Fundamental Studies of the Flotation Process:

The Work of the National Institute for Metallurgy

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SYNOPSIS

The concepts involved in flotation research are discussed and aims are presented. Three different method. of investigation can be used, all of which are applied at the National Institute for Metallurgy (N.I.M.), and these are the empirical, trial and error method, the chemical engineering method, and the physicochemical approachs This paper is devoted to the last of these.

Because of the complexity of the physicochemical interactions involved, the work has, to a large extent, been concentrated on only one aspect, viz. the interaction between the mineral surface and reagents in solution, which was considered of major importance in the understanding of the process. The aspects on which work has been done are the concentration of uranium, the reaction between salt minerals and fatty acids, mixed xanthate-cationic collector systems, and the reaction between sulphide minerals and thiol reagents. Selected problems from the first two of these are discussed in some detail and deal with the agglomeration flotation of uranium and the chemical control of the flotation process for phoscorite. A detailed discussion is also presented of the progress made in the understanding of the interaction between sulphide minerals and thiol reagents, which is of more general application.

Finally, an indication is given of the future direction of physicochemical research at the N.I.M.

SINOPSIS

Die begrip aangaande flotasie navorsing word bespreek en die doelstellings daarvan uiteengesit. Drie verskillende ondersoek metodes, almal tans deur die Nasionale Instituut van Metallurgie (N.I.M.) aangewend, kan van gebruik gemaak word; nl. die empiriese probeer en fouteer metode, die chemiese ingenieuriese metode, asook 'n fisies-chemiese benadering. Die laaste metode word in hierdie verhandeling behandel.

Asgevolg van die ingewikkeldheid van die fisies-chemiese wisselwerking word hierdie verhandeling grotendeels tot een aspek beperk; nl. die wisselwerking tussen die mineraal oppervlakte en die reagense in oplossing wat as baie belangrik beskou word om 'n volle begrip van die proses te verkry. Naderhand sal ander fases van die proses ook bestudeer word. Die aspekte waarop werk alreeds gedoen is, is die konsentrasie van uraan, die reaksie tussen sout minerale en vetsure, gemengde xanthate-kationiese versamelings systeem, en die reaksie tussen sulfiede minerale en 'thiol' reagense. Gekose probleme aangaande die eerste twee aspekte, wat grootliks handel oor ooreenhoping flotasie van uraan en die chemiese kontrole van die flotasie proses van foskoriet, word in besonder behandel. 'n Bespreking word ook gevoer in die fynste besonderhede oor die vooruitgang op die gebied van die wisselwerking tussen sulfiede minerale en 'thiol' reagense wat van meer alledaagse belang is.

Ten slotte word 'n rigsnoer gegee vir verdere fisies-chemiese navorsing deur die N.I.M.

INTRODUCTION

Flotation is acknowledged to be the most important process in use at the present time for the concentration of minerals. Flotation is used in the processing of the bulk of the world's non-ferrous metals, as well as of a growing proportion of its iron, non-metallic minerals, and coal. However, until the middle of the 1950's, the process played a less prominent part on the South African mineral-extraction scene than it did in other mining countries because hydrometallurgy was applied direct to the ores in the extraction and concentration of the two principal products of the industry and because sulphide minerals were relatively less important. During the past decade and a half, however, several very large flotation plants, as well as numbers of smaller operations, have been established in the country. The increase in production of flotation concentrates is clearly illustrated by the figures in Table I. A look into the future leaves no doubt that the importance of flotation to the South African mineral-extraction industry will continue to grow.

Before 1960 no long-term research and development devoted to the improvement and understanding of the flotation process were undertaken in South Africa. With the increase in application of the process, the need was felt for such an effort to be made, and work in this direction was initiated at the Government Metallurgical Laboratory, the forerunner of the National Institute for Metallurgy (N.I.M.). The progress of this programme has built up facilities and a body of know-how that should be of use to the South African industry in evaluating the significance of new developments and new ideas in this specialised field.

The present paper is intended to make the work more generally known to metallurgists in the country. It deals, first, with the general concept and planning of this long-term research, and goes on to describe one aspect — the study of the physicochemical basis of flotation — and to discuss the progress that has been made on several of its component projects.

AIMS AND DIRECTIONS IN FLOTATION RESEARCH

Research and development on the flotation process can be conducted with varying aims. Short-term work is generally directed towards the application of known processes, based on available machines and reagents, to a particular ore. Long-term investigations could be aimed at the following:

(1) The development of generalized methods of circuit design that will enable the performance of existing processes in particular situations, or the

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development of generalised methods for the control of flotation processes.

(2) The extension of the scope of the process to combinations of minerals that are not readily separated to be optimized, to minerals that are not flotable with existing reagents, and to the coarse and fine sizes of particles that are less amenable to the process. Within this aim is included the development of new reagents, new machines, and new techniques.

(3) A more-complete understanding of the mechanism of the different processes taking place during flotation. Understanding of the physical and mechanical aspects could be of importance in furthering aim (1) above; the understanding of the chemical aspects would assist in realizing aim (2), and is essential to the solution of the important problem associated with the fact that nominally identical minerals can show significantly different behaviour in flotation.

Three essentially different methods can be used in the investigation of flotation. Firstly, *the empirical (trial-and-error) method* in which previous experience is applied to new material by way of systematic process testing. For all its unwieldiness, this is the only technique by which processes can be developed and proved at the present time. Secondly, *the chemical-engineering method.* This is a synthetic approach that concentrates on the mixing and transport aspects, and is designed to meet the first and, to a lesser extent, the second of the aims set out above. It seeks to characterize flotation as a rate process and express characteristics of a plant as a mathematical model that relates all the most important factors governing the operation of the process. A satisfactory model would indicate how the process should be operated for greatest efficiency. Thirdly, *the physicochemical approach.* This analytical approach is directed towards the realization of both the second and third aims set out above. It is based on the premise that the primary, if not the most important, factor governing the efficiency and selectivity is the proper conditioning of the solid-solution and air-solution interfaces so that collisions between them are fruitful and selective. It therefore seeks to understand the nature and the mechanism of the chemical and physical reactions taking place at and between the interfaces.

At the N.I.M. all three approaches are applied to the study of flotation. The Ore Dressing Division carries out empirical development in relation to specific ores, the University Research Group in the Department of Chemical Engineering at the University of Natal concerns itself with an engineering approach based on mathematical models[1], and the Mineral and Process Chemistry Division studies the physicochemical aspects of flotation.

PHYSICOCHEMICAL RESEARCH WORK

Fig. 1 presents a break-down of the flotation process in the form of a flow diagram, which shows the most important stages that take place and the interaction take over between them. The process is manifestly a complex one. The heterogeneous mixture of solid particles that make up a typical flotation feed is concentrated and separated through interaction with chemical reagents, air, and energy. Important interactions take place at three interfaces—the solid-solution, solid-air, and air-solution interfaces—and in the solution phase.

Before a detailed consideration of some of the various research projects that have been undertaken and are under way in the Mineral and Process Chemistry Division, it is necessary to explain the principles that have governed the general direction of the work.

At the outset it was accepted that it would not be possible to work immediately on all stages of the process (c, d, e, and g of Fig. 1) in which important chemical interactions take place. It would be preferable to direct a concerted effort at one of the stages and to acquire on that one aspect a sound foundation of knowledge and experience on which a wider understanding could be built. Militating against a more general attack on the subject was not only the considerable complexity of the physicochemical interactions taking place, but also the uncertainties and contradictions in the existing knowledge of the subject — a circumstance that made it difficult to choose a secure point of knowledge from which to mount new research programmes.

It was decided that all studies should be conducted on as rigid and quantative a basis as rigidly as possible. At the time the work was started, there existed a certain general framework of understanding that explained, probably correctly, how hydrophobicity developed from the oriented absorption of collector molecules at the mineral surface. However, this general understanding did not explain the processes taking place in sufficient detail to be of practical assistance in process design and control, or in the prediction of the behaviour of flotation systems. It was considered that further progress would be possible only on the basis of a very much more quantitative and exact knowledge of the reactions taking place. The decision to adopt this type of very thorough approach carried with it the acceptance that the progress of the work might necessarily be slow and that, initially at least, the field of endeavour would have to be severely restricted.

The aspect of the process chosen for initial study was the interaction between the mineral surface and reagents in solution (see Fig. 1, stage (d)), and the fields in which work has been carried out are shown in Fig. 2. The following sections describe a few of the specific problems that have been undertaken and the conclusions that have been reached will be outlined and placed in context with the general state of knowledge of the particular subject.

THE INTERACTION BETWEEN SULPHIDE MINERALS AND THIOL REAGENTS[14]

To place the work that has been done at N.I.M. in its context, it is necessary to summarize the general state of knowledge of the interactions that take place between thiol reagents and sulphide minerals.

By the early 1950's, a clear picture of the events taking place when thiol reagents interact with sulphide mineral surfaces appeared to be emerging. It was known that sulphide surfaces abstracted thiols from aqueous solution and that in the process anions such as sulphates,

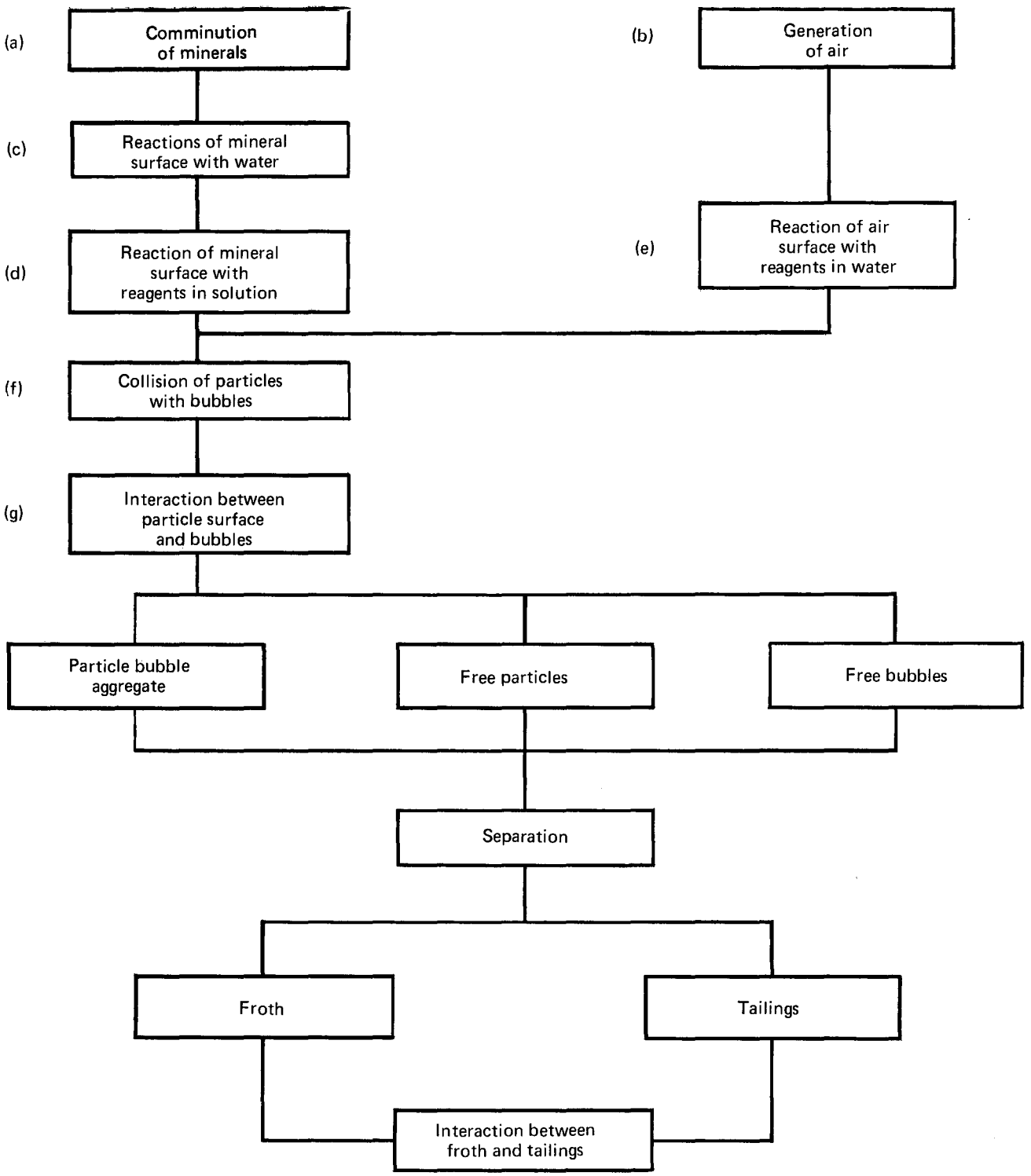

FIGURE 1 - Schematic flow diagram of flotation process

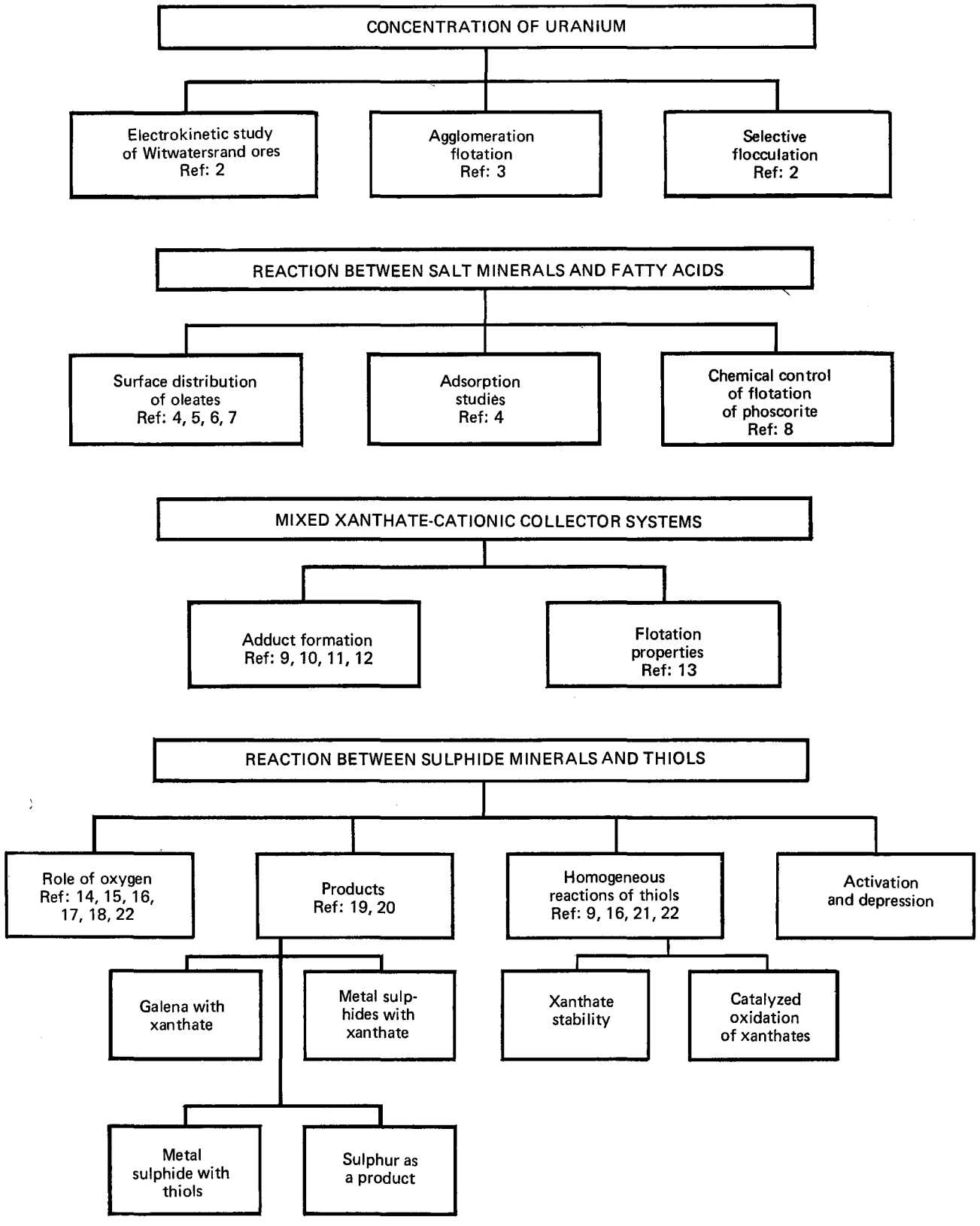

FIGURE 2 - Fields of physicochemical flotation studies

hydroxides, or carbonates appeared in solution in equivalent quantities. The product of the reaction was considered to be the metal-thiolate, and it was tacitly assumed that this adsorbed regularly, layer by layer. There was some evidence that the first layer was more strongly held than the subsequent ones. The reaction was generally regarded as one that rapidly reached a reversible state of equilibrium. This conclusion carries the important implication that the state of the surface is uniquely related to the state of the solution — concentrations of different ions, pH, temperature, etc.—with which it is in contact. There was some controversy whether clean sulphidemineral surfaces were floatable, but it was accepted that the surfaces encountered in practice would, to a greater or lesser extent, be oxidized and that this would make them hydrophilic. It was thought that hydrophobic properties were conferred on such surfaces by the adsorbed metal xanthates that were known to be so oriented that the hydrocarbon portion extended away from the solid and into solution.

During the mid 1950's facts began to accumulate that were not in harmony with this picture. The doubts crystallized around the work of the Russian school, which published a series of imported papers at about this time. These showed that the presence of oxygen was essential if there was to be reaction between sulphide minerals and thiol reagents, and if the minerals were to be rendered flotable. They also showed that the disposition of the adsorbed reagents at the surface, far from being regular, consisted of a number of isolated multilayer patches. It was suggested that the adsorption of reagent was controlled by the semiconductor properties of the surface, which were favourably influenced by interaction with oxygen.

During the past ten to fifteen years, a number of investigations have been undertaken in which sophisticated modern techniques have been applied to the study of the chemistry of these interactions. These investigations have concentrated on the following problems.

(i) How does oxygen participate in the interaction between thiol reagents and sulphide minerals?
(ii) What are the products of reaction?
(iii) What makes the surface flotable after reaction with thiols?

The work programme of N.I.M. has been directed primarily at the first and second of these problems.

THE ROLE OF OXYGEN IN THE INTERACTION BETWEEN XANTHATE AND GALENA[15, 16, 17, 18, 22]

One of the mechanisms that have been proposed to account for the participation of oxygen in the interaction between xanthates and sulphide minerals involves the oxidation of xanthate by oxygen in solution to form dixanthogen, which then adsorbs and reacts at the surface:

$$2X^- + \tfrac{1}{2}O_2 + H_2O \rightarrow X_2 + 2OH^-$$

$$|\ PbS + X_2 \rightarrow\ |\ PbS - \text{Surface Products}$$

A series of simple experiments showed that this mechanism could be eliminated from consideration. The rate of decomposition of xanthates in pure, alkaline solutions was found to be the same in the presence and in the absence of dissolved oxygen, and no dixanthogen could be detected among the products of decomposition. Reaction with oxygen and the formation of dixanthogen was found to be catalysed by the presence of ions of several transition metals. (See Table III). However, the rate of the catalysed formation of dixanthogen was too low for it to be of importance in flotation, where all reaction must take place within a few minutes.

It is clear, therefore, that oxygen must play its role by direct action at the mineral surface. There are essentially two ways by which this interaction might take place. The first of these involves the oxidation of the surface to form insoluble products that subsequently undergo an exchange with xanthate ions from solution, for example,

$$|\ PbS + 2O_2 \rightarrow\ |\ PbSO_4$$

$$|\ PbSO_4 + 2X^- \rightarrow\ |\ PbX_2.$$

It has been convincingly demonstrated[29, 30] that xanthate can react with heavily oxidized surfaces in this way, but this does not preclude the second direct mechanism — the simultaneous interaction of xanthate and oxygen at the surface — which may be written schematically as follows:

$$|\ PbS + O_2 + nX^- \rightarrow\ |\ PbS \begin{matrix}\text{Surface}\\ \text{product(s)}\end{matrix} + \begin{matrix}\text{Solution}\\ \text{product(s)}\end{matrix}$$

The N.I.M. group has devoted a major effort to the elucidation of this mechanism and has concentrated on galena and ethyl xanthate as a model system. This investigation is one of considerable experimental difficulty, which stems from two sources: firstly, the requirement that the sulphide surfaces used should be free of oxidation initially and, secondly, the need for the concentration of oxygen in the reaction system to be controlled and measured, and for the system to be isolated from contact with the abundant oxygen of the surrounding atmosphere. Thus, the progress of the investigation is conveniently followed through the development of experimental techniques.

The first stage of the investigation was the development of a means by which oxidation products could be removed from the surface of a sample of ground galena and by which the surface could subsequently be contacted with solutions containing either no oxygen or some oxygen[16]. The apparatus consisted essentially of a column through which solutions flowed upwards, maintaining a bed of ground galena in fluidized condition. Contact with sodium sulphide solution at pH 8, followed by rinsing with water, was found to effectively free the surface of oxidation: the resulting 'clean' surface did not react with an oxygen-free xanthate solution. As expected, when oxygen was introduced to the xanthate solution, reaction between xanthate and the surface, as indicated by a decrease in concentration of xanthate in solution, was observed. Quite unexpected, however, was the observation that this reaction did not reach completion after a time, as would be expected if it was limited by the build-up of a layer of adsorbed product on the surface. On the contrary, reaction persisted for as long — and experiments extended over several days — as oxygen and xanthate were kept in contact with the mineral surface.

The finding that the abstraction of xanthate by galena is a continuing process that does not reach completion or equilibrium is of the greatest importance and has necessarily influenced the course of subsequent work. It implies that the reaction is not reversible and that the *extent of reaction* is no longer a primary parameter that can be related simply to such variables as the concentrations of xanthate and of oxygen, pH, and temperature. The system can effectively be studied only with reference to the *kinetics of reaction*. Therefore, the next stage of the work emphasized the determination of rates of reaction.

The second stage of development was carried out with an apparatus[17] shown in Fig. 3 that was similar to that used previously, in that solutions having passed through a fluid bed of mineral were analysed for their xanthate content and then discarded. However, provision was made for the concentration of oxygen in the entering solution to be precisely controlled. It was found[17] that two distinct reactions between xanthate, oxygen, and galena could be distinguished. The first of these results in the adsorption of xanthate, and the second gives rise to soluble products. The adsorption reaction predominates in the early stages of contact between oxygen-containing xanthate solutions and 'clean' galena, and follows an exponential rate equation:

$$dq/dt = \beta \exp. (-\alpha q),$$

where q is the quantity of xanthate adsorbed and α and β are constants. At any time, both the rate and the extent of adsorption vary directly with the square root of the partial pressure of oxygen in solution. The second type of reaction becomes predominant once the rate of adsorption has been sufficiently reduced by the accumulation of adsorption products. This reaction is responsible for the continuing abstraction of xanthate from solution, which had been noted in the first stages of experimentation. After several hours of contact between the surface and the reagent, this reaction proceeds at a constant rate, which also varies with the square root of the partial pressure of oxygen in solution. Although it was not found possible to identify the chemical changes taking place, it was noted that the reaction was associated with the appearance of a water-soluble product that was tentatively identified as the monothiocarbonate $ROCOS^-$. It can be seen that this substance can be obtained from the equivalent xanthate, $ROCS_2^-$, by replacement of one of the sulphur atoms with oxygen.

The design of the second apparatus did not allow meaningful observations to be made within the first 20 minutes of contact between the solutions and the mineral. This meant that the results do not apply to the reactions that are of primary importance in flotation. Accordingly, attention was focused on the development of an apparatus that would allow this early period to be studied, and would also allow the consumption of oxygen during reaction to be monitored. After a prolonged period of unsuccessful innovation, the apparatus shown in Fig. 4 was developed[31]. In use, suitably pretreated galena is dropped into the upward-flow column, which contains a solution of the reagents that are required for the particular experiment. The column is then sealed in closed circuit with a spectrophotometer cell for determining the concentration of xanthate, a Clark electrode for monitoring the concentration of dissolved oxygen, and a completely sealed glass centrifugal pump. This system is capable of yielding meaningful results within 2 minutes of the commencement of reaction and has proved itself to be extremely productive. The results are very much more reproducible than those obtained by the previous techniques.

Whereas numbers of reliable observations have been made by this technique, the work of interpretation is still in progress. At this time, however, a number of interesting findings can be mentioned.

1. The two stages of reaction, which are again clearly revealed, are characterized by different values of the stoichiometric ratio — number of molecules of xanthate reacted to number of molecules of oxygen reacted. The ratio has a value of two in the first stage of reaction and, depending on the conditions, varying values of less than one in the second stage.
2. Clear confirmation was obtained that the final, continuing stage of the abstraction of xanthate is due to the formation of monothiocarbonate.
3. Under certain conditions of pH and xanthate concentration, adsorbed xanthate is converted to monothiocarbonate (MTC^-) at the surface, which then desorbs. It is thought that this effect might take place by reaction between adsorbed lead xanthate and lead hydroxide:

$$Pb(OH)_2 + PbX_2 + 2OH^- \longrightarrow 2MTC^- + 2PbS + H_2O.$$

4. The new experimental technique allows the quantity of monothiocarbonate formed at any time to be accurately determined and, therefore, the amount of xanthate adsorbed at the surface to be estimated. Thus it has been shown that the adsorption of xanthate can be reversed if suitable adjustments are made to the concentration or pH of the solution with which it is in contact. Whereas it is not yet certain how quantitative and complete this reversibility is, it seems highly probable that former indications of the adsorption of xanthate as irreversible derived from confusion between adsorption and the side reaction by which xanthate is converted to monothiocarbonate — and the latter certainly could not be reversed under the conditions obtaining in flotation.
5. The total rate of consumption of oxygen by galena is decreased by the presence of xanthate.

PRODUCTS OF REACTION BETWEEN THIOLS AND METAL SULPHIDES[19, 20]

The investigation of the nature of the products of reaction was prompted by the controversy that has grown up in the literature between those authors who believe the product of reaction between xanthates and sulphide minerals to be the metal xanthate, those who believe it to be dixanthogen, and those who believe it to be a mixture of the two. In the case of galena, the most convincing piece of evidence in favour of dixanthogen was provided by the work of Abramov[32], who used infrared spectroscopy to identify the products extracted from the surface of xanthated galena. When

members of the N.I.M. team repeated this work, they were unable to identify dixanthogen in extracts from xanthate-treated galena surfaces but, instead, found only lead xanthate to be present. Further investigation of the detailed procedure used by Abramov revealed that one of its stages — the evaporation of the organic extract from the mineral surface — had the effect of converting any lead xanthate present to dixanthogen and showed Abramov's finding to be an experimental artifact. It was therefore confidently concluded that metal xanthate was a major product of the reaction between galena and xanthate solutions. Since dixanthogen is more soluble than lead xanthate in the solvents used, and since there is no reason to believe that it is more strongly held at the surface than is the lead xanthate, it was also concluded that dixanthogen is not a major product. However, it could not be concluded that lead xanthate was the only product of reaction because there was no assurance that all the products formed at the surface were extracted by the methods used.

The investigation was extended to the determination of the products of reaction between some twelve different sulphide minerals and several different xanthate homologues. The purpose of this work was to establish whether the different minerals would form the same type of product (metal xanthate or dixanthogen) and to see whether any observed differences could be explained. The results, which are summarized in Table IV, show that, where minerals react to form an extractable product, this product tends to be either metal xanthate or dixanthogen. The formation of mixtures of the two is a rarity. Which of the two products is formed correlates with the potential that the mineral assumes in a solution of the xanthate. Those minerals that take up a potential more positive than the equilibrium potential for the reaction

$$X_2 + 2e \rightarrow 2X^-$$

form dixanthogen; those that assume a more negative potential either form the metal xanthate or do not react.

The reactions between the same suite of minerals and different types of thiol flotation reagents are currently being studied. The reagents are mercaptobenzthiazole, and alkyl dithiophosphates, thiocarbamates, and thionocarbamates. Results are being obtained that are in harmony with the behaviour observed in reaction with xanthates. Again it is found that, where reaction takes place, it is either the metal thiolate or the dithiolate that is formed; and, again, the formation of the dithiolate takes place on those minerals that assume a potential in a solution of the reagent that is higher than the equilibrium potential for the appropriate reduction reaction.

Although this work has provided an overall view of the behaviour of a number of related reagents with a whole range of metal sulphide minerals, and has thrown some light on a controversial subject, it by no means provides a complete or an adequate understanding of the products that are formed at the mineral surface. There is evidence that some minerals, at least, form a tightly-bound thiol-containing product that is not amenable to extraction by common organic solvents and hence cannot be detected by the techniques used at the N.I.M. For galena and xanthate, this product is thought to be a species in which a surface lead atom is attached to one xanthate, instead of to the normal two xanthates. Furthermore, there is reason to suspect that elementary sulphur is always formed as a primary product of the reaction between oxygen and sulphide surfaces in the presence of thiol reagents and that this sulphur may play an important part in rendering the sulphide mineral surfaces floatable.

THE CAUSE OF FLOATIBILITY

Both the metal xanthate and dixanthogen have been suggested as the entities that confer hydrophobic properties on sulphide mineral surfaces after they have been treated with xanthate. The finding that sulphide minerals react with xanthates to produce, in general, either xanthate or dixanthogen makes it extremely unlikely that either of these can be the sole cause of hydrophobicity at sulphide surfaces after treatment with xanthates. Indeed, it is now not even certain that either of them need necessarily be the primary hydrophobic entity. In an attempt to explain their observations on the role of oxygen, the workers at N.I.M. have been led to postulate reactions in which elemental sulphur is always one of the products — whether the reaction is adsorption or the formation of monothiocarbonate. The question now arises whether sulphur can be either solely or partly responsible for hydrophobicity. Whereas the suggestion is by no means a new one and some objections to it have been proposed, it is thought to warrant re-examination.

AGGLOMERATION FLOTATION OF URANIUM-BEARING ORES[2, 3]

For some time, interest has been shown by the mining industry in the development of processes for the concentration of uranium from minerals present in Witwatersrand ores. That none of the processes thus far proposed has been adopted might be ascribed to their failure to recover the uranium values that are associated with the finer particle sizes. Much of the uranium occurs in the slime fractions as is shown in Table II, which gives the analyses of the various size fractions from a sample of ore from Western Deep Levels, and which shows that 23 per cent of the uranium is associated with the fraction smaller than 12 μm. The uranium in the ores is usually associated with the phyllosilicate fraction (which limits the extent of beneficiation that is possible), and the concentration problem therefore resolves itself into the separation of the phyllosilicates from the quartz gangue.

It was decided to try a new approach that would take into account the special requirements of the slime fractions. This approach was based on the principle that the fine particles must be induced to associate selectively into larger aggregates as a precursor to eventual separation. Two separation procedures can be considered, viz., settling and flotation. When settling is used, the overall process is called 'selective coagulation' or 'flocculation', and the agglomerated particles settle faster than those that remain dispersed. When flotation is used, the process becomes 'agglomeration flotation' and here agglomeration is induced by the presence of finely

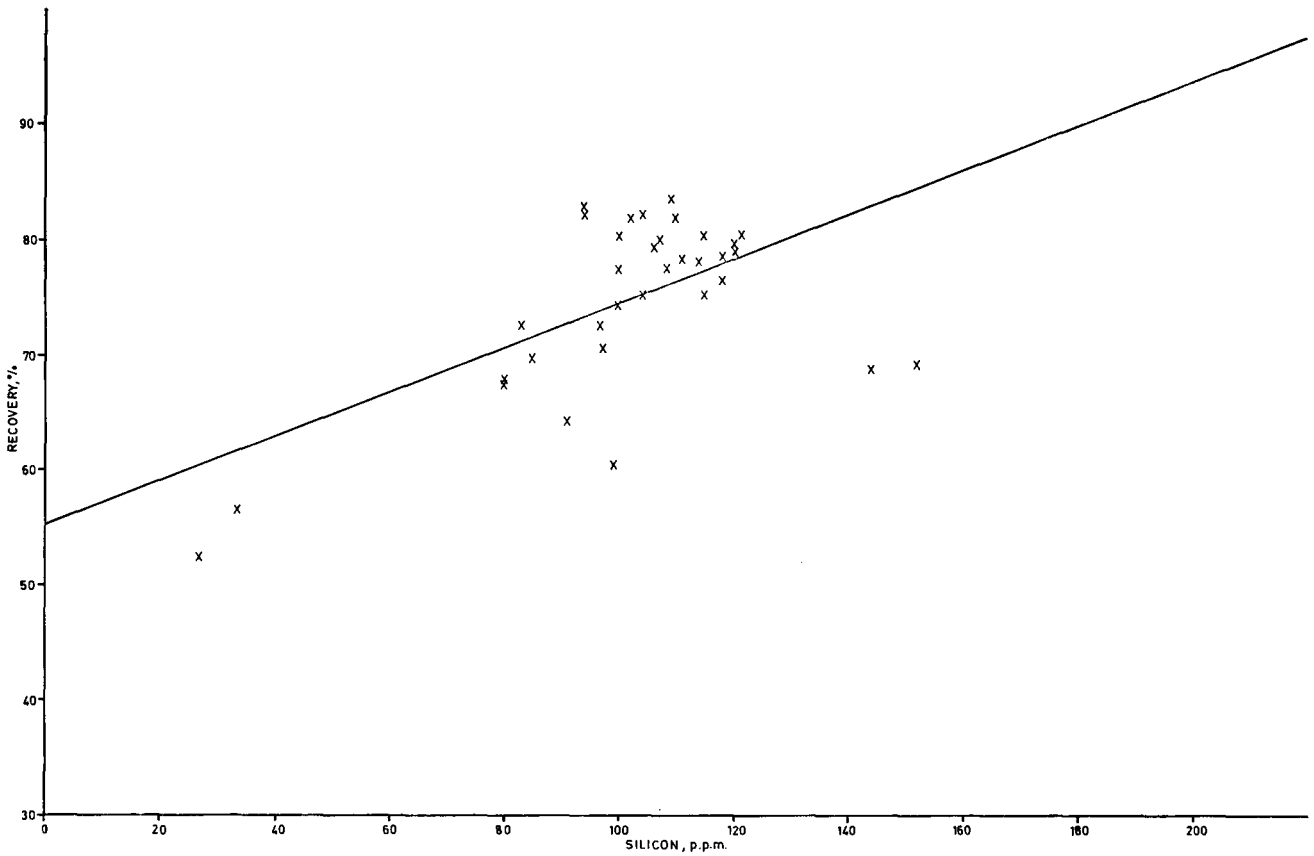

Fig 1

TABLE I

PRODUCTION OF FLOTATION CONCENTRATES IN THE REPUBLIC OF SOUTH AFRICA. METRIC TONS

	1950	1955	1960	1965	1970
Pyrite	12 775	357 292	500 008	428 294	607 851
Fluorspar:					
Acid	—	—	—	4 835	71 199
Ceramic	—	—	—	4 828	5 257
Copper*	113 273	148 893	161 333	201 666	464 673
Apatite	26 213	64 310	134 469	501 068	929 671
Antimony	13 600	23 200	20 200	20 600	28 800
Platinum†	15 000	20 000	25 000	50 000	100 000
Total	180 861	613 695	841 010	1 211 291	2 207 451

*Calculated from data for metal by assuming 30 per cent contained in flotation concentrate.
†Approximate figures.

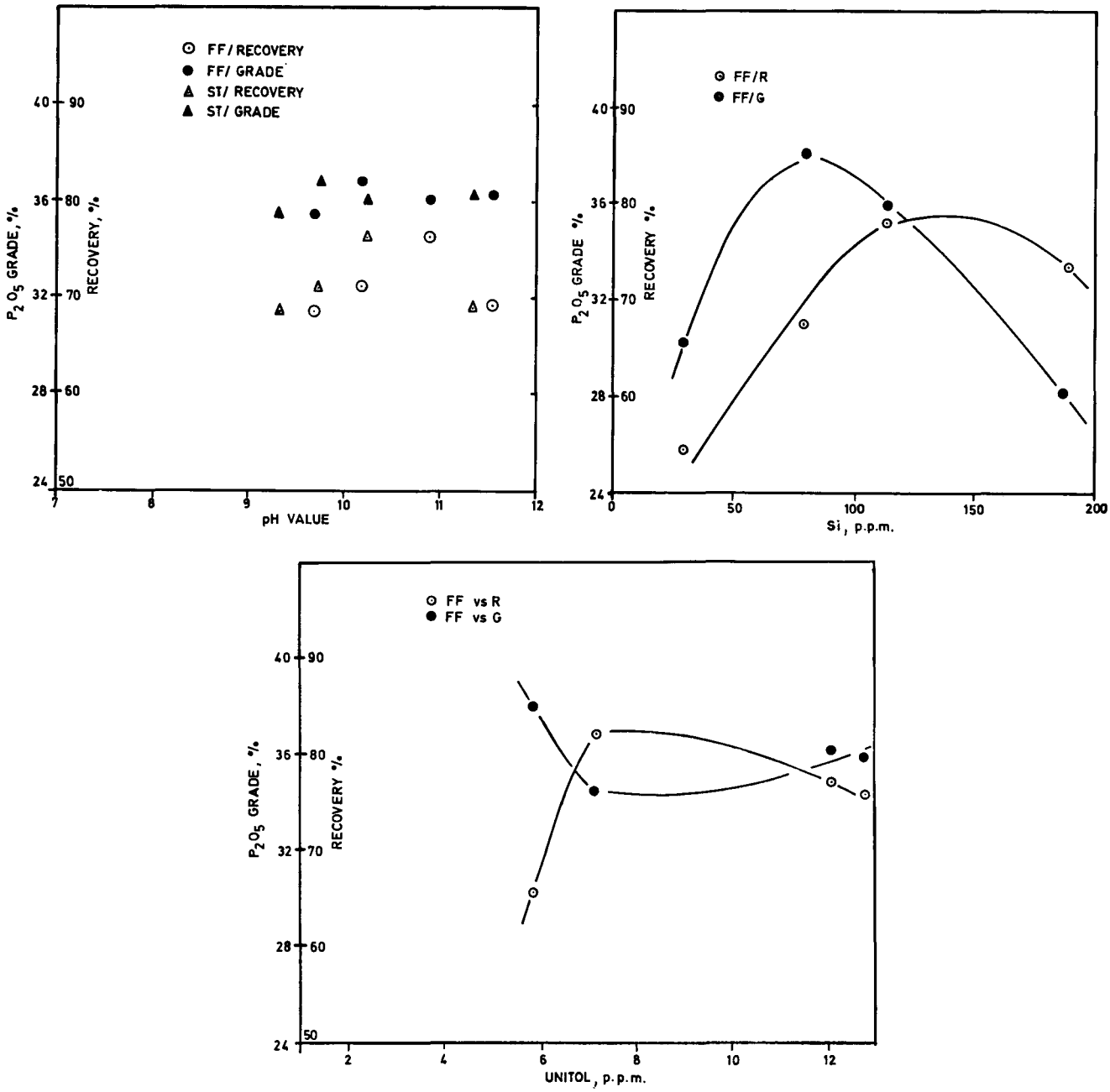

Fig 2

TABLE II

EFFECT OF PARTICLE SIZE ON THE OIL-AGGLOMERATION FLOTATION OF A SAMPLE OF ORE FROM WESTERN DEEP LEVELS

Nominal size of cyclosizer fraction μm		Mass of feed %	U_3O_8 in feed p.p.m.	U_3O_8 distribution in feed %	U_3O_8 in concentrate p.p.m.	Recovery of U_3O_8 in concentrate %
	> 41.6	23.46	622	37.0	2 080	85
< 41.6	> 32.3	21.82	323	18.0	1 380	85
< 32.3	> 23.1	16.03	326	13.0	1 212	89
< 23.1	> 15.7	10.54	308	8.0	832	88
< 15.7	> 12.0	4.97	205	3.0	419	87
< 12.0		23.18	349	21.0	717	97

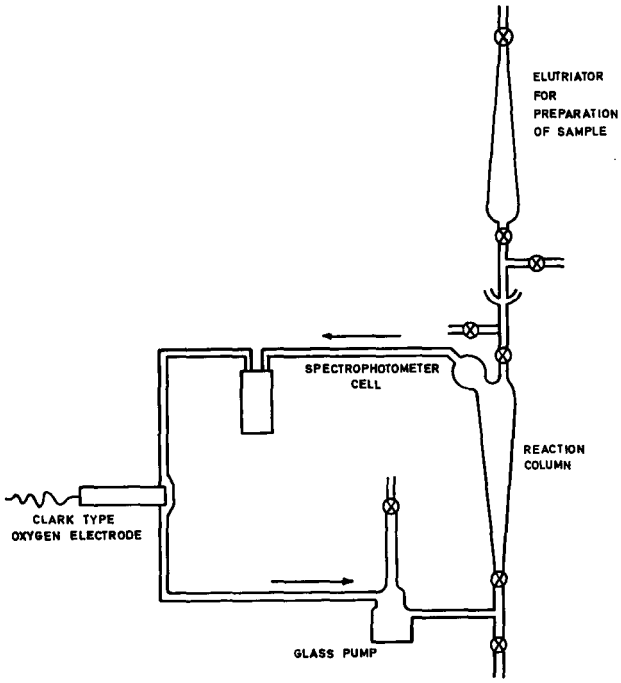

Fig 3

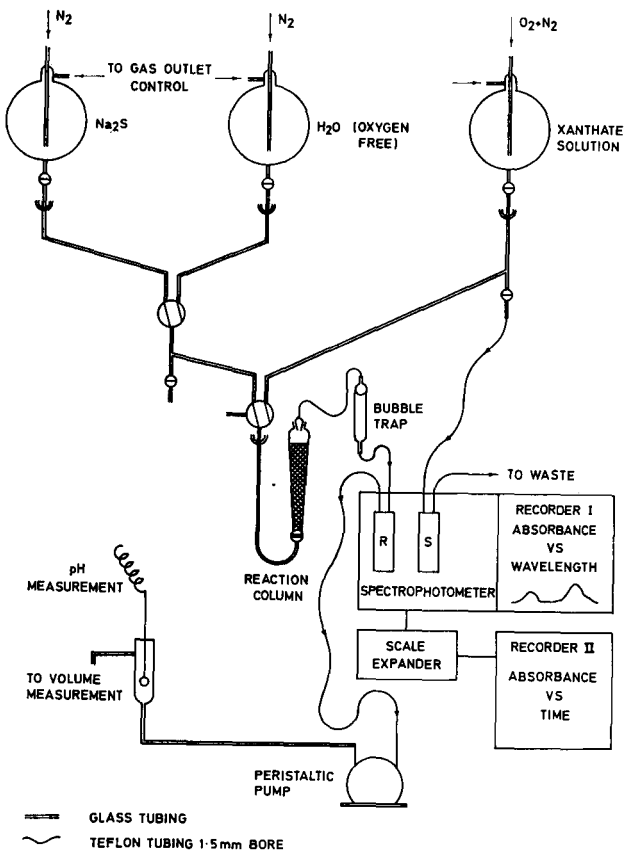

Fig 4

divided oil droplets. The resulting agglomerates are strong enough to survive the severe mechanical stresses of flotation and massive enough to attach to air bubbles.

The success of both the above approaches depends on the existence of reagents that produce aggregation of only one of the mineral fractions present, i.e., either phyllosilicates or quartz. It was considered that the choice of suitable reagents could be simplified if more were known about the structure of the interface between the mineral surface and its aqueous environment — in particular the sign and magnitude of the charge at the interface. Accordingly, electrokinetic investigations on a uranium-rich fraction and a low-uranium (mainly quartz) fraction from a typical Witwatersrand ore were carried out. The aims of this investigation were as follows:

(a) To see whether exploitable differences in the zeta potentials of the two fractions could be induced by variation in the electrolyte concentrations. For example, if conditions could be found under which the potential of one species was negative and the potential of the other positive, then a negatively charged reagent might be expected to adsorb selectively to the positive surfaces and either selectively coagulate them or render them selectively floatable.

(b) To detect whether chemisorption of reagents to one or other, or both, of the two types of mineral takes place.

It was found that most of the range of electrolytes and other reagents studied brought about very similar changes in the potentials of the uranium-rich and the uranium-poor fractions. With sodium oleate, however, the decrease in zeta potential was significantly greater for the uranium-rich fraction. Since this might indicate a greater affinity of oleate for the uranium-containing minerals than for the quartz, attempts were made to use this reagent in laboratory tests on selective coagulation and agglomeration flotation.

The agglomeration flotation tests gave promising results. The method involved the addition to the pulp of an emulsion comprising a non-polar hydrocarbon (kerosene, 25-30 lb/ton), oleic acid, and a non-ionic emulsifying agent. Addition of sulphuric acid in amounts of 0.4 to 0.8 lb/ton was also necessary, the usual effect being an increase in grade and a decrease in recovery with increasing additions. The amounts of oleic acid added in the tests were high (varying between ca 3 and 7 lb/ton), but no attempt was made to optimize the process and additions as low as 1.5 lb/ton may well prove to be adequate. The emulsifying agent used was an alkyl aryl polyether alcohol, Triton X.100, and was added in amounts of ca 0.75 lb/ton.

An important difference from the techniques of conventional flotation was the requirement of long conditioning times at high energy inputs and of high pulp densities in the conditioning stage. The use of high conditioning energies in agglomerate flotation is essential and may arise from the need for the removal of collector that becomes loosely attached to the gangue during the early stages of conditioning[23]. The manner in which high conditioning energies achieve this removal is to unnderstood, but it may be brought about by the

attrition of the more weakly held collector at the surface of the gangue minerals. In the tests, conditioning carried out at impeller speeds of 1 800 rev/min and times of 30 minutes was found to give good results. Pulp densities in the conditioning stage varied from 30 to 50 per cent solids, although the pulp was diluted to 20 per cent solids before aeration and collection.

Recoveries of high-grade ore (400 p.p.m. of U_3O_8) were usually between 85 and 92 per cent, with grades of approximately 1 200 p.p.m. of U_3O_8 in concentrates containing about 30 to 35 per cent by mass of the feed. Low-grade ores (ca 100 p.p.m. of U_3O_8) gave recoveries of about 75 to 80 per cent from concentrates containing 25 to 35 per cent of the feed, with grades varying between 200 and 400 p.p.m. of U_3O_8.

Of considerable importance is the fact that significant recovery of uranium from the fines was achieved. This is shown in Table II, where the response of different size fractions to the flotation process is shown.

Laboratory-scale tests on selective coagulation of the uranium-containing species were not successful in bringing about differential coagulation[2]. However, tests using high energies and pulp densities in the conditioning stage comparable with those used in agglomeration flotation did achieve some concentration, although this was not of sufficient magnitude to generate optimism about the future of the process in the treatment of Witwatersrand conglomerate ore.

FLOTATION OF PHOSCORITE ORES[8]

In conjunction with the research department of the Phosphate Development Corporation, a search was made for correlations between the concentration of flotation reagent in the solution phase of phoscorite pulp and the metallurgical performance of the flotation. This search was prompted by the possibility that the composition of the solution phase of the flotation pulp might govern the concentrations of the collector adsorbed at the different mineral surfaces, on which differential flotation of the minerals ultimately depends. Hence, the solution concentrations might provide an important factor for the control and optimization of the float. Such correlations for the flotation of galena by xanthate have been demonstrated by Bushell and used in the control of a large concentrator[24]. The initiation of the work was prompted by the availability, as a result of more fundamental studies of the Mineral and Process Chemistry Division, of suitable methods for the determination of the concentrations of most of the principal reagents used in the flotation of phoscorite.

In the flotation of phoscorite, four reagents are added to the pulp in the conditioning stage, viz., caustic soda, sodium silicate ($Na_2O.2SiO_2$), Unitol DSR (fatty acid, collector) and Berol EMU (polyglycol ether, frother and depressant). In this work, the levels of concentration in solution of three of these, viz., caustic soda (pH), sodium silicate, and Unitol DSR, were determined. The concentration of the remaining additive, Berol EMU, was not measured, mainly because no analytical procedure was readily available. The concentrations of calcium and magnesium were also determined, although previous work at Foskor[25] suggested that correlations with these ions would be unlikely.

The investigation was carried out on the 1-ton per hour pilot plant at Foskor, and the procedure was briefly as follows. Samples of pulp were withdrawn from the plant at various points in the circuit, as shown in the schematic diagram of the pilot plant in Fig. 5, and at regular intervals of one hour to 90 minutes. After the pH value had been measured, the samples were centrifuged and the supernatant solutions were analyzed for Unitol DSR, silicate, calcium, and magnesium. The phosphate content of the solids was also determined. The levels of concentration of the various species in solution were established when the pilot plant was operating under standard conditions, i.e., conditions of reagent addition that were required for maximum recovery at merchant-grade (36.5 per cent P_2O_5). A series of runs was then performed in which the addition of the three relevant reagents (caustic soda, sodium silicate, and Unitol DSR) was varied. This was to establish the effect of different concentrations on grade and recovery.

When the plant was running under 'standard conditions', a pronounced variation in concentration of the reagents was obtained, although the metallurgy of the plant was normal. Similar behaviour has been observed by two other groups of workers. Woodcock and Jones[26, 27], in measuring up to 19 chemical parameters in flotation pulps in six Australian lead-zinc plants, observed that vastly different chemical environments existed in the six plants, with a great variability at many points in each circuit. Although this finding suggests that chemical control of these plants is unlikely to be effective, this deduction cannot be confirmed because Woodcock and Jones do not quote metallurgical performance data. However, correlations between some of the variables measured, viz., pH, redox potential, and oxygen concentration in solution, were obtained. Plaksin et al[28] made measurements of the residual xanthate concentrations at various points in a flotation plant processing copper-lead-zinc-pyrite ore. They, too, found that the residual concentration of xanthate varied within wide limits, although the performance of the plant remained satisfactory. Decrease in the xanthate dosage rate likewise did not adversely affect plant performance, although it lowered the residual xanthate concentration.

Although this result was disappointing from a control point of view, some interesting figures concerning the uptake of the reagents during the conditioning stages were obtained.

Comparison of the concentration of Unitol DSR in solution in the flotation feed (8.1 p.p.m.) with the theoretical initial concentration (105 p.p.m.) indicated that a large proportion had apparently been removed from solution in the 2-minute period after its addition. However, from a previous study of the absorption of sodium oleate on pure apatite[4], it was shown that the amount of Unitol DSR that could be absorbed on the apatite fraction of the phoscorite was only ca 4 per cent of the amount that appeared to have been removed from solution. A hypothesis that could be put forward to explain this anomaly is that there was not time for

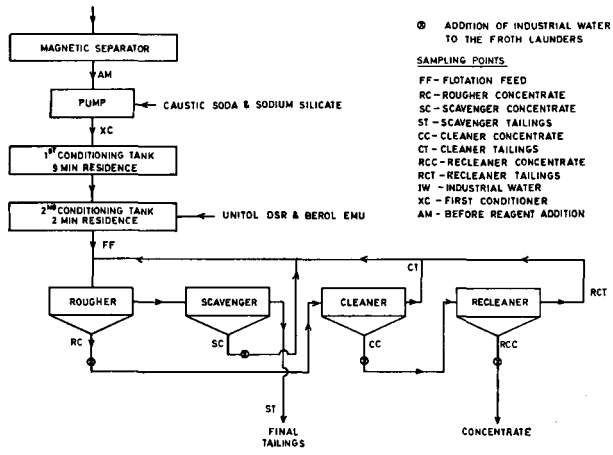

Fig 6

saponification to be completed before sampling took place and that the droplets of unsaponified material were separated from the solution during centrifugation.

The corresponding decrease in soluble silicate concentration (from 150 to 108 p.p.m. of silicon) could be explained by its precipitation as calcium and magnesium silicate, especially since the levels of these two ions in solution decreased sharply when sodium silicate was added to the circuit.

Variation in the addition of caustic soda to the plant had the expected effect on pH, but these changes had little effect on the flotation performance (Fig. 6). The levels of Unitol DSR and silicate in solution increased with increase in pH, whereas magnesium decreased, persumably because of formation of the hydroxide. However, the results did suggest that, within the range of values tested, the concentration of caustic soda is not a controlling variable.

TABLE III
RATES OF DECOMPOSITION OF SOLUTIONS OF POTASSIUM ETHYL XANTHATE AT pH 8[22]

Atmosphere	Metal ion added	Half-life of decomposition h
N_2	—	520
O_2	—	520
O_2	Zn^{2+}	520
	Mn^{2+}	500
	Ba^{2+}	450
	Al^{3+}	435
	Pb^{2+}	435
	Ni^{2+}	373
	Hg^{2+}	352
	Cu^{2+}	335
	Sn^{2+}	310
	Co^{2+}	310
	Fe^{3+}	236
N_2	Any of the above	520

The effect of silicate concentration on grade and recovery was more pronounced and is shown in Fig. 6. These results are unusual in that variations in grade and recovery are parallel.

The effect of Unitol DSR concentration on performance is also shown in Fig. 6. No real effect on either grade or recovery is apparent beyond a solution concentration of ca 8 p.p.m., and this surprising observation may indicate that the species of Unitol that is important in flotation is not measured in solution. This would be the case if the unsaponified material—whose existence was suggested earlier—was to govern the hydrophobicity of the particles. The failure of different additions of Unitol to affect the pH value of the pulp provides some confirmation of this mechanism.

More detailed analysis of the results by multilinear, stepwise regression analysis did not produce any meaningful correlations with flotation performance, although silicate was shown to be a significant variable. That silicate concentration is not an important variable for control purposes, however, is apparent in Fig. 7, where recovery is plotted against silicate concentration in the feed. The figure includes the results of the 'standard' runs as well as those of the runs in which the addition rates of both silicate and the other reagents were varied. The best computed straight line is shown. However, if the distribution of points is such that a large number fall within a narrow range of recoveries and concentrations (as occurs here), such a line is misleading because the least squares treatment gives undue weight to the few data that lie outside these ranges. These extreme conditions, however, are artificial and would not be likely in practice. Therefore, without a more complete understanding of the part played by silicate, this variable could not be used as a control of the process.

It was established, therefore, that solution-concentration variables cannot provide a useful basis for the control of the Foskor process. Such a conclusion, however, raises some important considerations. It suggests that the interaction between calcite and apatite and the fatty acid collector, the magnitude of which should be indicated by the residual concentrations in solution, is not an important factor in this process. Alternatively, if the essential relationship between adsorption of collector and floatability is accepted, it suggests that this adsorption is not relately uniquely to the concentration of reagent in solution. From this particular study, neither of these alternatives can be invalidated, although there are strong indications that the amount of Unitol DSR at the conditioned apatite surfaces was not related to the concentration in solution because of the presence on the mineral surface of unsaponified material. However, further work is necessary to substantiate this picture.

PROSPECT

In the future, the work of the N.I.M. group on the physicochemical aspects of flotation will be broadened to

TABLE IV

PRODUCTS EXTRACTED FROM SULPHIDE SURFACES

MX=metal xanthate X_2=dixanthogen NPI=no positive identification

Mineral	Normal Alkyl Xanthates					
	Methyl	Ethyl	Propyl	Butyl	Amyl	Hexyl
Orpiment	NPI	NPI	NPI	NPI	NPI	MX
Realgar	NPI	NPI	NPI	NPI	NPI	MX
Sphalerite	NPI	NPI	NPI	NPI	NPI	MX
Stibnite	NPI	NPI	NPI	NPI	NPI	MX
Antimonite	NPI	MX	MX	MX	MX	MX
Cinnabar	NPI	NPI	NPI	NPI	NPI	MX
Galena	MX	MX	MX	MX	MX	MX
Bornite	NPI	NPI	MX	MX	MX	MX
Chalcocite	NPI	NPI	MX	MX	MX	MX
Covellite	X_2	X_2	X_2+MX	X_2+MX	X_2+MX	X_2+MX
Chalcopyrite	X_2	X_2	X_2	X_2	X_2	X_2
Pyrite	X_2	X_2	X_2	X_2	X_2	X_2
Pyrrhotite	NPI	X_2	X_2	X_2	X_2	X_2
Arsenopyrite	X_2	X_2	X_2	X_2	X_2	X_2
Alabandite	NPI	X_2	X_2	X_2	X_2	X_2
Molybdenite	X_2+?	X_2+?	X_2+?	X_2+?	X_2+?	X_2+?

cover aspects of the process other than the interaction between reagents and mineral surfaces. Although the knowledge gained of this aspect confirms the group's initial belief that it is one of the keys to the understanding and the more systematic development and operation of flotation processes, it is certainly not the only one.

Least understood and, according to present thinking at N.I.M., most vital of these key areas is the link between the chemical reactions that take place at a surface and the flotation properties that result. To lend this opinion point, reference has only to be made to the study described here of the products of reaction between various sulphide minerals and thiol reagents. Although the products of reaction are now known, it is not possible to gauge the significance for flotation of the observed differences. To provide this link will be one of the goals of the expanded programme of the group. Being planned at present is an investigation of the interaction of air bubbles with hydrophobic surfaces — the ultimate aim of which is to provide an explanation of the way in which the attachment and detachment of bubbles depend on the chemical composition of the surface. This work will naturally include studies of the mechanism by which non-polar additives operate in processes such as agglomeration flotation.

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