floc breakage is more likely to be at the polymer-solid junction rather than at the -C-C- bond of the polymer chain due to the relative strength of the bonds. For more homogenous distribution of the flocculant stepwise addition of the optimum quantity is generally found suitable on an industrial scale (134). In one case however, (207) a "Polyteric" flocculant of low molecular weight was reported to flocculate a typical washery tailing completely in 10 seconds, without the need for agitation. (Even so, mixing must have occurred; and the process could have been improved by finding the optimum conditions).

In figure 27 is shown the effect of the intensity of

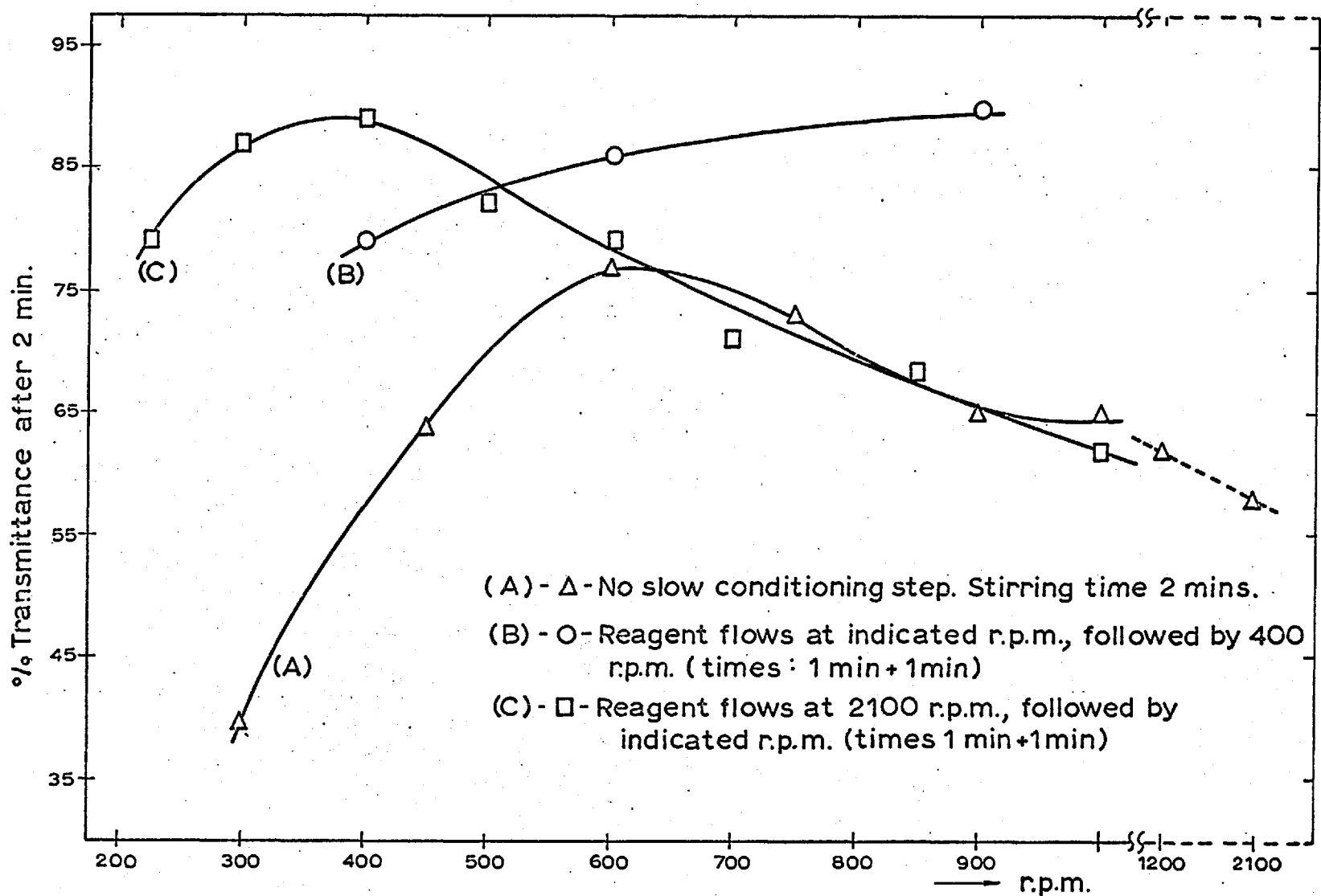


Fig. 27 Effect of intensity of agitation on the flocculation of 0.8%  $\text{CaCO}_3$  by 1.5 p.p.m A-100

agitation on the effectiveness of clarification for the system  $\text{CaCO}_3$ -Al<sub>2</sub>O<sub>3</sub>. It can be seen in this figure that too low or too high an intensity of agitation is harmful, whereas better clarification is obtained if the flocculant is added under high intensity of agitation followed with a slow step of conditioning, giving particles time to collide less vigorously and thus retain the mineral-polymer bridges. Table 14 shows that the mode of addition of flocculant is of not great consequence providing the initial conditioning at high shear rate is such that the polymer is as evenly distributed as if it is added in a very dilute form. The system in this table: 2 ppm A80 + 0.8%  $\text{CaCO}_3$  and the conditioning steps were 2100 r.p.m. conditioning for 1 min (including flocculant addition time) followed by 1 minute of 400 r.p.m.

Table 14

Mode of flocculant addition	Addition Time	% Trans.
All at once	-	92
10 times diluted	15 sec.	92
25 times diluted	35 sec.	92

Optimum shear conditions for flocculant addition, namely, 1 minute agitation at 2100 r.p.m. - including flocculant flow time - followed by 1 minutes agitation at 400 r.p.m. were adopted for all experiments. The optimum quantities of flocculants were determined for the three mineral studied and are given in table 15.

Table 15

Optimum flocculant concentrations and relative flocculating powers of the flocculants.

Mineral	Quartz 0.5%		Calcite 0.8%		Galena 0.4%	
	optimum ppm	% Trans at optimum	optimum ppm	% Trans at optimum	optimum ppm	% Trans at optimum
No flocculant	-	0	-	0	-	19
Cyanamer P250	4	95	1	82	1.5	80
BTL-C110	2.5	95	1	42	2	89
" -C100*	7	85	-	-	-	-
" -A100	-	-	1.5	85	0.2	72
" -A130	-	-	1.5	63	0.5	68
" -A150	-	-	2	54	0.25	42
" -A70	-	-	2	82	0.5	76
" -A80	-	-	1.5	92	1.5	82
Polyteric S-1	-	-	1	75	-	-

\* This sample of C100 does not dissolve completely.

## 8. COAGULATION AND FLOCCULATION OF MINERALS IN MIXTURES

When a mixture of two or more minerals is placed in an aqueous medium the resulting suspension does not always have the sum of the properties of the two minerals individually suspended in a similar medium. In such a mixture the stability of one mineral is effected by the factors outlined below.

(a) The altered ionic composition of the suspending medium if one of the minerals is relatively soluble or carries soluble oxidation products, as in the case of galena + quartz,

(b) the increase in the medium of charged colloidal particles due to dispersion of one component, which in turn act as bridging agents between the particles of the other mineral, as in the case of quartz + calcite

(c) the alteration of the pH of the medium which may change the electro-kinetic potential of one component or lead to the formation of hydrolysis products which produce coagulation, as in the case of calcite + galena,

(d) the different surface chemical properties of individual minerals having opposite charges.

(e) The above effects may take place immediately when the two minerals are mixed together; however, if the conditions are such that the two minerals do not immediately coagulate, upon the introduction of a polymeric flocculant mutual flocculation can take place owing to the activation of one mineral by the traces of metal ions introduced into the medium by the other mineral.

These points are considered below for calcite, quartz and galena.

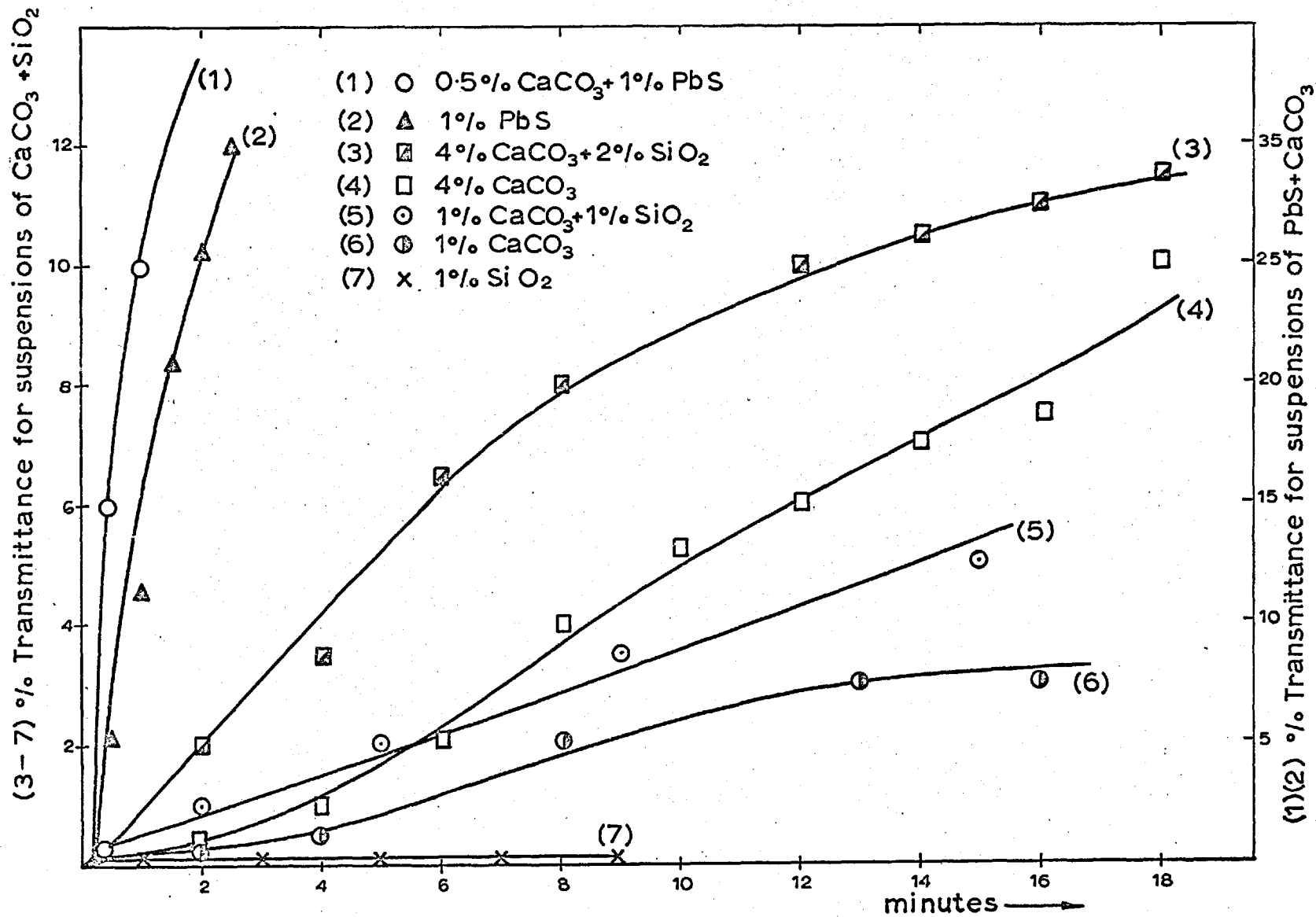


Fig. 28 Mutual coagulation of minerals



### 8.1 Mixture of calcite and quartz

An aqueous suspension containing calcite is always alkaline, and at equilibrium the pH of the medium becomes  $8.5 \pm 0.5$ . The ionic strength of the medium is  $10^{-3.4}$  and a considerable quantity of  $\text{Ca}^{2+}$  is present. Also the zeta-potential of  $\text{CaCO}_3$  at this pH is about +20mV. On the other hand quartz, in such an ionic medium has a zeta-potential of -45mV.

The two minerals when individually suspended with appropriate solids content in the medium, are fairly stable under these conditions. However, when they are mixed together, mutual coagulation takes place as is shown in figure 28. In figure 29 a photomicrograph of a mixture of  $\text{SiO}_2 + \text{CaCO}_3$  is shown, where it is seen that the coarse quartz particles are covered with fine calcite slimes, which can not be removed by ordinary washing. This is due to the opposite surface charges of the particles.

Different oxide minerals when mixed together at a constant pH, can also mutually coagulate if they have opposite surface charges. This depends on the corresponding z.p.c. values of the oxides and since  $\text{H}^+$  and  $\text{OH}^-$  are potential determining ions for oxides in general, at  $\text{pH} < \text{z.p.c.}$  they are positively charged whereas the charge is negative at  $\text{pH} > \text{z.p.c.}$  Consequently, the mutual coagulation of a number of oxides was observed as is shown in table 16. These results were obtained simply by preparing about 1% solid suspensions of each oxide at the indicated pH value in a 50cc glass stoppered cylinder and mixed by agitation. Coagulation of the mixtures could easily be observed after 15 minutes standing, while no change took place in the single solid suspensions.

For table 16 see overleaf.

Table 16 Mutual coagulation of oxide minerals

No.	Oxide	i.e.p. (pH)	Mixture	pH	
				Coagln.	No Coagln.
I	Al <sub>2</sub> O <sub>3</sub>	5-9.2	I+VIII	5	11
II	Cr <sub>2</sub> O <sub>3</sub>	7	II+VIII	5	11
III	Fe <sub>2</sub> O <sub>3</sub>	4.5-8.6	III+VIII	5	10
IV	MgO	12	-	-	-
V	SnO <sub>2</sub>	7.3	-	-	-
VI	TiO <sub>2</sub>	3.5-6.2	VIII+VI	5	11
VII	ZnO	8.7-9.2	VI+VII	7.8	11
VIII	SiO <sub>2</sub>	2-3.6	VI+VIII	5	11

Obviously mutual coagulation presents a problem if selective flocculation of one component of the mixture is required.

An obvious solution would be to make the two minerals similarly charged by some modifying reagent. This can be effected by altering the concentrations of potential - determining ions for the two minerals. Since that of quartz cannot be made positive by reducing the pH, the alteration has to be made for the calcite. It was shown in section 5.3, however, that the zeta-potential of CaCO<sub>3</sub> becomes negative at relatively high concentrations of added carbonate (i.e.  $\approx 10^{-2}$ M) which in turn increases the ionic strength and the pH of the medium. (cf. figures 16 and 17). Observing from figure 17 that at pH>10

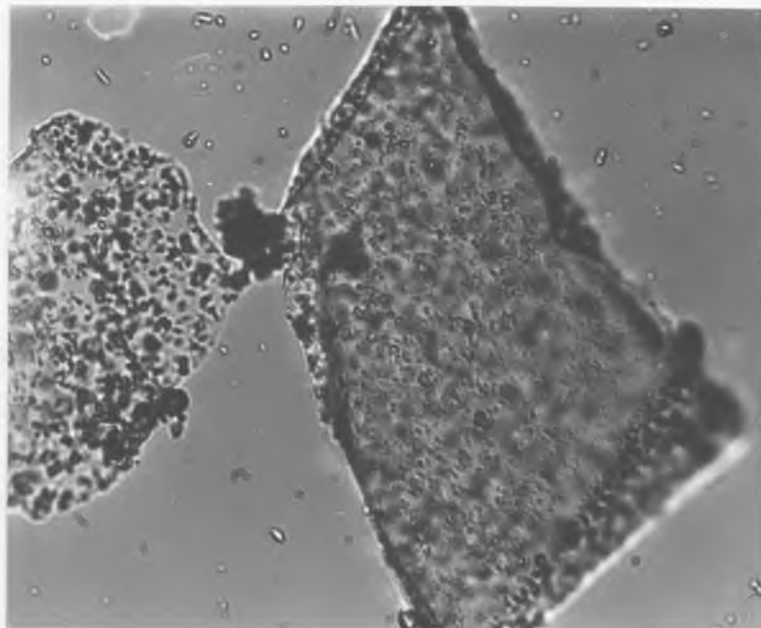


Figure 29  
Photomicrograph of quartz grains  
coated by calcite slimes  
Magnification = 625 x

$\text{CaCO}_3$  is negatively charged and remembering that the medium contains  $\sim 10^{-4} \text{M Ca}^{2+}$ , from figure 8 since under these conditions quartz does not coagulate, it would be expected that calcite and quartz should remain separate at  $\text{pH} > 10$  without mutual coagulation.

### 8.2 The Galena + Quartz and Galena + Calcite systems:

Since galena is negatively charged in distilled water, as quartz is, mutual coagulation of the two minerals would not be expected to take place for reasons of opposite surface charge signs. However, the ground galena stored for a time oxidizes to a considerable extent. It introduces relatively large quantities of  $\text{Pb}^{2+}$  ions to the medium. The conductivities of the supernatant liquids obtained after suspending various quantities of galena powder washed once, were measured and compared with those of  $\text{Pb}(\text{NO}_3)_2$  of known concentrations. The results given below indicate that the free  $\text{Pb}^{2+}$  present in the medium may be of the order of  $10^{-4}$  mol/l.

g. $\text{PbS}/100\text{cc}$	:	1.4	2.71	5.47	8.0
Conductance of supernatant liquid ( $\mu\text{mho}$ )	:	34	42.5	56	65
Corresponding $[\text{Pb}^{2+}]$ mol/l	:	$1.5 \times 10^{-4}$	$2 \times 10^{-4}$	$2.3 \times 10^{-4}$	$3 \times 10^{-4}$

Nonetheless, as seen in figure 10, at this  $\text{Pb}^{2+}$  concentration quartz suspensions do not coagulate. It would be expected however, at  $\text{pH} > 9.5$  that because of the increased number of colloidal silica particles (see section 4.6 and figure 14) galena particles might be bridged together. The  $\zeta$ -potential of galena at such pH values is weakly negative but the charge density is low enough and would allow the inclusion of negatively charged silicate dendrites on local sites of galena which due to crystal defects would form a scattered negative charge distribution.

Experiments on the local electrode potential for grains of galena have always revealed great variations from point to point; presumably this also effects the local electrical double layers.

In the case of the galena + calcite system, the factors favouring mutual coagulation of the two minerals are further increased since upon mixing the two, the pH and the ionic strength of the medium is increased and the two minerals have opposite signs of surface charge. The accelerated rate of coagulation of calcite by the introduction of galena into the medium is shown in figure 28; figure 30 is a photo-micrograph of the mutually coagulated galena and calcite. In this photomicrograph it is possible to observe aggregated calcite particles possibly bridged together by the formation of localized pockets of  $Pb(OH)_2$ . In systems involving two such minerals the formation of surface chemical compounds such as  $PbCO_3$  is also possible (as mentioned on p 58). Increase of pH does not make the mixture any more stable; this observation supports the possibility of the interparticle bridging due either to  $Pb(OH)_2$  or  $PbCO_3$  formation. In any case it was shown in section 6.2 that the stability of galena suspensions is not greatly altered by increasing the pH from 8.2 to 11.

### 8.3 Effects of added ions on the flocculation of minerals by polymers.

It is known from froth flotation that negatively charged minerals can be rendered floatable by anionic flotation reagents after conditioning with added metal ions, as in the well known case of ZnS being activated by  $Cu^{2+}$  prior to flotation by xanthates and the flotation of quartz by fatty acids after activation by  $Ca^{2+}$  at alkaline pH. Analogous results of activation of a number of minerals not normally flocculable in the absence of

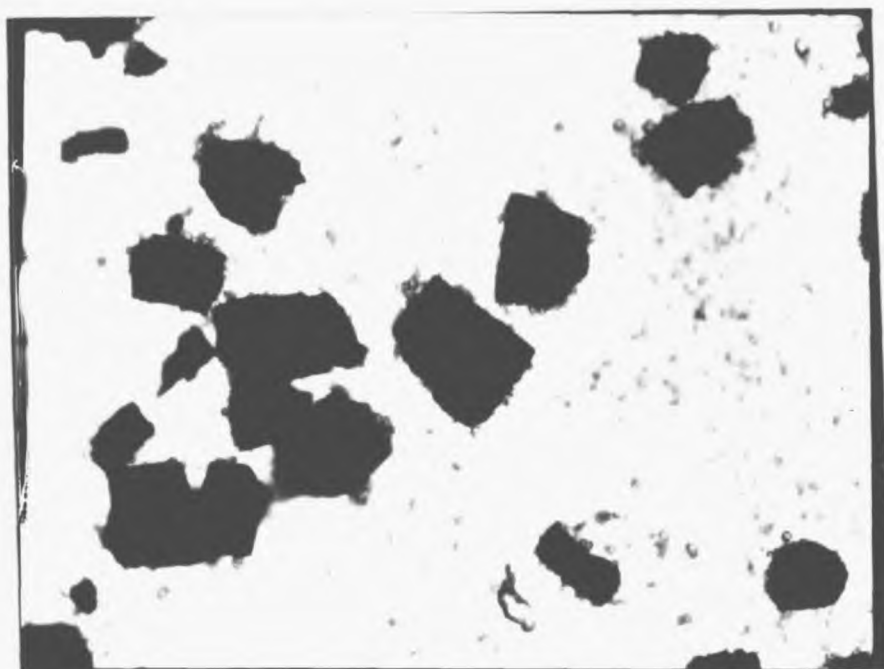


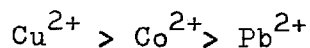
Figure 30

Photomicrograph of calcite fines  
adhering to galena grains.

Magnification: 250 x

added ions by PAM - based flocculants were discovered by Slater, Clark and Kitchener (179). Cations were found to activate some negatively charged minerals and in one case of the opposite kind  $PO_4^{3-}$  was found to activate  $Al_2O_3$ , not normally flocculable by a cationic flocculant at  $pH < 6$ .

From the analysis of the results of the experiments establishing the factors effecting the stabilities of  $CaCO_3$  and  $SiO_2$  it was concluded in section 8.1 that quartz and calcite, at or below the maximum solid concentration where they would individually form stable suspensions, their mixtures too should be stable at  $pH > 10$ . However, when a flocculant specific to one of the minerals is introduced into the medium, the  $Ca^{2+}$  ions produced due to the solubility of  $CaCO_3$  and adsorbed on quartz provide sites for the adsorption of the flocculant on quartz, thus leading to the mutual flocculation of the two minerals. In fact, at  $pH > 10.6$   $Ca^{2+}$  concentrations much lower than those likely to be provided by  $CaCO_3$  takes place as illustrated by line 2 of figure 31. Also in figure 31 the activation of 0.5g quartz in a solution of  $2.6 \times 10^{-4} M Ca^{2+}$  is shown by lines 1-6. It is noteworthy that there is a critical pH of activation (c.p.a.) for each flocculant in the presence of a constant concentration of  $Ca^{2+}$ , and as the concentration of  $Ca^{2+}$  increases, the c.p.a. becomes smaller (compare curves 2 and 4 in figure 31). Furthermore as the anionic character of the flocculant increases the c.p.a. decreases. The non-ionic PAM flocculants on the other hand (A100 being more akin to non-ionic PAM than to a truly hydrolyzed PAM) respond to activation as well as the highly hydrolyzed flocculants (curves 3 and 5 in the same figure). Activation of quartz by cations other than  $Ca^{2+}$  also follows the same pattern, and the order of activation at the same pH and metal ion concentration for  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Co^{2+}$  is



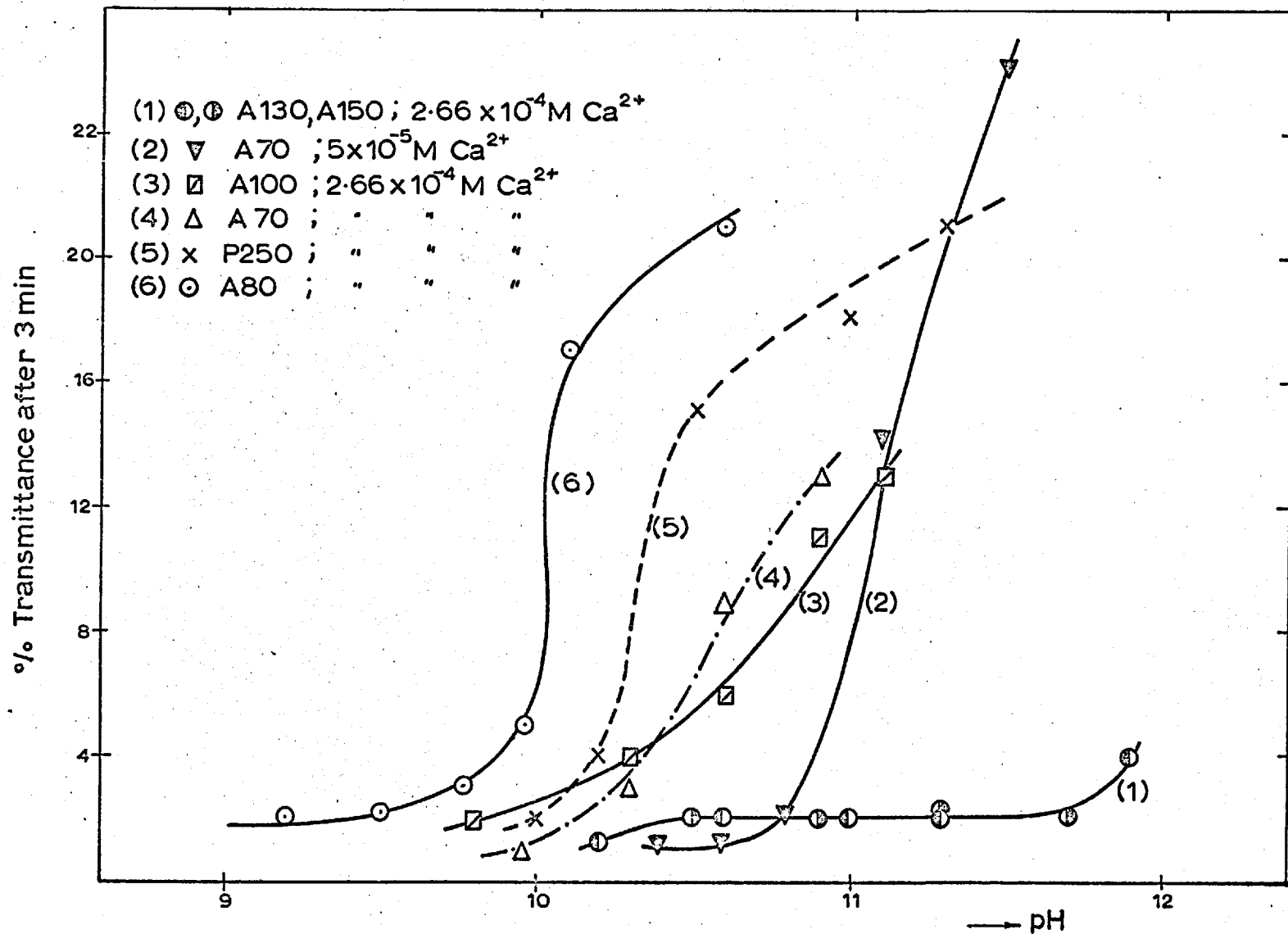
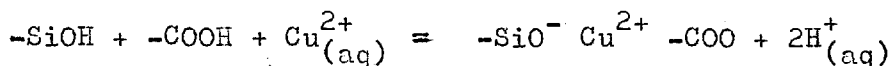


Fig. 31 Activation of 0.5% quartz suspensions by  $\text{Ca}^{2+}$ . (Flocculant quantities: 2 p.p.m)



In figure 32, the effects of  $\text{Cu}^{2+}$  and  $\text{Co}^{2+}$  as activators for quartz in the presence of AlOO is illustrated. It is interesting to note that activation starts at the beginning of  $\text{Me}(\text{OH})_2$  formation and as the hydroxide formation is practically complete flocculation is inhibited. Slater, Clark and Kitchener (179) concluded that  $\text{Cu}^{2+}$  ions act as bridges for joining  $-\text{COO}^-$  ions of the hydrolyzed PAM to silicate ions as in the following reaction



and since  $\text{Cu}^{2+}$  does not activate aged quartz which is known to lose its hydrogen bonding sites upon ageing, they concluded that  $\text{Cu}^{2+}$  acts simply by reducing the electrostatic repulsion between silica and the polymer chains.

In flotation of minerals where  $\text{Ca}^{2+}$  ions and  $\text{COO}^-$  groups are involved the formation of surface compounds is known from infra red spectrographic studies (189). Where hydrolyzable metal ions and  $\text{COO}^-$  groups are involved, the role of hydroxy complexes is stressed (190). Other adsorption mechanisms were mentioned in section 7-4. Therefore the adsorption mechanism in each system might be different, and also, the same ion could act by more than one mechanism. For instance, in addition to the hydrogen bonding mechanism of  $\text{Cu}^{2+}$  mentioned in the work of Slater, Clark and Kitchener, it appears that there is a direct correlation between the i.e.p. of  $\text{Cu}(\text{OH})_2$  (i.e.  $9.4 \pm 0.4$ ) (19) and the activation illustrated in figure 32 curve 5. At  $\text{pH} < \text{i.e.p. Cu}(\text{OH})_2$  is negatively charged and flocculation is enhanced and at  $\text{pH} > \text{i.e.p.}$  flocculation ceases. By analogy and from curve 6 of the same figure the i.e.p. of  $\text{Co}(\text{OH})_2$  could be estimated as  $\text{pH } 10.5 \pm 0.5$ , which is in agreement with the value of 11.4 found by Mattson and Pugh by zeta-potential measurements (19).

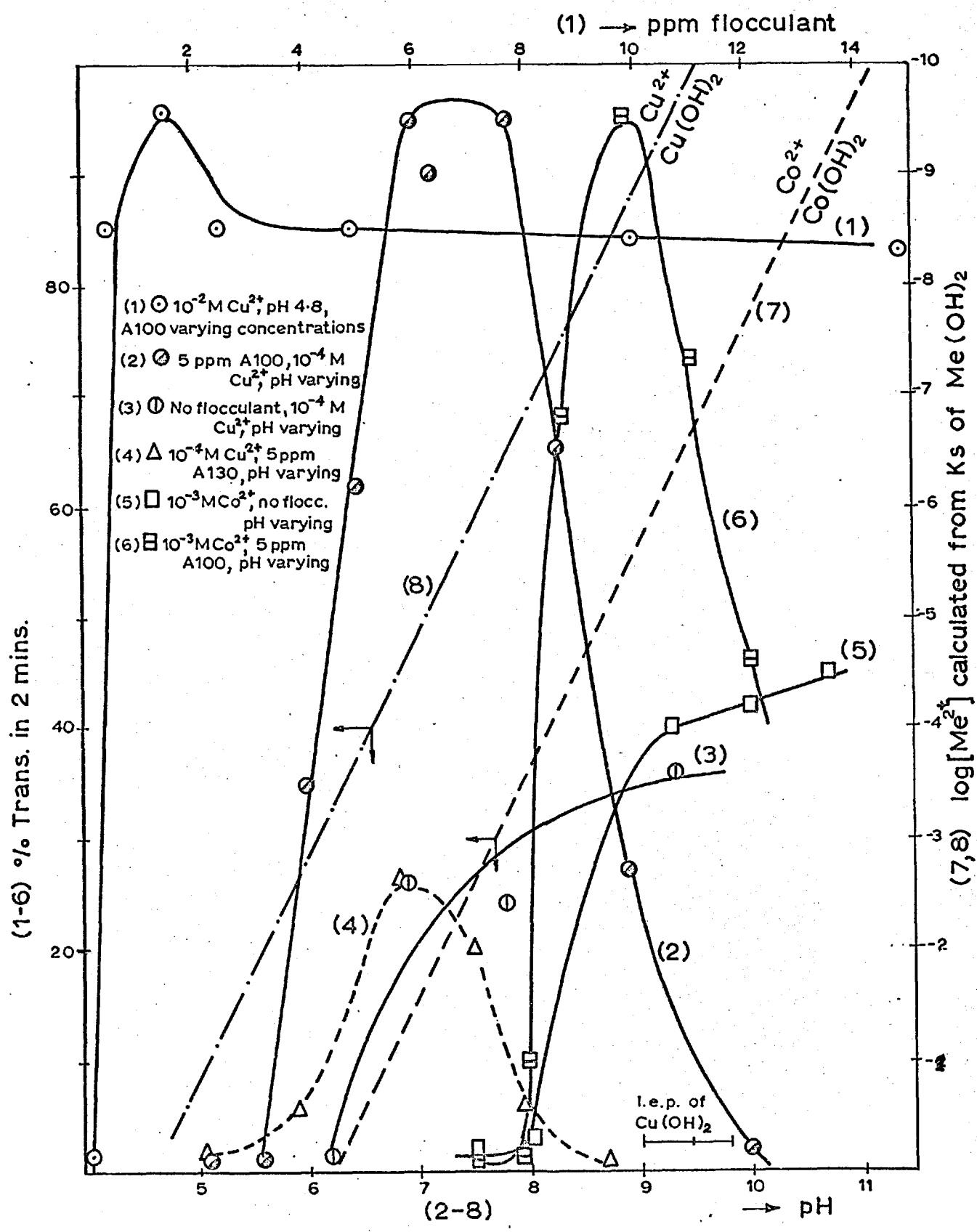
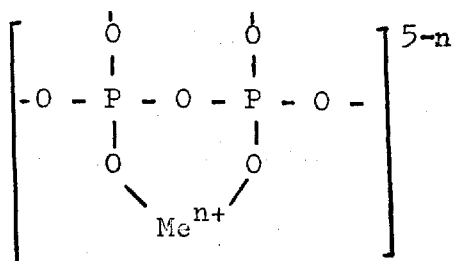


Fig. 32 Activation of 0.5% quartz by  $Me^{2+}$  ions

In addition to the "positive activation" (or promotion of flocculation), the action of ions inhibiting flocculation could be termed "negative activation" (analogous to depression in flotation). This involves the preferential adsorption of the added ion instead of the flocculant if the negative activator is added before the flocculant, or desorption of the flocculant if the order of addition is reversed. For instance the adsorption of anionic flocculants on galena and calcite is inhibited by  $\text{Na}_2\text{S}$  and  $\text{PO}_4^{3-}$  respectively. Similarly, flocculated calcite and galena are re-dispersed by the addition of these anions, suggesting that the carboxylate groups are displaced.

It is known that phosphate ions form a negatively charged complex with metal ions, having the following structure (191)



Similarly,  $\text{S}^{2-}$  forms metal sulphide precipitates. In both cases  $\text{PO}_4^{3-}$  and  $\text{S}^{2-}$  compete with the  $-\text{COO}^-$  groups of the flocculant for the surface adsorption sites.

The prevention of flocculation of  $\text{CaCO}_3$  and  $\text{PbS}$  by anionic flocculants was tested in parallel with  $\zeta$ -potential measurements.  $\text{Na}_2\text{S}$  prevented the flocculation of  $\text{PbS}$  by all the BTI-A flocculants except  $\text{AlOO}_3$ , the effect of which was only reduced but not prevented. The effect on "Cyanamer P-250" was like on BTI- $\text{AlOO}_3$ . The  $\zeta$ -potential of  $\text{PbS}$  varied as shown in table 17. In the case of  $\text{CaCO}_3$ , however, tripolyphosphate stabilized the mineral at a concentration of 5mgs phosphate/g  $\text{CaCO}_3$  and prevented the adsorption of all flocculants but the cationic ones\* and desorbed the

\*Polyteric LS was used instead of BTI-C110 which becomes anionic at  $\text{pH} > 7$ .

already adsorbed flocculant. The  $\zeta$ -potentials of calcite under deactivation conditions are given in table 17. In both the cases of PbS and CaCO<sub>3</sub> agitation for 30 seconds was enough to break all the flocs irreversibly, whether the flocs were formed with an under-dose, optimum, or over-dose quantity of flocculant.

Table 17

System	$\zeta$ -potential at 25°C (mV)
PbS (pH 11)	: -25
PbS+Na <sub>2</sub> S (1x10 <sup>-3</sup> M)	: -54
PbS+Al <sub>3</sub> O (1 ppm)	: No particle mobility
PbS+Al <sub>3</sub> O+Na <sub>2</sub> S	: -55
CaCO <sub>3</sub> (pH 8.2)	: +22
CaCO <sub>3</sub> +Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub> (5mg/g)	: -47
CaCO <sub>3</sub> +A70 (1 ppm)	: No particle mobility
CaCO <sub>3</sub> +A70+Na <sub>5</sub> P <sub>3</sub> O <sub>10</sub>	: -43

The effect of Na<sub>2</sub>S and tripolyphosphate could however, be reversed by the addition of a cation which would interact with the reagent. For instance, the addition of a quantity of Cu<sup>2+</sup>, Co<sup>2+</sup> or Pb<sup>2+</sup> so as to form a 0.05% solution to an already stabilized PbS suspension reversed the effect of Na<sub>2</sub>S. Ca<sup>2+</sup> as well as Cu<sup>2+</sup> and Ba<sup>2+</sup> at the same concentrations reversed the effects of Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> on CaCO<sub>3</sub>. Similarly, the addition of a fresh quantity of untreated solid to the already stabilized suspension consumed the respective dispersing reagents, and removed their effects. Table 18 illustrates the action of these cations for the case of PbS. In this table + indicates flocculation and - indicates no effect while  $\bar{+}$  indicates partial flocculation with a haze remaining.

Table 18. Re-activation of galena treated with  $\text{Na}_2\text{S}$

Cation Flocculant	Ba	Ca	Cu	Pb	Zn	Co
A-100	+	+	+	+	-	+
A-130	+	+	+	+	-	+
A-150	+	+	+	+	-	+
A-70	+	+	+	+	-	+
A-80	+	+	+	+	-	+

#### 8.4 Summary

From the facts so far established, the conditions for the separation of the three minerals can be summarized as follows :

(a)  $\text{CaCO}_3 + \text{SiO}_2$  : The mixture can be prepared in a solution of pH greater than 10 and smaller than 11.5. A130 and A150 can be used to flocculate  $\text{CaCO}_3$  selectively leaving quartz suspended. Non-ionic PAM cannot be used to flocculate quartz selectively since  $\text{Ca}^{2+}$  in the medium activates **the mineral for** this type of flocculant.

(b)  $\text{PbS} + \text{SiO}_2$  : This system does not present the problem of mutual coagulation; however, a cationic flocculant cannot be employed for selectively flocculating one component only since both would flocculate. Any of the anionic or non-ionic flocculants should be suitable to flocculate galena while quartz remains suspended. For the use of a non-ionic flocculant quartz has to be aged by increasing the pH of the suspension.

(c)  $PbS + CaCO_3$  : Since the two minerals give relatively unstable suspensions and also present a problem of mutual coagulation, an initial stabilization of the mixture by making  $CaCO_3$  negatively charged is essential. Mutual coagulation can be prevented by making the pH greater than 10. However, this does not solve the problem completely since all types of flocculants still do flocculate the two components. The solution of this problem was achieved by initially stabilizing the two components by a protective colloid ("Dispex") and preferentially desorbing it from  $PbS$  by the addition of  $Na_2S$ . This process is described below.

(d)  $CaCO_3 + PbS + SiO_2$  : For the separation of the three components two approaches should be possible:

a.  $PbS + CaCO_3$  can be initially flocculated together by the use of A130 or A150 at  $10 < pH < 11.5$  leaving  $SiO_2$  suspended.

b.  $PbS$  can be flocculated alone as in (c) above leaving  $SiO_2 + CaCO_3$  suspended; and finally  $SiO_2 + CaCO_3$  can be separated as in (a) above.

In testing the feasibility of these processes the total solids content of the suspension and the ratio of one component to the other present a special problem of "entrapment". Entrapment here refers to the fact that although a mineral in a mixture is not flocculated by a polymeric flocculant, it is carried down in the porous structure of the flocs of the flocculating component, and in extreme cases a total precipitation of solids takes place, leaving a clear supernatant liquid. The conditions leading to this situation and a possible way of overcoming it are described in section 9-2 below.

9. SELECTIVE FLOCCULATION OF  $\text{PbS}$ ,  $\text{CaCO}_3$   
AND  $\text{SiO}_2$  FROM MIXTURES

Artificial mixtures of minerals were prepared and dispersed in 50 cc of water, by vigorous agitation at 2100 r.p.m. and by treatment with ultrasonics for three minutes. Then the flocculant was added at high shear as in the case of the flocculation of individual minerals (cf section 75 ) and finally the mixture was conditioned at low shear for 1 minute. The unflocculated upper part was then sucked off with a suitable arrangement and each fraction analyzed quantitatively by wet analytical methods described below. In some cases the flocculated part was further agitated at low shear after the addition of a certain volume of water and the resulting fractions analyzed similarly. The added water, depending on the system, sometimes contained a certain quantity of flocculant, as mentioned in relevant sections below.

The percent recovery (%R) of one mineral in a fraction was calculated from  $\%R = \frac{W_s}{W_i} \times 100$ , where  $W_s$  is the weight of the component in a fraction of the separated mixture, and  $W_i$  is the initial total weight of this component placed in the mixture before the separation process. The percent grade (%G) was calculated from  $\%G = \frac{W_s}{W_t} \times 100$ , where  $W_s$  is as above and  $W_t$  is the total weight of solids in a fraction of the separated mixture.

The methods of analysis were as summarized below:

i. Determination of  $\text{CaCO}_3$ . Fractions containing calcite were dried on a Gooch crucible previously lined with asbestos, dried and weighed. After the determination of the total weight of the mixture,  $\text{CaCO}_3$  was leached with dilute HCl, the residue washed with water and the crucible re-weighed after drying

to constant weight. The weight percentages of the components were then determined from the data obtained.

ii. Determination of PbS. Galena was first dissolved with conc.  $\text{HNO}_3$  and the  $\text{Pb}^{2+}$  solution obtained was gravimetrically determined as  $\text{PbCrO}_4$  (197). When in some cases elemental sulphur was produced due to oxidation it was first evaporated by heating, and the dissolution operation repeated. The PbS content was calculated from  $\text{PbCrO}_4$ .

iii. Determination of  $\text{SiO}_2$ . In all experiments  $\text{SiO}_2$  was determined from the weights of the residues after leaching.

#### 9.1 Experimental results of separations:

a.  $\text{CaCO}_3 + \text{SiO}_2$ : Since A130 and A150 are the only flocculants which do not flocculate quartz through activation by  $\text{Ca}^{2+}$  and A 150 is the least effective flocculant for  $\text{CaCO}_3$ , the former was preferred for separation experiments. The results of these experiments are given in table 19 overleaf.



Table 19 Separation of  $\text{SiO}_2 + \text{CaCO}_3$  mixtures

Test No.	p.p.m of flocculant	Fraction	Initial mixture		Calcite		Quartz	
			$\text{CaCO}_3$ (g)	$\text{SiO}_2$ (g)	Recovery %	Grade %	Recovery %	Grade %
1	1	1	0.50	0.50	0	-	40.7	99.9
		Residue			100	63	39.3	37
2 <sup>#</sup>	1	1	0.50	0.50	0	-	30.2	99.9
		Res			100	59	69.8	41
3 <sup>#</sup>	1	1	0.50	0.71	0	-	16.5	99.9
		Res			100	45.2	83.9	54.5
4	1	1	0.50	1.10	0	-	27.8	99.9
		Res			100	34.5	72.7	65.5
5	1	1	0.50	2.10	0	-	18.7	99.9
		Res			100	22.7	81.3	77.3
6	1	1	0.54	3.03	0	-	20.4	99.9
		2 Res			10.7 89.3	20 18	7.6 72	80 82
7	1	1	0.56	4.0	0	-	19.9	99.9
		2 Res			11.3 88.7	18 15	7.1 73	82 85
8	2	1	1.07	0.50	0	-	8.36	99.9
		Res			100	72	21.64	28

Table 19 (continued)

		1			0	-	2.9	99.9
9	2	2	1.96	0.52	0.57	50.7	2.1	49.3
		3			0.43	50.7	1.5	49.3
		Res			99	83.7	94.5	16.3

\* pH made 11 after agitating the mixture for 2 min. with 50cc H<sub>2</sub>O of pH 5.

In this process the main point leading to separation is the fact that quartz and calcite, which initially have opposite surface charges, were made similar by making the pH 11 and thus changing the surface charge of the latter to negative. Under these conditions the uptake of Al<sub>3</sub>O by calcite is not prevented.

Operating on the same basis of changing the surface charges it should be possible to use a reagent other than NaOH to make the surface charge of calcite negative. Making the surface charge of quartz positive would prevent mutual coagulation; however, in this case an anionic flocculant cannot be used to flocculate one component only. Poly-vinylpyrrolidone (PVP), a product used as a stabilizing additive in syndets (196) and as a protective colloid (11), was found to prevent the mutual coagulation of quartz and calcite, and not prevent the uptake of an anionic flocculant by the latter. Comparative stability tests on suspensions containing 0.8% CaCO<sub>3</sub> and 1.8 to 36 mg PVP in 100cc revealed no difference between the treated and untreated suspensions in 1½ hours and 24 hours. Neither did 0.5% quartz suspensions at low PVP concentrations; but at PVP concentrations higher than 2mg/100cc flocculation of silica to a very small sediment volume could be observed after 24 hours of standing. Similarly, the zeta-potentials of silica and calcite showed a gradual decrease with increasing PVP concentration. An inhomogenous adsorption of PVP on quartz was revealed by the

great variation in particle mobilities in the same suspension. Zeta-potential averages of quartz and calcite in PVP solutions are given in table 20 below.

Table 20

Effect of PVP on the zeta-potentials of  $\text{SiO}_2$  (0.5% solids) and  $\text{CaCO}_3$  (0.8% solids) at 25°C.

PVP (mg)	Zeta-potential(mV)	
	$\text{SiO}_2$	$\text{CaCO}_3$
0	-55	+20.8
1.8	-34	+20.5
3.6	-32	+20.1
10.8	-24	+19
21.6	-18	- *
34	- *	- *

\* the zeta-potential is negative but too low to be measured accurately.

In separating the PVP-treated  $\text{CaCO}_3 + \text{SiO}_2$  mixtures it was found that A80, a flocculant of high anionic character in the BTI-A series was more efficient than others, which were seemingly unable to compete with PVP for surface charge sites of  $\text{CaCO}_3$ . Artificial mixtures of  $\text{CaCO}_3 + \text{SiO}_2$  were prepared, conditioned with PVP and flocculated with A80. The results are given in table 21 overleaf.

Table 21

Separation of  $\text{SiO}_2$  -  $\text{CaCO}_3$   
(17mg PVP + 5ppm A80)

Test No.	Fraction	Initial Mixture		$\text{CaCO}_3$		$\text{SiO}_2$	
		$\text{CaCO}_3$ (g) <sup>3</sup>	$\text{SiO}_2$ (g) <sup>2</sup>	%R	%G	%R	%G
1	1			1.27	7.9	13.43	92.07
	2	0.76	1.95	58.97	80.23	13.16	19.76
	Residue			39.75	32.93	73.41	67.06
2	1			1.91	13.02	7.74	86.98
	2	2.22	2.02	0.80	6.81	6.68	93.19
	Residue			97.34	40.73	85.58	59.27
3	1			0.9	13.9	1.10	86.10
	2	3.3	1.73	0.79	72.9	0.5	27.10
	Residue			99.20	65.74	98.39	34.26
4	1			1.92	5.15	15.34	94.85
	2	1.3	3	2.38	6.82	14.08	93.18
	Residue			95.69	36.96	70.58	63.04

b.  $\text{PbS} + \text{SiO}_2$  : Since galena and quartz are both negatively charged, mutual coagulation of the two minerals does not usually take place. However, when galena is highly oxidised, although at low solids content (0.5%  $\text{PbS}$  + 0.5%  $\text{SiO}_2$ ) mutual coagulation did not take place, at higher solids content (5%  $\text{PbS}$  + 1%  $\text{SiO}_2$ )

a considerable quantity of quartz settled, together with galena. The main problem brought about when galena became oxidized was the enhancement of mutual flocculation of quartz in the presence of a polymer, rather than straightforward mutual coagulation.

All the flocculants flocculated galena, as was shown in table 2 , in fact the role of the flocculants was essentially to accelerate the rate of sedimentation of the slowly coagulating mineral.

It was noted with this system that A70 and A80, which formed big flocs when added to a pure galena suspension, were not the most selective. This was not due to activation of quartz by  $Pb^{2+}$  but rather because the fast formation of big flocs tends to enclose much of the quartz. The less effective flocculants such as A150 on the other hand formed smaller flocs which took longer to settle but reduced the degree of entrapment.

The results of flocculating PbS selectively from mixtures of PbS +  $SiO_2$  are given in table 22 overleaf. In some tests more than one extraction was performed as follows:

After the low shear conditioning stage the slurry was transferred to a 100ml glass stoppered cylinder and the first supernatant suspension extracted after 5 minutes' standing. The volume was then completed to the 100ml level by a 1 p.p.m solution of A 150, the cylinder inverted 6 times and the extraction process repeated after another 5 minutes.

Table 22  
Separation of SiO<sub>2</sub> + PbS mixtures (pH 5.4)

Test No.	Flocculant p.p.m.	Fraction	Initial mixture		PbS		SiO <sub>2</sub>	
			SiO <sub>2</sub> (g)	PbS (g)	%R	%G	%R	%G
1	A70	1	2.0	0.50	0	-	96	100
	1	Residue			100	98.5	4	1.5
2	A70	1	2.0	3.07	0	-	16.3	100
	2	Res.			100	65	83.7	35
3	A150	1	2.0	1.32	0	-	94	100
	1	Res.			100	92.5	6	7.5
4	A150	1	1.01	0.982	2.4	1.8	97	98.2
	1	Res.			97.6	98	3	2
5	A150	1	2	5	0.59	-	32.5	96.5
		2			0.65	-	13.5	90
		3			0.78	-	12.5	86
		4			0.48	-	9.5	94.5
	5	Res.	97.50	89.5	32.3	-		
6	A150	1	2	8.4	0	-	40.61	100
		2			0.298	-	10.45	95.5
		3			0.643	-	10.0	90
		4			0.880	-	6.90	82
	5	Res.	98.179	84	32.04	-		

Table 22 (continued)

Test No.	Flocculant p.p.m.	Fraction	Initial mixture		PbS		SiO <sub>2</sub>	
			SiO <sub>2</sub> (g)	PbS (g)	%R	%G	%R	%G
7	A150	1			0.34	-	67.17	99
		2			0.17	-	14.02	"
	5	3	10.	3.	0.59	-	10.32	"
		4			0.39	-	3.45	61
		Res.			98.51	85	5.04	-
8	A150	1			-	-	1.71	99.9
		2			-	-	0.66	"
	5	3	5.	15.	-	-	2.32	"
		4			-	-	2.96	"
		Res.			99.9	76	92.35	-
9	A150	1			-	-	62.81	99.9
		2			-	-	17.80	"
	5	3	5.	5.	-	-	8.80	"
		4			-	-	4.50	"
		Res.			99.9	94.5	6.15	-
10 <sup>#</sup>	A70	-	2	2	Complete mutual			
	2	-	(oxidized)		flocculation			
11 <sup>#</sup>	A150	-	5	10	Complete mutual			
	2	-	(oxidized)		flocculation			

\* Galena oxidized by leaving a wet powder to dry in contact with air.

c. PbS + CaCO<sub>3</sub> : As mentioned on p181 above, this mixture presents the problem of mutual coagulation. When a slurry of the two minerals is prepared, the pH of the medium becomes

alkaline owing to the presence of  $\text{CaCO}_3$ , and all the flocculants studied, flocculate the two minerals. Mutual coagulation could initially be prevented by increasing the pH to make the surface charge of  $\text{CaCO}_3$  negative or sodium tripolyphosphate can be used to stabilize the two minerals. These modifications of surface charges, however, do not favour the selective action of one flocculant. A cationic flocculant would flocculate the two components together and the adsorption of an anionic flocculant will either be totally prevented if the zeta-potential is made too highly negative, or both will take up the flocculant under conditions favouring adsorption. The competition between flocculants and stabilizing agents for both  $\text{CaCO}_3$  and PbS was illustrated on page 179.

"Dispex", which is believed to be the sodium salt of a synthetic polyacrylic acid, acts as a protective colloid for both  $\text{CaCO}_3$  and PbS. It is probably chemisorbed by these minerals. When solutions of  $\text{CaCl}_2$  and "Dispex" were mixed, a white precipitate (which is presumably Ca-polyacrylate) formed. It was experimentally found that 2 mg of this product per 1g of calcite produce a stable suspension which slowly flocculates in the course of 2-4 hours. Under these conditions the  $\zeta$ -potential of calcite is negative, whereas, it is positive in the absence of "Dispex". Similarly, galena is stabilized by 3mg "Dispex"/g PbS.

Addition of small quantities of  $\text{Na}_2\text{S}$  de-stabilizes the suspended galena selectively apparently by desorbing "Dispex". The quantity of  $\text{Na}_2\text{S}$  required is relatively small as illustrated in table 23 below, and the slowly coagulating PbS can be made to settle faster by the addition of a flocculant. In this case A100 appears to cause the best separation. Results of separation experiments for mixtures of  $\text{CaCO}_3$  + PbS are given in table 23 below.



Table 23

Separation of  $\text{CaCO}_3$  +  $\text{PbS}$ .  
 $[\text{Na}_2\text{S}]$  added: 0.17mM unless  
 otherwise indicated.

Test No.	Flocculant p.p.m.	Dispex (mg)	Fraction	Initial mixture		PbS		$\text{CaCO}_3$	
				PbS (g)	$\text{CaCO}_3$ (g)	%R	%G	%R	%G
1	A70 2	6	1	2.47	1.04	6.62	36	28.0	64
			2			3.38	51	64.5	49
			Residue			90	77	7.5	23
2	"	8	1	2.37	2.78	26.84	33.80	44.89	66.19
			2			2.66	25.78	6.54	74.21
			Res.			70.49	55.33	48.57	44.66
3	"	12	1	2.43	2.55	15	36.89	10.01	63.1
			2			14	40.87	11.71	59.12
			Res			71	51.17	78.26	48.82
4	"	12	1	2.55	2.46	20	20	82	80
			2			3	81	1	19
			Res.			77	83	17	17
5	A100 2	12	1	2.42	2.62	6	11	44	89
			2			2	12	14	88
			Res			92	67	42	33
6	A100 2	12	1	2.44	2.62	5	20	19	80
			2			16	41	20	59
			Res.			79	55	61	45

Table 23 (continued)

Test No.	Flocculant p.p.m.	Dispex (mg)	Fraction	Initial mixture		PbS		CaCO <sub>3</sub>	
				PbS (g)	CaCO <sub>3</sub> (g) <sup>3</sup>	%R	%G	%R	%G
7	A70 2	20	1	4.75	5.37	0.3	4.5	5.65	95.5
			2			9.4	29.4	20.2	70.6
			Residue			90.3	51.8	75.15	48.2
8	A70 2	20	-	4.7	5.3	No flocculation unless Na <sub>2</sub> S added.			
9	A70 3	20	1	5.	4.95	1.2	16	6.72	84
			2			4.1	23	14.05	77
			Res.			94.7	53.6	79.23	46.4
10	A70 2	20	-	2.5	2.5	All fractions stable			
11	A70 4	12	-	5.	5	Complete mutual flocculation.			
12	A70 4	20	1	5.	5	0.85	21	3.18	79
			2			2.47	27.5	6.21	72.5
			Res.			96.68	51.8	90.61	48.2
13	A70 4	24	1	5.	5.37	26.5	55	20.2	45
			2			4.5	28.6	10.45	71.4
			Res			69	48.5	69.35	51.5
14	A70 4	24	1	5.	5.06	2.4	17.2	11.3	82.8
			2			11.5	33.2	22.8	66.8
			Res			86.1	56.6	65.9	43.4

\* Notes on table, see overleaf.

\*Notes on table 23

Added  $\text{Na}_2\text{S}$  concentrations: 0.34mM in test 10 and 0.13mM in test 15.

In test 7,  $\text{Na}_2\text{S}$  added before the flocculant.

In test 8,  $\text{Na}_2\text{S}$  added after the flocculant.

In test 9,  $\text{Na}_2\text{S}$  and flocculant added simultaneously.

In test 11,  $\text{PbS}$  was oxidized by leaving the wet powder to dry in the open.

-----

d.  $\text{PbS} + \text{SiO}_2 + \text{CaCO}_3$ : A mixture containing these three minerals presents a number of problems which have to be overcome before an actual separation could be attempted. Firstly mutual coagulation of  $\text{PbS} + \text{CaCO}_3$  and  $\text{CaCO}_3 + \text{SiO}_2$  prevents the formation of an initially dispersed suspension which is essential for an actual separation. Secondly, the ionic strength of the medium is highly increased due to the solubilities of  $\text{CaCO}_3$  and  $\text{PbS}$  oxidation products.

By controlling the concentrations of potential-determining ions of  $\text{CaCO}_3$  only (for instance, by making the pH greater than 10 and smaller than 12) all the three minerals can be made negative. In such a state of the mixture, although the minerals are not stuck together, a C-flocculant cannot be used as it flocculates all, and only A130 or A150 can be used to flocculate  $\text{PbS} + \text{CaCO}_3$  leaving  $\text{SiO}_2$  unflocculated. As the stabilization of  $\text{PbS}$  by  $\text{S}^{2-}$  is not permanent under experimental conditions its use as a stabilizer is not favourable. In practice it is more convenient to attempt a flocculation of  $\text{PbS}$  first. The process of separating  $\text{PbS} + \text{CaCO}_3 + \text{SiO}_2$  thus has to be in 2 stages. First it should be possible to flocculate  $\text{PbS} + \text{CaCO}_3$  by A130 or A150 at pH 11, taking off  $\text{SiO}_2$  in the supernatant suspension and then the components of the residue should be separated by stabilizing  $\text{CaCO}_3$  as discussed on p 181.

An alternative method is to stabilize the whole mixture

by a protective colloid such as "Dispex" and then flocculate PbS alone leaving the other two components dispersed.

Attempts were made to test the feasibility of the two processes.

i. An initial flocculation of PbS + CaCO<sub>3</sub> alone leaving PbS suspended appeared to be essentially impracticable with mixtures containing as little as 0.5g of each component all in 100 cc of solution. All the components flocculated together leaving a clear supernatant liquid at pH 11 and with 1ppm Al<sub>2</sub>O<sub>3</sub>. With mixtures containing less solids under similar conditions complete mutual flocculation did not occur. Only one series of tests was partly analyzed by leaching the soluble components with conc HNO<sub>3</sub> and the results were as follows.

Table 24

Flocculation of PbS + CaCO<sub>3</sub> leaving SiO<sub>2</sub> suspended  
PbS 0.5g, CaCO<sub>3</sub> 0.3g, SiO<sub>2</sub> 0.5g  
pH 11, Al<sub>2</sub>O<sub>3</sub> = 1 p.p.m.

---

First supernatant suspension	0.092g SiO <sub>2</sub> 0.001g PbS + CaCO <sub>3</sub>
------------------------------	---

---

RESIDUE

Treated by "Dispex" and Na<sub>2</sub>S

- No further Al<sub>2</sub>O<sub>3</sub> added -

Supernatant suspension	0.280g SiO <sub>2</sub> 0.188g CaCO <sub>3</sub> + PbS
Residue	0.168g SiO <sub>2</sub> 0.570g CaCO <sub>3</sub> + PbS

With the alternative method of initially stabilizing  $\text{CaCO}_3 + \text{PbS}$ , the total solids content could be as high as 8%. In this case the presence of  $\text{SiO}_2$  did not introduce extra complications, and the separation process was as in the case of  $\text{PbS} + \text{CaCO}_3$  described on p 181.

Results of the few experiments carried out are given below

Table 25  
Separation of  $\text{PbS} + \text{CaCO}_3 + \text{SiO}_2$   
pH 5.2, "Dispex" 12mg, flocculant: 5p.p.m. A70

SUPERNATANT			SUSPENSION			FLOCCULATED			RESIDUE		
% Recoveries			% Grades			% Recoveries			% Grades		
$\text{SiO}_2$	PbS	$\text{CaCO}_3$	$\text{SiO}_2$	PbS	$\text{CaCO}_3$	$\text{SiO}_2$	PbS	$\text{CaCO}_3$	$\text{SiO}_2$	PbS	$\text{CaCO}_3$
Test I. 0.97g $\text{SiO}_2$ + 2.31g PbS + 1.02g $\text{CaCO}_3$											
33.5	2.4	66.5	30.6	5.2	64.4	66.5	<u>97.6</u>	35.6	19.9	<u>69.2</u>	10.8
Test II. 1.04g $\text{SiO}_2$ + 3.20g PbS + 1.10g $\text{CaCO}_3$											
29.5	1.47	24.5	50.	7.5	42.7	70.5	<u>98.53</u>	75.5	15.6	<u>68</u>	24.3
Test III. 2.73g $\text{SiO}_2$ + 3.45g PbS + 1.49g $\text{CaCO}_3$											
11.4	8.45	8.32	42.6	40.1	17	88.6	91.55	91.68	35.	45.5	19.6

9.2 The problem of entrapment

It was shown in table 22 that as the solids content of the medium increases the recovery of the mineral from the first supernatant suspension decreases, and the rest of it settles together with the flocculated mineral. This is mainly due to the entrapment of the mineral not intended to flocculate, being enmeshed in the open structure of the flocs which may be up to 80-90% void space (see figure 20). Entrapment is enhanced if i. the solids content of the medium is high, and ii. if the flocculation process is fast, as that brought about by a highly effective flocculant such as A70 or A80.

If a portion of a mutually flocculated slurry was placed in a further volume of suspending liquid (thus, in effect, reducing the % solids in the medium) and the mixture gently agitated it was possible to liberate the majority of the mineral not intended to flocculate.

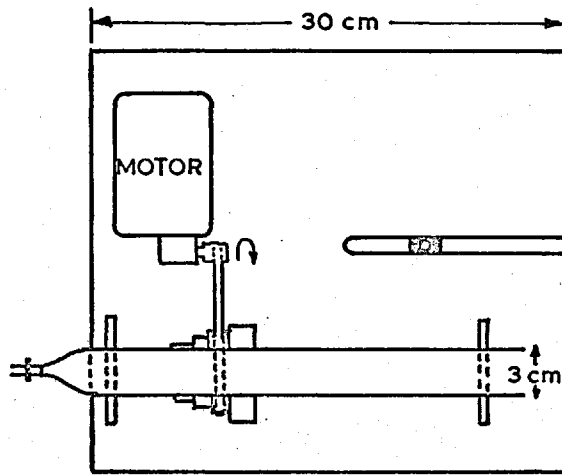
For instance, 5g SiO<sub>2</sub> + 5g PbS were completely flocculated with 2 p.p.m. of A70. When part of the flocculated slurry was taken out with a pipette and placed in 50ml of distilled water in a cylinder, part of the quartz was already freed and formed a white suspension before agitation. The cylinder was gently agitated a few times and the supernatant suspension separated from the residue after 3 minutes. The analysis of both fractions gave the following results.

	SiO <sub>2</sub>		PbS	
	%R	%G	%R	%G
PbS + SiO <sub>2</sub> = 2.72g				
Supernatant	85.2	99.9	0	-
Residue	14.8	-	100	94.5

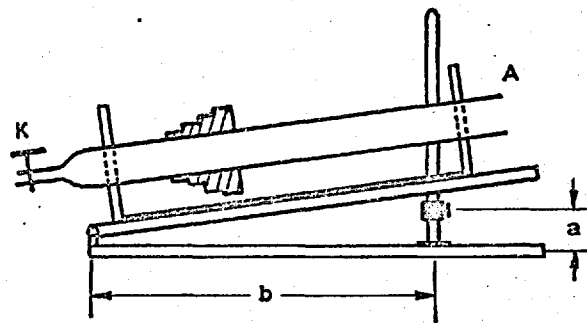
The fact that mutual flocculation takes place in the presence of a less effective flocculant if the solids content is too high was illustrated in table 22 , test 8. It is also seen in this table (see test 9 for instance) that up to 95% of the entrapped solid could be recovered by repeating the extraction process. These repeated extraction steps in effect are firstly reducing the total solids content of the medium and secondly, gentle agitation is partly opening the structure of the "host" flocs (without destroying them) to free the entrapped particles.

An alternative method of dealing with entrapment was found. Initially it was observed that during selective flocculation experiments, if the settling and growth of the flocs (after the initial high shear flocculant addition) is allowed to take place in a 16cm high cylinder the degree of entrapment was higher than if the cylinder was tilted. Furthermore, if the tilted cylinder was slowly revolved round its longitudinal axis separation was improved. This can be understood if the distance travelled by a growing floc before it touches the bottom of an upright or the wall of a tilted cylinder is considered. Slow revolution of the cylinder on the other hand assists the growth of the flocs and slowly "works" them to set free the entrapped particles.

The possibility of using this principle to separate mineral mixtures of rather high solid content was tested. For this purpose the apparatus shown diagrammatically in figure 33 was constructed. It consisted of a revolving glass cylinder, the speed of revolution and angle of inclination of which could be controlled. The mineral slurry was initially treated with a flocculant under high shear and transferred to the cylinder. Initially the cylinder was revolved for 5 minutes at an inclination of  $13^{\circ}$  ( $a/b = 5/22$  see figure 33 ) with the outlet K



Top view



Side view

Fig. 33 Diagrammatic representation of the "revolving cylinder" apparatus



closed, and then the inclination was increased to about  $35^\circ$  ( $a/b = 15/22$ ) to facilitate the sliding of the flocculated fraction, and K was opened. The cylinder was revolved at its slowest (i.e. 50 r.p.m.) throughout the experiments. It appeared that the process could be operated continuously by receiving the flocculated slurry from K, while collecting the suspended part from A. In this case the initial feed would have to be made to flow into the middle of the cylinder by a suitable arrangement. Batch tests were carried out and 3 fractions were obtained from each batch, namely, first a concentrate of the flocculated mineral, followed by a middle fraction and finally the suspension of the unflocculated mineral. The results of the experiments carried out are given in table 26 below.

Table 26  
Separation of  $PbS+SiO_2$  by the revolving cylinder apparatus  
(flocculant: 5p.p.m. Al50, pH=5)

	Fraction	$SiO_2$		PbS	
		%R	%G	%R	%G
Test I 5g $SiO_2$ +10g PbS	PbS concentrate	31.0	17	75.2	83
	$SiO_2$ "	60.4	79	8.1	21
	Middling	8.6	20.5	16.7	79.5
Test II 5g $SiO_2$ +15gPbS	PbS concentrate	6.6	-	75.5	92.5
	$SiO_2$ "	54.2	87.5	2.9	-
	Middling	39.2	38	21.6	62
Test III 10g $SiO_2$ +10g PbS	PbS concentrate	28.0	30.5	63.3	69.5
	$SiO_2$ "	39.3	88.5	5.21	-
	Middling	32.7	51	31.5	49

When it is considered that complete flocculation takes place at such high solids content under ordinary flocculation conditions, the results obtained with the revolving cylinder apparatus are significant. Probably the design of this apparatus particularly with regard to the receiving stage of the flocculated residue was not the best possible. Because although PbS and SiO<sub>2</sub> appeared fairly free from one another in the cylinder when K was opened, the escape of one component with the other could not be prevented. Nonetheless the principle is clearly feasible and machines for operating it continuously on a large scale could certainly be developed.

### 9.3 Effect of grinding minerals together on selectivity

In the actual application of a selective flocculation process the slimes to be treated would have normally passed a number of crushing and grinding circuits and thus the constituents would have had ample chance of rubbing against one another. To simulate such a process, PbS + SiO<sub>2</sub> and SiO<sub>2</sub> + CaCO<sub>3</sub> powders were mixed in different proportions and subjected to dry and wet grinding in a silica crucible, with a heavy glass rod. PbS + SiO<sub>2</sub> could visually be observed to separate when the process described on p 180 was applied irrespective of wet or dry grinding. However, before the flocculant addition stage, the mixture had to be dispersed by ultrasonics (apparently to shake the particles apart) otherwise, complete mutual flocculation took place. In view of the distinct separation of the mixtures to a black (PbS) residue and a white (SiO<sub>2</sub>) supernatant suspension, no analyses of the fractions were required.

As results could not be visually judged in the CaCO<sub>3</sub>+SiO<sub>2</sub> system, separated fractions were analyzed and a representative number of results are given in table 27 below.

Table 27

Separation of mutually ground calcite + quartz mixtures

Test No.	Initial mixture		Fraction	CaCO <sub>3</sub>		SiO <sub>2</sub>	
	CaCO <sub>3</sub> (g) <sup>3</sup>	SiO <sub>2</sub> (g) <sup>2</sup>		%R	%G	%R	%G
1 D	0.53	0.49	1 Res	8.1 91.9	62.5 51	5.5 94.5	37.5 49
2 W	0.53	0.54	1 Res	9.5 90.5	54.7 49	7.7 92.3	45.3 51
3 W	0.47	0.53	1 Res	14.1 85.9	54.5 46.5	12.6 87.4	45.5 53.5
4 D	0.58	0.53	1 2 Res	14.7 11.7 73.6	65 59.7 43.8	7.2 7.2 85.6	35 40.3 56.2
5 W	0.40	0.77	1 2 Res	28.6 10.0 61.4	54.4 46.6 28	12.3 6.0 81.7	45.6 53.4 72.
6 W	1.0	0.51	1 Res	6.6 93.4	86 66	2.2 97.8	14 34
7 D	0.37	0.5	1 Res	13.8 86.6	23.9 49.1	<u>32.8</u> 67.2	<u>76.1</u> 50.9
8 W	0.48	0.57	1 Res	10 90	32.4 49.7	<u>17.5</u> 82.5	67.6 52.1
9 W	0.51	0.53	1 Res	20.4 79.6	58 47.4	14.0 86	42 52.6
10 W	0.54	0.47	1 Res	14.6 85.4	50 54.3	16.9 83.5	50 45.7
11 W	0.50	0.50	1 Res	82.9 17.1	67.4 21.7	39.5 60.5	32.6 78.3

Notes on table

(see overleaf)

Notes on table 27

D: Dry ground, W: Wet ground

Tests 1-3 no ultrasonic agitation applied

" 4-11 mechanically + ultrasonically dispersed

" 1,3,4,7,9,11: Dispersion and flocculant addition made at pH 11.

Tests 2,5,6,8,10: Ground with 10cc of H<sub>2</sub>O of pH 12 and the rest of the operations made with H<sub>2</sub>O of pH 5.2

Tests 7 and 8: "Fransil" used instead of quartz.

" 9 and 10: Ground with 10cc of 10<sup>-2</sup>M Na<sub>2</sub>CO<sub>3</sub>

Test 11 : Ground with 1cc of solution containing 1.26 mg Na<sub>5</sub>P<sub>3</sub>O<sub>10</sub> + 5cc H<sub>2</sub>O of pH 11

Flocculant quantity in all the experiments: 1p.p.m. Al<sub>3</sub>O

It can be seen from this table that in most of the experiments (except test 11 which is discussed below) more than 80% of the two components were flocculated and if the mixture was treated by ultrasonics the total SiO<sub>2</sub> + CaCO<sub>3</sub> received as a supernatant suspension was higher than in the cases where only mechanical agitation was used for the initial dispersion of the solids. It appears that the main problem is associated with the sticking together of the minerals during grinding, so that they do not completely separate even with high intensity agitation. Support for this assumption is provided from the fact that if an extremely fine silica powder such as "Fransil" - which is a commercial silica powder with spherical particles of less than 1μ - is used the amount of silica which does not flocculate is much higher than in the cases where relatively coarser silica powder is used (see test 7). Where very fine silica is used, probably some particles are so fine that they are never rubbed against the coarser (and softer) CaCO<sub>3</sub> particles during grinding. The use of Na<sub>2</sub>CO<sub>3</sub> alone or together with

alkali does not prevent sticking of the two minerals completely although more  $\text{CaCO}_3$  appears to be rendered unresponsive to  $\text{Al}_3\text{O}$  (see test 9); probably the added  $\text{CO}_3^{2-}$  ions have blocked some of the  $\text{Ca}^{2+}$  sites where the  $-\text{COO}^-$  groups of the flocculant would have normally adsorbed. Such a competitive effect is more pronounced if a phosphate salt is used (see test 11). In this case more than 80% of the calcite remains unflocculated and 60% of the quartz collects in the residue. In this test no floc formation at all was observed. It was already mentioned on p 179 that a flocculated calcite suspension would be re-stabilized irreversibly by the addition of this phosphate salt.

In mineral processing practice  $\text{SiO}_2 + \text{CaCO}_3$  are usually separated as gangue from the valuable minerals and the separation of these two minerals is rarely required. However, in cement production the proportions of calcite and siliceous components in the feed have to be controlled. In such cases the slimes are initially separated from the coarser fractions by physical means and calcite is floated with fatty acids at pH 11 (2) 187. The reason appears to be that the  $\text{CaCO}_3 + \text{SiO}_2$  in the extremely fine form (slimes) are not easily separable. In view of the observed activation by ions and effects of mutual grinding of minerals on recoveries, it seems possible to state as a general conclusion; "the slimes of minerals can be separated or upgraded by selective flocculation if these minerals are ones which can be separated by froth flotation".

## 10. SUMMARY OF CONCLUSIONS

The selective flocculation of  $-37\mu$  powders of galena, calcite and quartz from aqueous suspensions by use of water-soluble polymeric flocculants has been investigated. The effects of simple inorganic ions and water-soluble polymeric flocculants on the individual mineral suspensions and on their mixtures as well as the effects of various ions on the mineral-flocculant interactions were studied. Turbidity, electrokinetic measurements and chemical analyses were the main techniques used. From the results and observations an attempt was made to establish the principles governing the selective flocculation of mineral slimes from mixtures.

The following information was obtained as a result of these investigations:

- i) Quartz forms stable suspensions in the range  $3 < \text{pH} < 11.5$  at solids concentration of 2-4%, whereas calcite forms suspensions stable only for a few hours at solid concentrations of less than 0.8% and galena suspensions in distilled water are practically unstable.
- ii) The cations  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  coagulate quartz more effectively at increasing pH and the order of adsorbability for these ions is  $\text{Ba}^{2+} > \text{Pb}^{2+} > \text{Ca}^{2+}$ .
- iii) The slow coagulation of quartz suspensions with the above ions seems to be by a charge neutralization mechanism, rather than by metal silicate formation and is accompanied by a reduction of (negative) zeta-potential to a value of about 30mV.
- iv) The coagulation of quartz suspensions by NaCl is accelerated by  $\text{OH}^-$  ions and quartz suspensions "aged" by immersion in water for two months require less NaCl to coagulate than those of freshly ground and dispersed quartz.

- v) The dissolution of dry-ground quartz takes place by the breaking of fragments of the disturbed surface layer into colloidal particles which in turn dissociate into silicic acid.
- vi) Calcite suspensions in distilled water have a pH value of about 8.2 in accordance with ionic equilibria calculations and under these conditions  $\text{CaCO}_3$  has a positive zeta-potential.
- vii)  $\text{H}^+$  and  $\text{OH}^-$  ions are potential-determining for  $\text{SiO}_2$ ,  $\text{CaCO}_3$  and  $\text{PbS}$ ; however, in the case of the latter two minerals,  $\text{H}^+$  and  $\text{OH}^-$  act by controlling the relative concentrations of the actual lattice ions in the suspending medium. (i.e.  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  for  $\text{CaCO}_3$  and  $\text{Pb}^{2+}$  and  $\text{S}^{2-}$  for  $\text{PbS}$ ).
- viii) The z.p.c. of quartz is at about pH 2 and a positive zeta-potential for this oxide has not been observed by increasing the acid concentration.
- ix) The z.p.c. of  $\text{CaCO}_3$  is at  $\text{pH } 9.5 \pm 0.5$  and by varying the pH or the concentrations of  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$  ions the zeta-potential can be varied at will.
- x) Although low positive zeta-potential values can be imparted to galena by use of  $\text{Pb}^{2+}$ , the mineral in water has a negative zeta-potential, the magnitude of which can be increased by  $\text{S}^{2-}$ ; however, on standing in contact with water containing dissolved air, its potential drops to smaller values.  $\text{S}^{2-}$  appears to be more strongly adsorbed on  $\text{PbS}$  than  $\text{Pb}^{2+}$  but the precise z.p.c. is at inaccessibly low concentrations.
- xi) The properties of a suspension containing more than one mineral are different from the properties of the suspensions of the individual minerals because of the mutual chemical effects of dissolved ions etc.
- xii) Flocculant adsorption is a prerequisite for flocculation; however, not every adsorption leads to flocculation.

- xiii) Flocculant addition has to be made under controlled conditions of shear, and providing the flocculant is evenly distributed in the pulp, whether the flocculant is added as a dilute solution or not, is then immaterial.
- xiv) The flocculation of PbS and  $\text{CaCO}_3$  by anionic flocculants and of quartz by cationic flocculants is accompanied by a charge neutralization process and with an over-dose of flocculant the charges of  $\text{SiO}_2$  and  $\text{CaCO}_3$  can be reversed, while that of PbS is made more negative.
- xv) Quartz, which cannot normally be flocculated by anionic flocculants, can be "activated" by metal cations, and there is a narrow range of pH for each metal ion concentration at which a particular flocculant operates.
- xvi) In the  $\text{SiO}_2 + \text{Ca}^{2+} + \text{flocculant}$  system, as the anionic character of the flocculant increases the pH at which flocculation takes place becomes smaller. Non-ionic PAM (e.g. P250) responds to activation as well as the most anionic flocculants (e.g. A70 and A80) in this system, and A100 appears to be more akin to a non-ionic flocculant than an anionic one.
- xvii) Selective adsorption of flocculants on minerals is essential for selective flocculation.
- xviii) Even in an "over-dosed" system the mineral surface is not completely covered by the flocculant, and there are sites not occupied by the polymer chains.
- xix) The minerals in a mixture must initially be dispersed so that an efficient selective flocculation can be carried out and at least one component must inherently form a stable suspension or be made to form one.
- xx) One or more minerals in a mixture can be made to form a stable suspension by the use of a modifying agent such as



potential-determining ions, their combinations or a protective colloid.

xxi) The selective adsorption or desorption of flocculants can be effected to fulfil the conditions set out in xix and xx above by the use of "surface site competitors".

xxii) As the solids content of a suspension increases the recovery of the mineral not intended to flocculate decreases due to "entrapment".

xxiii) Entrapment also occurs if one component is flocculated with a highly effective flocculant which leads to the formation of big porous flocs.

xxiv) This undesirable effect can be overcome by repetitive removal of the supernatant suspension, the use of a "revolving cylinder apparatus" described in the text, or working at low solids content.

xxv) Unlike "bulk flocculation"; in selective flocculation the formation of very fast settling, big flocs is not essential. The main requirement is that the flocs should be just big enough to settle relatively faster than the suspended particles.

xxvi) Although it is not essential to selectively flocculate the mineral with the higher specific gravity from a mixture the consideration given in xxv above may make such an order of flocculation more practicable.

xxvii) Binary or ternary mixtures of PbS,  $\text{CaCO}_3$  and  $\text{SiO}_2$  can be separated with recoveries and grades in favourable cases up to 99%.

xxviii) Mutual grinding of minerals may in some cases change the flocculation properties of a mixture; however, the conclusions derived above remain operative.

xxix) From the surface-chemical point of view, there appears to be a close parallel between the principles operative in froth flotation and selective flocculation, and it can be concluded that if given minerals which can be separated by flotation their slimes can be separated by **selective flocculation**.

References

1. Taggart, A.F., "Handbook of Mineral Dressing" J.Wiley, London. (1960)
2. Gaudin, A.M., "Flotation" Mc Graw-Hill, London, (1957)
3. Klassen, V.I. and Mokrousov, V.A., "An Introduction to the Theory of Flotation" (translated by J. Leja and G.W. Poling), Butterworths, London, (1963)
4. Gaudin, A.M., Schuhmann, R. and Schlechten, A.W., J.Phys. Chem., 46, 902, (1942)
5. Tomlinson, H.S. and Fleming, M.G., "VI. International Min. Processing Congr. (Cannes) 1965"
6. Del Guidice, G.R.M., Trans. A.I.M.E., 112, 398, (1934)
7. Ince, C.R., Ibid., 87, 261, (1930)
8. Sun, C.R., Ibid., 153, 476, (1943)
9. Fuerstenau, D.W., Gaudin, A.M. and Miaw, H.L., Ibid., 211, 792, (1958)
10. Iwasaki, I., et. al., Ibid., 223, 37, (1962)
11. Jirgenson, B., and Straumanis, M.E., "A Short Textbook of Colloid Chemistry", Pergamon Press, London, (1954)
12. Kitchener, J.A., J. Oil and Color Chemists' Assoc., 37, 355, (1954).
13. Alexander, A.E. and Johnson, P., "Colloid Science" Clarendon Press, Oxford, (1950)
14. Sennett, P. and Olivier, J.P., "Chemistry and Physics of Interfaces" Am. Chem. Soc. Publication Washington D.C. (1965) p.75.
15. Parsons, R., "The Structure of the Electric Double Layer and its Influence on the Rates of Electrode Reactions", Adv. in Electrochem and Electrochem. Eng., Vol. 1. Interscience, New York (1961)
16. Kruyt, H.R., (editor) "Colloid Science, Vol. 1" Elsevier, London, (1952)

17. La Mer, V.K., J. Colloid. Sci., 19, 291, (1964)
18. Parks, G.A., and de Bruyn, P.L., J. Phys. Chem., 66, 967, (1962)
19. Parks, G.A., Chem. Revs., 65, 177, (1965)
20. Benson, A.C. and Thomas, C.M., "Effluent and Water Treatment Convention," London, (1965)
21. Matijevic, E., and Kolak, N., J. Colloid. Intf. Sci., 24, 441, (1967)
22. Van Arsdale, G.D., "Hydrometallurgy of Base Metals", Mc Graw-Hill, New York, (1953)
23. Bachler, F.R., U.S. Patent, 1,170,868 (1916)
24. Packham, R.F., Proc. Soc. Water Treatment and Examination, 12, 15, (1963)
25. Audsley, A., Miner. Proc. Inform. Note 5., (Warren Spring Laboratory Stevenage) (1965)
26. Minz, D.M. (Editor), Intern. Water Supply Congress, (Stockholm 1964), General Report No. 5.
27. Purchas, D.B., Process Biochem., 3, 17, (1968)
28. Stock, D.I., Nature, 170, 423, (1952)
29. Smith, H.M., and Puddington, I.E., Canad. J. Chem., 38, 1911, (1960)
30. Farnand, J.R., and Puddington, I.E., Canad. Inst. Met. Bulletin., 62 (683), 267, (1969)
31. Siranni, A.F., Capes, C.E., and Puddington, I.E., Canad. J. Chem. Eng., 47, 166, (1969)
32. Bartnik J.A. and Giermak, C.F., Canad. Inst. Met. Bull., 62, 263, (1969)
- 33 a) Oliver, R.H., Trans. A.I.M.E., 220, 434, (1911)  
b) " " , Eng. Min. J., June (1963) p.1.

34. Adorjan, L.A., Coal Preparation, 4(4), 125; (1968)  
and " " " " , 4(5), 171, (1968)
35. Cartwright, Z., U.S. Patent, 980, 143 (1910)
36. Schwerin, B., U.S. Patent, 1,029,579 (1912)
37. Feldheimer, W., U.S. Patent, 1,324,958 (1919)
38. Coddington, M.K., U.S. Patent, 1,402,740 (1922)
39. Gaudin, A.M., and Malozemof, P., J. Phys. Chem., 37,  
597, (1933)
40. Rowland, B.W., U.S. Patent, 2,981,630 (1961)
41. Haseman, J.F., U.S. Patent, 2,660,303 (1953)
42. Beavers, A.H. and Marshall, C.E., Proc. Soil.Soc., Amer.,  
15, 142, (1951)
43. Huber, J.M. Corporation, British Patent, 1, 115, 694, (1966)
44. Iwasaki, I., Carlson, W.J. Jr., and Parmerter, S.M.,  
Paper presented at the annual meeting of A.I.M.M. and  
Petroleum Engrs., New York (1968)
45. Frommer, S.W., Mining Eng., 16, 67, (1964)
46. " " and Colombo, A.F., U.S. Patent, 3,292,780 (1966)
47. Frommer, D.W., VIII. Int Min. Process. Congr., Leningrad  
(1968) Preprint D-9
48. Sher, P., Miloshevich, M., and Bulatovich, P., Ibid.,  
preprint D-16.
49. Usoni, L., et. al. Ibid, preprint D-13.
50. Collins, D.J., Dissertation, R.S.M. Imperial College  
(June 1963)
51. Ball, B., Dissertation, Ibid., (1966)
52. Griot, D., and Kitchener, J.A., Trans. Faraday Soc.,  
61, 1026, (1965)
53. Clark, J.P. R.S.M. Dept. Min. Tech. Imperial College (London)  
(1966) unpublished.

54. Kitchener, J.A., Filtrn., and Sepern., 6, 553, (1969)  
b. Contribution to the discussion of this paper.
55. Freundlich, H., and Cohn, H., Koll. Z., 28 (1926)
56. Kuz'kin, S.F. and Nebera, V.P., "Synthetic Flocculants in Dewatering Processes" (Moscow 1963). Trans. Nat. Lending Library, Boston, England, (1966)
57. Edwards, B.C., Ph.D. Thesis. Univ. London, (1967)
58. La Mer, V.K. and Smellie, R., J. Coll. Sci. 13, 589, (1958)
59. Slater, R.W. and Kitchener, J.A., Faraday Soc., Disc., 42, 267, (1966)
60. Perry, M.G. and Baird, R.D., Filtrn. and Separation, 5, 546, (1968)
61. Baskerville, R.C., and Gale, R.S., J. Inst. Water Pollution Control, 67, 233, (1968)
62. Gallenkamp Pamphlet, "Sedimentation Balance PC-650"
63. Edelman, L.I. and Sominskii, D.S., Koll. Zhur. 21, 126, (1959)
64. Michaels, A.S. and Bolger, C.J., I and EC Fundamentals., 1, 24, (1962)
65. Conmeta, C. and Van Rutten, F., J. Colloid, Intf. Sci., 25, 322 (1968)
66. Helmholtz, H., Wied. Ann., 1, 537, (1879)
67. Stern, O., Z. Electrochem., 30, 508, (1924)
68. Grahame, D.C., Chem. Revs. 41, 441 (1947)
69. Shaw, D.J., "Introduction to Colloid and Surface Chemistry" (Butterworths, London, 1966)
70. Davies, J.T., and Rideal, E., "Interfacial Phenomena", 2nd. ed., (Academic Press, London, 1967)
71. Overbeek, J.Th.G., Thesis, (Utrecht 1941)
72. Booth, F., Proc. Royal Soc., (London) A.203, 514, (1950)

73. Lykloema, J. and Overbeek J.Th.G., J. Colloid. Sci., 16, 501 and 595 (1961)
74. Shenkel, J.H., Thesis, Univ. of London (1968)
75. Hull, M., Thesis, Univ. of London., To be published
76. Saleeb. F.Z., Thesis, Univ. of London (1963)
77. Bangham, A.D., et. al., Nature. 182, 642, (1958)
78. Rank Bros., "Cylindrical Micro Electrophoresis Apparatus, Pamphlet".
79. Glasstone, S. and Lewis, D., "Elements of Physical Chemistry" Van-Nostrand Lcndon,(1964)
80. Shaw, D.J., "Electrophoresis" (Academic Press, London, 1969)
81. Moyer, L.S. and Abramson, H.A., J. Gen. Physiol.17,727, (1935-36)
82. Laskowski, J. and Kitchener, J.A., J. Colloid, Intf. Sci., 29, 670, (1969)
83. Rastogi, R.P., and Misra, B., Faraday Soc. Transactions, 63, 584, and 2926 (1967)
84. Crummett, W.B., and Hummel, R.A., J. Am. Water Works Assocn., 55, 209, (1963)
85. Uts, V.N., and Reiter, E.N., Tr. Khim. Met. Inst. Akad. Nauk. Kaz. U.S.S.R. 1, 125,(1963)
86. Wiberley, S.E., Sprague, J.W., and Campbell, J.E., Anal. Chem., 29, 210, (1957)
87. American Cynamid Co. "Polyacrylamide Pamphlet" (1955)
88. Nebera, V.P., C.A. 68, 53674h (1968)
89. Kuzkin, S.F., Nebera, W.P., and Zolin, S.N., VII. Int Min. Process. Congr. New York, (1964) prt 7, p.347
90. Slater, R.W., Thesis, Univ. of London (1967)
91. Griot, O., Thesis, Univ. of London (1964)

92. Gregor, H.P., et. al., J. Phys. Chem., 59, 990, (1955)
93. Zubay, G., Ibid. 61, 377, (1957)
94. Baykut, F., "Chromatography", Kimya Ve Sanayi Yayinlari, Istanbul (1965) in Turkish.
95. Gortikov, B.M., and Ostopinko, B.G., Koll. Zhur., (U.S.S.R.) 1, 303, (1935)
96. Laskowski, J., "Physical Chemistry in Mineral Processing Technology (in Polish)". (Wydawnactwo "Slask" katowice, 1969)
97. Gill, A.E., B.T.I. Chemicals Bradford. Personal communication.
98. Ghigi, G., Trans. I.M.M. 77(c), 212, (1968)
99. Gibb, J.G., Ritchie, P.D. and Sharpe, J.W., J. Appli. Chem., 3, 213, (1953)
100. Talbot, J.H., Bradley, A.A. and Kempis, E.L., Brit. J. Appl. Phys. 14, 399, (1963)
101. Paterson, M.S. and Wheatly, K.H., S.M.R.E. Res. Rep. No.24, (1955)
102. Bergman, I., J. Appl. Chem., 13 319, (1963)
103. Gordon, R.L., and Harris, G.W., Nature, 175, 1135, (1955)
104. Wadams, J.A., Research, 11, 370, (1958)
105. Lidström, L., Acta Polytechnica Scand., 75, 1, (1968)
106. Bergman, I., and Paterson, S., J. Applied. Chem., 11, 369, (1961)
107. Bergman, I., Ibid., 12, 336, (1962)
108. Holt, P.F., and King, D.T., J. Chem. Soc. , 773, (1955)
109. Bergman, I and Casswell, C., J. Appl. Phys., 13, 621, (1962)
110. Okkerse, C., Thesis, Technical Univ., Delft, (1961)
111. Van Lier, J.A., de Bruyn, P.L. and Overbeek, J.Th. G., J. Phys. Chem., 64, 1675 (1960)



112. Greenberg, S.A. and Price, E.W., Ibid. 61, 1539 (1957)
113. Gaudin, A.M., Spedden, H.R. and Laxen, P.A., Min. Eng., 4, 693, (1952)
114. French, C.M. and Howard, J.P., Chem. and Industry., p. 572, (1956)
115. Cooke, S.R.B., Trans., A.I.M.E. 184, 299 (1949)
116. Malati, M.A., J Coll. Intf. Sci., 22, 306, (1966)
117. " " , and Estefan, S.F., J. Appl. Chem. 17, 209, (1967)
118. Fuerstenau, D.W., Thesis, M.I.T. (1953)
119. Fahrenwald, A.E. and Newton, J. Eng. Min. I., 138, 23, (1937)
120. Roller, P.S. and Erwin, G. Jr., J. Am. Chem. Soc., 62, 461, (1940)
121. Greenberg, S.A., J. Phys. Chem., 60, 325 (1956)
122. Ruhrwein, R.A. and Ward, D.W., Soil Sci., 73, 485, (1952)
123. Ohyama, T., Shimoizaka, J. and Usui, S., Bull. Chem Soc. Japan, 34, 790, (1961)
124. Matijevic, E., Kratochvil, S. and Stryker, L.J.; Disc. Faraday Soc. 42, 187, (1966)
125. Watillon, A. and Petit, A.M.J., Disc. Faraday Soc., 42, 143, (1966)
126. Daluja, K.L. and Srivastava, S.M., Indian J. Chem., 5, 221, (1967)
127. Ottewill, R.H. and Rastogi, M.C., Trans Faraday Soc., 56, 866, (1960)
128. Watillon, A. and Gerard, Ph., Proc. IV. Int. Congr. Surf. Active Substances, Brussels (1964) 2B 1261
129. Bolt G.H., J. Phys. Chem., 61, 1166, (1957)
130. Honig, E.P. and Hengst, J.H.TH., J. Coll., Intf. Sci., 29 510 (1969)

131. Okamoto, G., Okura, T., and Goto, K., Geochimica et Cosmochimica Acta, 12, 123 (1957)
132. Omelga, C.R. and Stumm, W., J. Coll. Intf. Sci., 23, 437, (1967)
133. Packham, R.F., J. Coll. Sci., 20, 81, (1965)
134. Li, H.C. and de Bruyn, P.L., Surf. Sci. 5, 203, (1966)
135. Hazel, J.F., In "Principles and Application of Water Chemistry" Editors: Faust, S.D. and Hunter, J.V. John Wiley, (1967)p.301
136. Iler, R.K., "The Colloid Chemistry of Silica and Silicates", Cornell Univ. Press, New York, (1955)
137. Tucker, A., The Guardian, 14th Nov., (1968)
138. Holt, P.F., Personal Communication.
139. Strickland, J.D.H., J. Am. Chem. Soc., 74 862, (1953)
140. Alexander, G.B., Ibid., 75, 5655, (1953)
141. Aoki, F., J.Chem. Soc. Japan, Pure Chem. Sect., 72, 17, (1951)
142. Lange, A.N., "Handbook of Chemistry" Mc. Graw-Hill, London (1967)
143. Stöber, W., Fink, A. and John, E., J. Coll. Intf. Sci. 26, 62, (1968)
144. Heller, L. and Taylor, H.F.W., "Crystallographic Data for the Calcium Silicates" H.M.S.O., London (1956)
145. Krüger, G. and Thilo, E., Z. Anorg. u. Alg. Chemie. 308, 242, (1961)
146. Latimer, W.M., "Oxidation Potentials" 2. ed. Prentice Hall, Englewood Cliffs. (1959)
147. Tsukioka, K. Repts. Res. Lab. Ashai Glass Co., 5, 163, (1955)
148. Long, R.P. and Ross, S., J. Coll. Intf. Sci., 26, 434, (1968)
149. Turner, R.C., Soil Sci., 86, 32, (1958)
150. Garrels, M.R. and Christ, C.L., "Solutions, Minerals and Equilibria". Harper and Row, London, (1965)

151. Borisov, V.M., Chem. Ind. Moscow (1955) in Classen and Mokrausov p.297
152. Reed, L.S., Müller, W.H. and Fredrickson, R.E., Eng. Min. J. 167, 87, (1966)
153. Somasundaran, P. and Agar, G.E., J. Coll. Intf. Sci., 24, 433, (1967)
154. Douglas, H.W. and Walker, R.A., Trans. Faraday Soc., 46, 559, (1950)
155. Katsin, L.V. and Kogan, D.I., Nauch. Trud. (Irgiredmet) Vyp. 13, 216 (1965)
156. Somasundaran, P., J. Coll. Intf. Sci., 27, 659, (1968)
157. Rootare, H.M., Deitz, A.R. and Carpenter, R.G., J. Coll. Sci., 19, 87, (1964)
158. Douglas, H.W. and Adair, D., Trans. Faraday Soc., 50, 1251, (1954)
159. Parks, G.A., In "Adv. In Chem. Ser. 67". Ed., R.F. Gould, Am. Chem. Soc. Washington (1967) p.121
160. Gaudin, A.M. and Sun, S.C., Min Tech. New York, (1946)
161. Freyberger, W.L. and de Bruyn, P.L., J. Phys. Chem., 61, 586, (1957)
162. Reuter, B. and Stein, R., Z. Electrochem., 61, 440, (1957)
163. Tolun, R., Personal communication.
164. Blackader, D.A., Ratcliff, G.A. and Sutherland, D.N., IV. Int. Congr. Surf. Activit. Substances, Brussels (1964) C/V.4
165. Fischer, E.W., Koll. Zeit. 160, 120, (1958)
166. Audsley, A. and Fursey, A., Nature, 208, 753, (1958)
167. a) Ries, E.H.Jr. and Meyers, B.L., Science, 160, 1449, (1968)  
b) " " Ibid., 162, 379, (1968)
168. Linke, W.F. and Booth, D.R. Trans. A.I.M.E., 217, 364, (1960)

169. Spetch, D., Presented to the Midlands section of the Coal Preprn. Soc., (1965)
170. Jones, G.D., Friedrich, P.F. and MacWilliams, D.C., Presented at the Am. Inst. Chem. Eng. Spring Meeting, New Orleans (1961)
171. Whistler, R.L., "Industrial Gums", Academic Press, New York (1959)
172. Perkel, R. and Ullman, P., J. Polymer Sci., 54, 127, (1961)
173. Drozskowski, A. and Lambourne, R., Presented at the Informal Symposium on the Applications of Surface Chem. to Technology, Brunel University, 16 May, (1969)
174. Michaels, A.S. and Morelos, O., Ind. and Eng. Chem., 47, 9, (1955)
175. Kohl, R.A., and Taylor, S.A., Soil Sci. 91, 223, (1951)
176. La Mer, V.K. and Smellie, R.H., J. Coll. Sci., 11, 710, (1956)
177. Crawford, J. and Smith, B.R., J. Coll. Intf. Sci., 21 623, (1966)
178. Nestler, C.H., Ibid., 26, 10, (1968)
179. Slater, R.W., Clark, J.P., and Kitchener, J.A., VIII. Int. Min. Process Congr. Leningrad. (1968) preprint C-5
180. Matijevic, E. and Kolak, N., J. Coll. Intf. Sci. 24, 441, (1967)
181. Steiner, H.J., Radex-Rdsch. 6, 733, (1965)
182. Sutherland, K.L. and Wark, I.W., "Principles of Flotation", Aust. Inst. Min. Met. Melbourne (1955)
183. La Mer, V.K. and Healy, T.W., Rev. Pure. Appl. Chem., 13, 112, (1963)
184. Fleer, G.J. and Lyklema, J., Proc. Int. Congress Surf. active Substances. Barcelona (1968) Paper B/o (132)
185. Healy, T.W., J. Coll. Sci. 16, 609, (1961)

186. Peterson, C. and Kwei, T.K., J. Phys. Chem., 65, 1330, (1961)
187. Lee, D., U.S. Bur. Mines Investigation Rep. No. 2744 (1926)
188. Glovers Chemical Ltd., Chem. In Britain 5, adv. 17, (1969)
189. Peck, A.S., U.S. Bur. of Mines Rep. 62202 (1963)
190. Fuerstenau, M.C. et al.
  - a) Trans. A.I.M.E., 226, 443, (1963)
  - b) Ibid., 238, 321, (1967)
191. Cruchfield, M.M. and Rani, M.M., J. Am. Chem. Soc., 87, 2815, (1965)
192. Ahmed, S.M. and Maksimov, D., Min. Res. Rept. R196 . Can., Dept. Energy, Min and Resources Mines Branch. Ottawa (1968)
193. Erkut, H., Revue Fac. d'Sci. l'Univ. Istanbul, 30 (C), 157, (1966)
194. Abramov, A.A., Obogasch., Rud, Leningrad, 5, 21, (1960)
195. Jasjukevic, S.M. et. al. Freiberger Forschungshefte, (A) 437, 11, (1968)
196. Grijo, R.A. and Berni, R.P., Soap and Chem. Spec. 44, 49, (1968)
197. Vogel, A.I., "A Textbook of Quantitative Inorganic Analysis" Longmans, London (1966)
198. Sakaguchi, K. and Nagase, K., Bull. Chem. Soc. Japan, 39, 88, (1966)
199. Kragh, A.M. and Langston, W.B., J. Coll. Sci., 17, 101, (1962)
200. Lenher, V., J. Am. Chem Soc., 43, 391, (1921)
201. Hitchen, C.S., Min. Met. Bull., 44, 255, (1936)
202. Paterson, M.S. and Wheatley, K.H., Safety In Mines Res. Ist. Rep. No. 124, (1955)
203. Krauskopf, K.B., Geochim. Cosmochim. Acta, 10, 1, (1956)

204. White, D.E., Bull. Geol. Soc. Amer., 68, 1659, (1957)
205. Siever, R., Amer. Mineralogist, 42, 821, (1957)
206. Smith, F.G., Can. Mineralogist, 6, 210, (1958)
207. Mosebach, R., J. Geol., 65, 343, (1957)
208. Fournier, R.D., Bull. Geol. Soc. Amer., 71, 1867, (1960)
209. Morey, G.W. et. al., Geochim. Cosmochim. Acta., 26, 1029, (1963)
210. StÜber, W., in "Equilibrium Concepts in Natural Water Systems"  
Ed. R.F. Gould, Advances in Chem. Series No. 67  
Am. Chem. Soc., Washington D.C. (1967).

Appendix A

Critical ion concentrations for the formation of silicates  
(Total dissolved silica 10 mg/l.) cf. figures 8,9,10.

1	2	3	4	5	6	7
pH	lg [H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup> ]	lg [Ca <sup>2+</sup> ]	lg [H <sub>2</sub> SiO <sub>4</sub> <sup>2-</sup> ]	lg [Ca <sup>2+</sup> ]	lg [Ba <sup>2+</sup> ]	lg [Pb <sup>2+</sup> ]
7	-5.98	+1.84	-8.78	+1.18	+4.28	- 6.72
8	-4.98	-0.160	-7.78	+0.18	+3.28	- 7.72
8.24	-4.78	-0.56	-	-	-	-
8.59	-4.47	-1.06	-	-	-	-
8.83	-4.30	-1.51	-	-	-	-
9.2	-4.08	-1.96	-6.75	-0.82	+2.26	- 8.74
9.37	-4.00	-2.12	-	-	-	-
9.56	-3.93	-2.29	-	-	-	-
9.80	-3.87	-2.38	-	-	-	-
10.15	-3.82	-2.47	-5.75	-1.82	+1.26	- 9.74
11.04	-3.82	-2.47	-4.78	-2.82	+0.28	-10.72
11.39	-3.87	-2.38	-4.47	-3.12	-0.02	-11.02
11.63	-3.93	-2.29	-4.30	-3.30	-0.20	-11.20
11.82	-4.00	-2.120	-4.17	-3.42	-0.32	-11.23
12.00	-4.08	-1.96	-4.08	-3.52	-0.42	-11.42
12.17	-4.17	-1.86	-4.00	-3.60	-0.50	-11.50
12.36	-4.30	-1.51	-3.93	-3.66	-0.56	-11.56
12.60	-4.47	-1.06	-3.87	-3.73	-0.63	-11.63
12.95	-4.78	-0.56	-3.82	-3.77	-0.67	-11.67

Appendix B

Critical ion concentrations for the formation of silicates  
(Total dissolved silica 100mg/l.) cf. figures 8,9,10.

1	2	3	4	5	6	7
pH	lg [H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup> ]	lg [Ca <sup>2+</sup> ]	lg [H <sub>2</sub> SiO <sub>4</sub> <sup>2-</sup> ]	lg [Ca <sup>2+</sup> ]	lg [Ba <sup>2+</sup> ]	lg [Pb <sup>2+</sup> ]
6	-5.98	+1.84	-	-	-	-
7	-4.98	-0.16	-7.78	+0.18	+3.28	-7.72
8	-3.98	-2.216	-6.78	-0.82	+2.28	-8.72
8.24	-3.78	-2.56	-	-	-	-
8.59	-3.47	-3.16	--	-	-	-
8.83	-3.30	-3.51	-	-	-	-
9.02	-3.17	-3.76	-5.78	-1.82	+1.28	-9.72
9.37	-3.00	-4.12	-	-	-	-
9.56	-2.93	-4.14	-	-	-	-
9.80	-2.87	-4.38	-	-	-	-
10.15	-2.82	-4.47	-4.76	-2.81	+0.27	-10.73
11.04	-2.82	-4.47	-3.78	-3.82	-0.72	-11.72
11.39	-2.87	-4.38	-3.47	-4.12	-1.02	-12.02
11.63	-2.93	-4.14	-3.30	-4.30	-1.12	-12.20
11.82	-3.00	-4.12	-3.17	-4.42	-1.32	-12.23
12.	-3.08	-3.96	-3.08	-4.52	-1.42	-12.42
12.17	-3.17	-3.76	-3.00	-4.60	-1.50	-12.50
12.36	-3.30	-3.51	-2.93	-4.66	-1.56	-12.56
12.60	-3.47	-3.16	-2.87	-4.73	-1.63	-12.63
12.95	-3.78	-2.56	-2.82	-4.77	-1.67	-12.67



Appendix C

Stabilities of precipitated PbS suspensions.

(+) : Coagulated

(-) : Stable

Added reagent (mol/l)		Resulting PbS (mol/l)	Excess reagent (mol/l)		Stability of Precipitate
Na <sub>2</sub> S	Pb(NO <sub>3</sub> ) <sub>2</sub>		Na <sub>2</sub> S	Pb(NO <sub>3</sub> ) <sub>2</sub>	
1.64x10 <sup>-3</sup>	1.64x10 <sup>-3</sup>	1.64x10 <sup>-3</sup>	Nil.	Nil.	+
1.34x "	1.67x "	1.34x "	"	3.37x10 <sup>-4</sup>	+
1.01x "	"	1.01x "	"	6.74x "	+
6.74x10 <sup>-4</sup>	"	6.74x10 <sup>-4</sup>	"	1.01x10 <sup>-3</sup>	+
3.37x "	1.68x10 <sup>-4</sup>	3.37x "	"	1.34x "	+
2.69x "	"	2.69x "	"	1.41x "	+
2.0 x "	"	2.0 x "	"	1.48x "	+
1.34x "	1.70x10 <sup>-3</sup>	1.34x "	"	1.57x "	+
6.75x10 <sup>-5</sup>	1.71x "	6.7 x10 <sup>-5</sup>	"	1.65x "	-
1.68x10 <sup>-4</sup>	1.68x10 <sup>-4</sup>	1.68x10 <sup>-4</sup>	"	Nil	+
1.34x "	"	1.34x "	"	3.37x10 <sup>-5</sup>	+
1.01x "	"	1.01x "	"	6.74x "	+
6.75x10 <sup>-5</sup>	"	6.76x10 <sup>-5</sup>	"	1.01x10 <sup>-4</sup>	-
3.37x "	"	3.37x "	"	1.34x "	-
2.69x "	"	2.69x "	"	1.41x "	-
2.0x ""	"	2.0 x "	"	1.48x	-
1.34x "	1.70x10 <sup>-4</sup>	1.34x "	"	1.57x "	-
6.7 x10 <sup>-6</sup>	1.71x10 <sup>-4</sup>	6.7 x10 <sup>-6</sup>	"	1.65x "	-

Continued overpage

Appendix C (continued)

Added reagent (mol/l)		Resulting PbS(mol/l)	Excess reagent (mol/l)		Stability of Precipitate
Na <sub>2</sub> S	Pb(NO <sub>3</sub> ) <sub>2</sub>		Na <sub>2</sub> S	Pb(NO <sub>3</sub> ) <sub>2</sub>	
1.68x10 <sup>-5</sup>	1.68x10 <sup>-5</sup>	1.68x10 <sup>-5</sup>	Nil	Nil	-
1.34x "	"	1.34x "	"	3.37x10 <sup>-6</sup>	-
1.01x "	"	1.01x "	"	6.74x "	-
6.74x10 <sup>-6</sup>	"	6.74x10 <sup>-6</sup>	"	1.01x10 <sup>-5</sup>	-
3.37x "	"	3.37x "	"	1.34x "	-
1.68x10 <sup>-3</sup>	1.68x10 <sup>-3</sup>	1.68x10 <sup>-3</sup>	"	Nil	+
"	1.34x "	1.34x "	3.37x10 <sup>-4</sup>	"	-
"	1.01x "	1.01x "	6.74x "	"	-
"	6.74x10 <sup>-4</sup>	6.74x10 <sup>-4</sup>	1.01x10 <sup>-3</sup>	"	-
"	3.37x "	3.37x "	1.34x "	"	-
"	2.69x "	2.69x "	1.41x "	"	-
"	2.0 x "	2.0 x "	1.48x "	"	-
1.70x10 <sup>-3</sup>	1.34x "	1.34x "	1.57x10 <sup>-3</sup>	"	-
1.71x "	6.7 x10 <sup>-5</sup>	6.7 x10 <sup>-5</sup>	1.65x "	"	-
1.68x10 <sup>-4</sup>	1.68x10 <sup>-4</sup>	1.68x10 <sup>-4</sup>	Nil	"	-
"	1.34x "	1.34x "	3.37x10 <sup>-5</sup>	"	-
"	1.01x "	1.01x "	6.74x "	"	-
"	6.75x10 <sup>-5</sup>	6.74x10 <sup>-5</sup>	1.01x10 <sup>-4</sup>	"	-
"	3.37x "	3.37x10 <sup>-5</sup>	1.34x "	"	-

Appendix D

Zeta-potentials of PbS.

G : Galena, Prec. : Precipitated

eo ; electro-osmosis ep : micro-electrophoresis

mb : moving boundary method

Pb(NO <sub>3</sub> ) <sub>2</sub> (mol/l)	Zeta- potential (mV)	Notes
1x10 <sup>-1</sup>	+5	G, eo
1x10 <sup>-2</sup>	+5	" "
3x10 <sup>-4</sup>	+5, +14	" "
1x10 <sup>-2</sup>	+19	Prec, mb.
3.6x10 <sup>-3</sup>	+26	" "
3 x10 <sup>-4</sup>	+30	" "
8 x10 <sup>-5</sup>	+ +19	" "
6 x10 <sup>-6</sup>	-6	" "
Na <sub>2</sub> S (mol/l)		
4.5x10 <sup>-2</sup>	-55	G, ep.
4.5x10 <sup>-3</sup>	-56	" "
9 x10 <sup>-4</sup>	-60	" "
4.5x10 <sup>-4</sup>	-56	" "
9 x 10 <sup>-5</sup>	-48	" "
4.5x10 <sup>-5</sup>	-32	" "
4.5x10 <sup>-6</sup>	-33	" "
7.6x10 <sup>-2</sup>	<del>-35.7</del>	Prec., mb
1 x "	-38	" "
5.5x10 <sup>-3</sup>	-44	" "

Appendix D (continued)

Na <sub>2</sub> S (mol/l)	Zeta- potential (mV)	Notes	
2.8x10 <sup>-3</sup>	-39	prec.,	mb.
2.3x "	-44.7	"	"
1.4x "	-42.6	"	"
1 x "	-59	"	"
6.7x10 <sup>-4</sup>	-67, -49	"	"
6 x10 <sup>-7</sup>	-16	"	"
pH		G,	eo
2.2	+4	"	"
3.2	-4	"	"
4.5	"	"	"
5.6	"	"	"
6.3	-8	"	"
7	-18.6	"	"
9.5	-21.5	"	"
10.9	-40	"	"
11	-30	"	"

APPENDIX - E

CATIONIC-ANIONIC CONVERSION OF C110 UNDER DIFFERENT CONDITIONS.

BTI-C110, which is said to contain quaternary ammonium compounds as the active groups, undergoes changes on standing for a long time at pH<6 or in a short time if placed in a solution of pH>7.

5 p.p.m. C110 was prepared at different pH values and applied to quartz dispersions at the same pH. The results of flocculation tests varied greatly between measurements. Sometimes complete sometimes no flocculation was observed. A correlation between the time of agitation before the flocculant was used and its subsequent flocculating power was observed. As seen in figure E-1 the flocculant lost its cationic capacity almost immediately at pH>8, whereas at lower pH values, longer agitation times were required. Once the flocculant was rendered inactive by alkali, subsequent alteration of the pH to neutral or acid did not produce any change. If quartz was treated by alkali and the pH made neutral subsequently, the flocculant acted perfectly, providing it was not itself previously treated by alkali. It appears that alkali acts on the flocculant in combination with oxygen from the air and mechanical agitation accelerates this action. This is seen from the results of flocculation experiments summarized in table E-1.

Table E-1

Shaking Time	With Air % Trans	With(N <sub>2</sub> ) %Trans	With(O <sub>2</sub> ) % Trans
No Shaking	84	20	76
10 min.	76	75	35
15 min	80	78	No flocs

The procedure was as follows:

10 p.p.m. Cl10 was placed in distilled water (pH=5.3) in shaking bottles and oxygen-free nitrogen or oxygen gas bubbled for 15 minutes. Then the bottles were placed on a mechanical agitator and shaken for different time intervals, and finally applied to 0.5% quartz suspensions at the same pH. A control sample which was treated with N<sub>2</sub> and O<sub>2</sub> but not agitated, did not show such a fast decrease in flocculating capacity as did the shaken ones.

The viscosity of a 100 p.p.m. solution of the flocculant at different pH values and in NaCl solutions of different concentrations at pH 5.4 was measured with an Ostwald viscometer at 25°C; results showed the pattern given in figure A-2. There does not seem to be a correlation between the loss of flocculating capacity of the polymer at high pH and the variation of viscosity under similar conditions. It was shown by the charring experiment described in section however, that the lack of adsorption of flocculation of quartz is due to the lack of adsorption of Cl10.

It appears that the flocculant at pH<7 has both cationic and anionic properties with the latter predominating and being maximal at 4<pH<5. The anionic character becomes maximal at pH 11. These conclusions are drawn from the following observations and the appearance of 2 maxima in figure A-2.

1. The flocculation of a number of ion-exchange resins was noted with Cl10 and a control anionic flocculant (Al30) at concentrations of 5 p.p.m. The results are given in table A-2 below, where + means flocculation and - means no flocculation.

Table E-2

Resin	Type of resin	Al3O	Cl10
Zeo-karb-225	Cation exchanger	-	+
I.C.R-50-H	" "	-	+
I.C.R-50-H	" "	-	- <sup>Ⓜ</sup>
I.C.R-45-OH	Anion exchanger	+	+

<sup>Ⓜ</sup> Cl10 first treated at pH 11 and then brought to pH 5 by HCl.

2. R. W. Slater reported that Cl10 has only a marginal flocculating effect on Degussa alumina (90). In fact, had this flocculant been purely cationic-assuming the absence of hydrogen bonding - it should not have had any flocculating action on this alumina which has a positive surface charge in distilled water (pH 5). On the other hand, modification of the flocculant by treating it at pH 11 and then making the pH 5 renders it a good flocculant for alumina.
3. Calcite, which has a positive surface charge at pH 8.2, behaved very much the same as alumina in example 2 above by flocculating only partially. With an overdose of Cl10 modified as above its zeta-potential dropped from +20.2 mV, in the absence of the flocculant, to -11 mV at 25°C.
4. At pH 4.5, Cl10 reverses the zeta-potential of quartz from negative to +8 mV.

The detailed organic chemistry involved in the change of functional groups from cationic to anionic with this material were not pursued further.

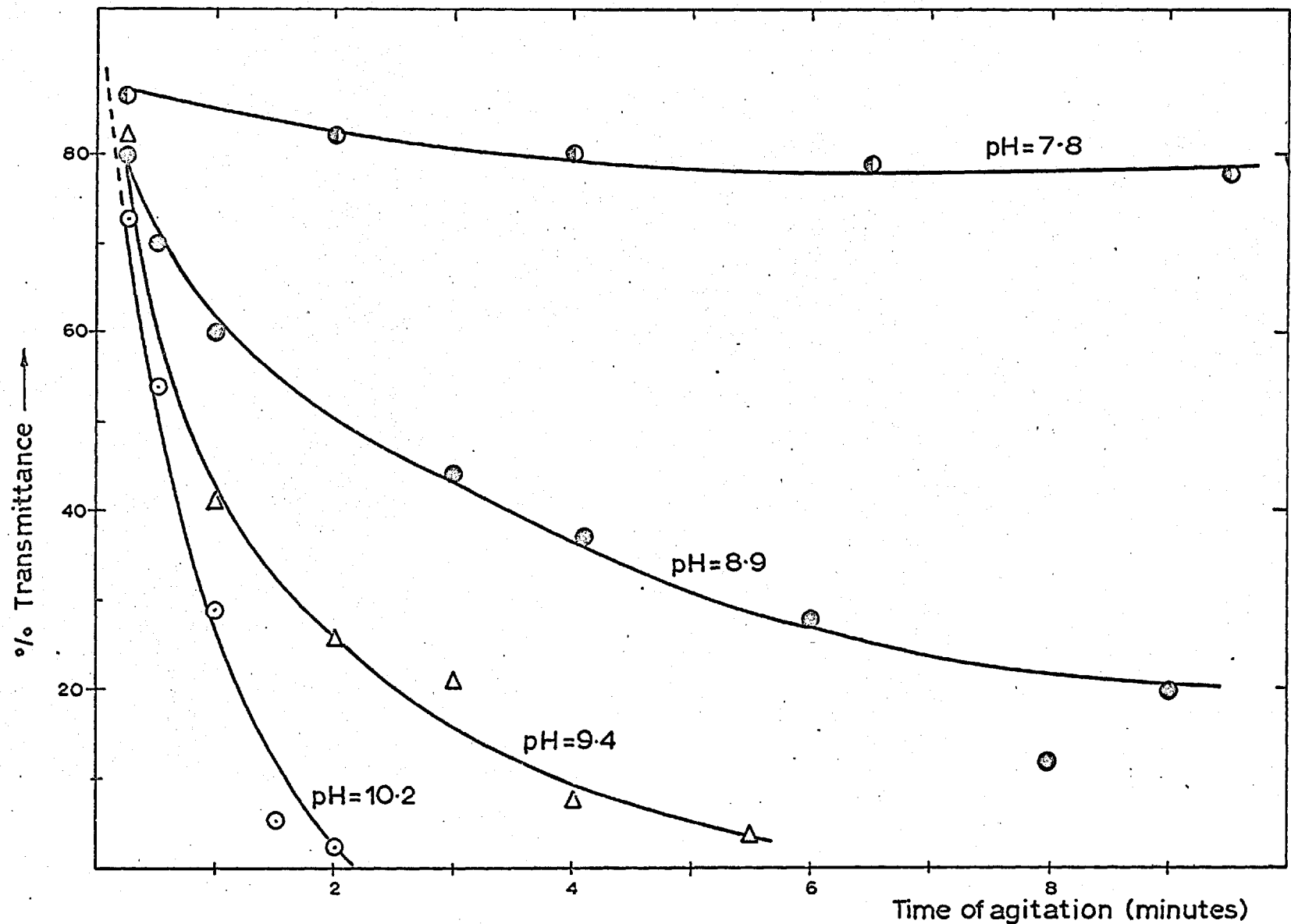


Fig. E1 Effect of pH on the flocculation capacity of BTI-C110 (solids 0.5% quartz flocculant 5%)



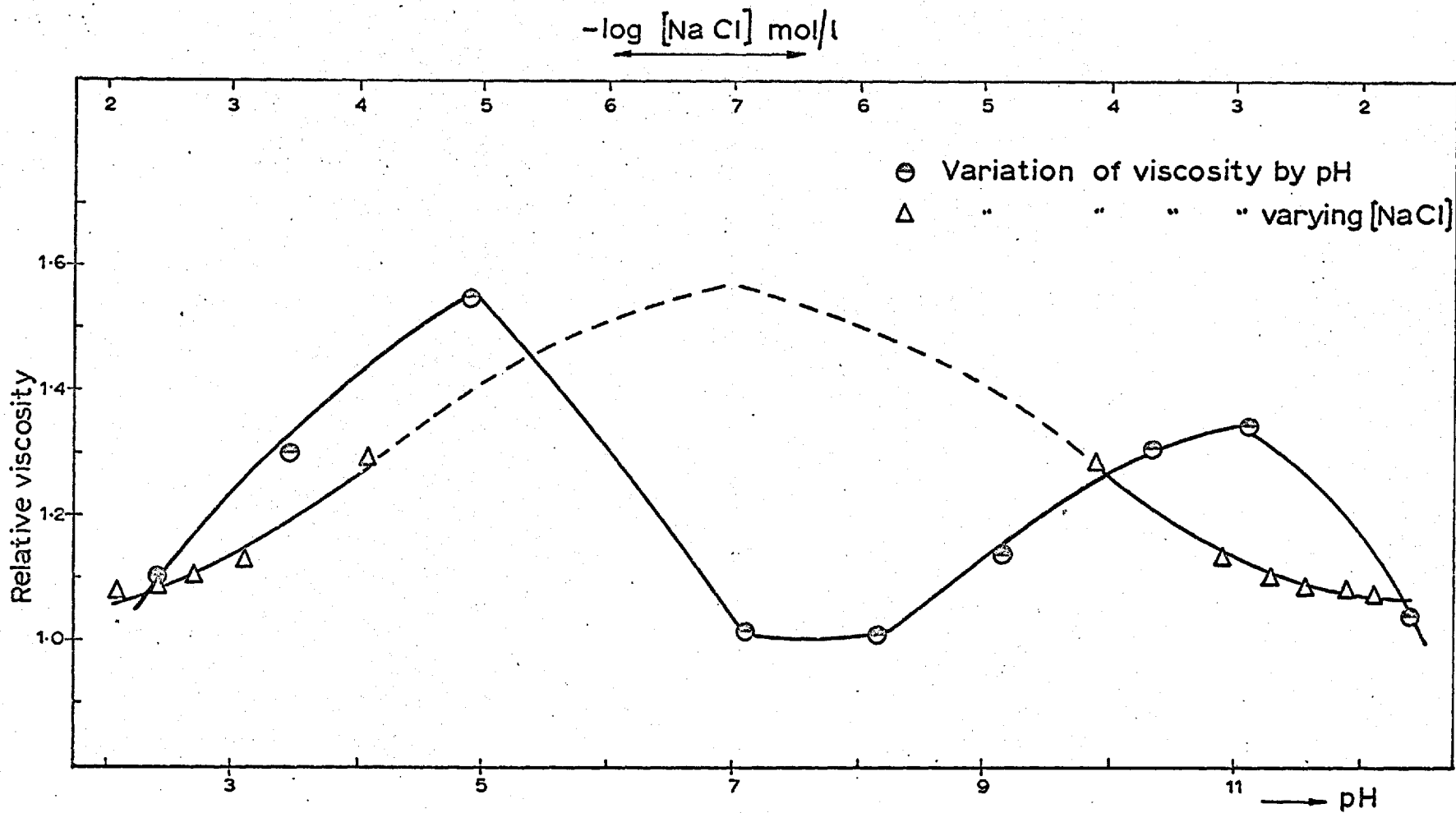


Fig. E2 Variation of the relative viscosity of BTI-C110 by varying pH and [NaCl] (flocculant conc. 100 ppm)