Complex sulphide ores

Role of surface chemistry of fine sulphides in their flotation

P. Somasundaran

their flotation

P. Somasundaran B.Sc., B.E., M.S., Ph.D.
Henry Krumb School of Mines, Columbia University, New York, U.S.A

Synopsis

Although the flotation of sulphide ores has been practised and studied for almost 75 years, the mechanisms that govern the interfacial processes that are involved in flotation and flocculation are poorly understood, mainly because of the difficulties of identifying and controlling the surface species, as well as the solution species, under various conditions. Complications arise from the effects of oxidation and surface mineralogical heterogeneity. The physico-chemical behaviour of sulphides is further complicated for complex sulphides when the minerals are present in a finely dispersed form.

The suggested mechanisms for flotation of sulphides with and without thiol collectors are reviewed. The effects of pretreatments, including oxidation, electrochemical polarization and surface heterogeneity are considered. In addition, the potentials for the use of selective flocculation processes and of special chelating reagents as float aids are reviewed and certain major research needs in this area are identified.

Résumé

Bien que la flottation des minerais de type sulfure ait été utilisée et étudiée depuis près de 75 ans, les mécanismes qui gouvernent les processus interfaciaux mis en oeuvre dans la flottation et la floculation sont mal compris. Cela est dû essentiellement aux difficultés rencontrées dans l'identification et le contrôle des produits en surface et en solution sous différentes conditions. Les complications sont dues aux effets de l'oxydation et à l'hétérogénéité minéralogique en surface. Le comportement physico-chimique des sulfures est de plus rendu plus compliqué dans le cas des sulfures complexes lorsque les minéraux sont finement dispersés.

Cet article passe en revue les différents mécanismes de flottation des sulfures proposés avec et sans thiols collecteurs. Les effets de la préconcentration comprenant, en outre, l'oxydation, la polarisation électrochimique, et l'hétérogénéité en surface, y sont abordés. L'avenir des méthodes de floculation sélective et des agents chélateurs spéciaux en tant qu'adjuvants de flottation est examiné et certains domaines où une recherche est vitale sont indiqués.

Zusammenfassung

Obwohl das Flotationsverfahren für schwefelhaltige Erze seit nahezu fünfundsiebzig Jahren ausgeübt und auch studiert wird, ist man sich über die Mechanik der sich während der Flotation und Ausflockung abwickelnden Grenzflächenvorgänge noch keineswegs im klaren. Das liegt in erster Linie am Problem der Identifizierung und Kontrolle der Oberflächen- sowie der Lösungsart unter verschiedenartigen Bedingungen. Weitere Schwierigkeiten erwachsen aus den Auswirkungen der Oxydation und der mineralogischen Oberflächen-Heterogenität. Im Fall verwachsener Erze wird das Verständnis des physikalisch-chemischen Verhaltens noch weiter durch die Anwesenheit der Mineralien in fein-dispergierter Form erschwert.

Der Artikel bietet eine Übersicht über Vorschläge zur Mechanik der Flotation von schwefelhaltigen Erzen mit und ohne Merkaptan-Sammler. Die Auswirkungen der Vorbehandlung, einschließlich Oxydation, elektrochemischer Polarisation sowie der Oberflächen-Heterogenität, werden ebenfalls behandelt. Die Möglichkeiten selektiver Ausflockung und besonderer Chelier-Reagenzien als Schwimmhilfen werden gleichfalls kritisch untersucht, und gewisse Gebiete, die eingehender Forschung bedürfen, werden aufgezeigt.

Riassunto

Sebbene la flottazione dei minerali di solfuro sia stata praticata e studiata per quasi 75 anni, la meccanica che presiede ai processi di interfacie coinvolti nella flottazione e flocculazione sono poco compresi. Ciò è principalmente dovuto alle difficoltà nell'identificare e controllare le specie di superficie come pure le specie in soluzione in diverse condizioni. Le complicazioni sorgono dagli effetti dell'ossidazione e dall'eterogeneità mineralogica della superficie. Il comportamento fisico-chimico dei solfuri è ulteriormente complicato per i solfuri complessi quando i minerali sono presenti in una forma di elevata dispersione.

In questo saggio viene passata in rassegna la meccanica proposta per la flottazione dei solfuri con e senza tiol collettori. Vengono presi in considerazione gli effetti dei pre-trattamenti, inclusa l'ossidazione, la polarizzazione elettrochimica e l'eterogeneità della superficie. Vengono anche passate in rassegna le possibilità per l'uso di processi particolari di flocculazione e di speciali reagenti chelanti come ausilii per la flottazione e vengono identificate alcune principali esigenze di ricerca in questo campo.

gathered unprecedented importance in recent years as we are being forced to treat finely disseminated ores to meet the increasing demand for minerals. It has also become necessary to develop techniques to process the fine wastes that are invariably generated in large tonnages during the beneficiation of such ores. Even though this problem has received more attention in the area of non-metallic ores, it is also significant and possibly more complex in the processing of sulphides. For example, in the processing of Climax molybdenum ore, which is of a finely disseminated nature, most of the loss in the flotation of the 85% −44-μm feed is in the −5-μm size fraction.[1] The problem of loss of finely disseminated values during the processing of sulphides has been illustrated best by Arbiter recently in his discussion of the processing of New Brunswick zinc–lead–copper ores and the McArthur River prospect in Australia.[2] In the case of the New Brunswick ore flotation of the −325 mesh feed is reported to recover only 70% of lead at 30% concentrate grade and 70% of zinc at 50% concentrate grade, whereas in the case of the McArthur River prospect pilot tests showed only a dismal 20% recovery of zinc (50% concentrate) and less than 50% recovery of lead (50% concentrate). With several ores, such as pentlandite–pyrrhotite ore, there is apparently no concentration below −20-μm size.[3] The dependence of flotation on particle fineness was clearly shown by Trahar and Warren[4] for the case of sphalerite flotation in laboratory as well as in operating mills (Fig. 1). It is seen that recovery falls substantially below about 10 μm as well as above 100 μm. For us to be able to beneficiate such fines it will undoubtedly be helpful to establish the reasons for the poor response of the fines. Inasmuch as very little basic work has been done with different sulphide fines, this problem can be analysed at this point only in general terms.

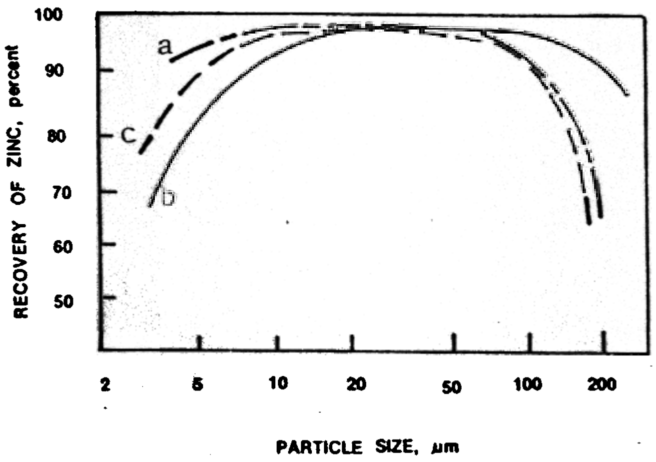

Fig. 1 Dependence of flotation recovery of sphalerite on particle size under batch and operating mills conditions: (*a*) batch flotation; (*b*) zinc circuit at Broken Hill South; (*c*) zinc circuit at Morning mill (data in literature compared by Trahar and Warren[4])

Factors in sulphide fines flotation

The problem of the flotation of sulphide fines results from a number of contributory factors that are not always mutually exclusive. They include general factors because specific to sulphides, such as oxidation and mineralogical alterations. Results given by Trahar and Warren[4] for the size range of various minerals for maximum recovery in increasing order (galena, 6–70 μm; sphalerite, 8–90 μm; pyrrhotite, 9–40 μm; chalcopyrite, 15–60 μm; arsenopyrite, 15–120 μm; and pyrite, 20–150 μm) do not suggest any correlation for either the maximum or minimum size with their specific gravities. Clearly, other factors, such as surface composition and oxidation, or even shape and dissolved ions concentrations, play an important role in determining the flotation of fines of these minerals.

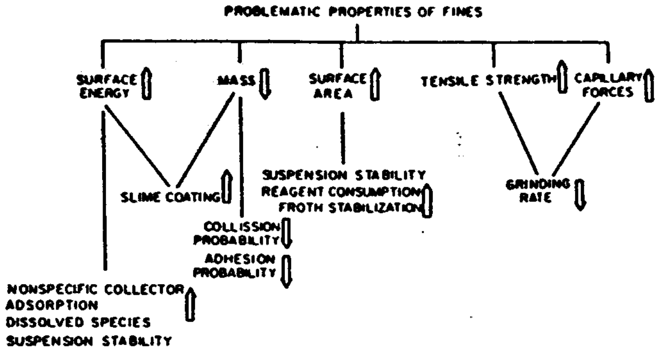

Fig. 2 Change in some major properties of particles with increase in fineness

Mineral properties that undergo significant changes in the fine and colloidal size range include mass, surface area, surface energy and rugosity (Fig. 2).[5,6,7] All these factors can contribute towards the poor flotation of fines. It should be noted that it will, however, be incorrect to suggest that there is an intrinsic lower size limit for flotation, since even ions can be floated, even though under different aeration and agitation conditions.[8,9]

Although increase in surface area or surface energy might not have any direct role in determining the lower size limit for flotation, decrease in mass will indeed lead to reduced momentum for collision by inertial impact and, hence, reduced flotation. On the other hand, the detachment rate of already attached particles on the bubbles in turbulence is also likely to be reduced with decrease in size. More important in determining adhesion during collision might be the change in roughness or shape of particles with decrease in size. Hematite samples of various size fractions that were examined for the change in rugosity clearly showed it to be significant as the size approached that of sub-micron slimes.[10] Recently, Finch and Smith[11] have compared the shape of 30-μm and −7-μm hematite particles. The coarser particles that were readily floated appeared to show higher angularity; the fines were, however, less clearly resolved in the micrographs, which made any definite conclusion difficult.

In contrast to the above possibility, certain ores can exhibit increased angularity when broken down to colloidal size range because of the dispersal of fibrous clay minerals. Our study with natural hematite, in fact, showed increased angularity in the slimes range (Fig. 3).

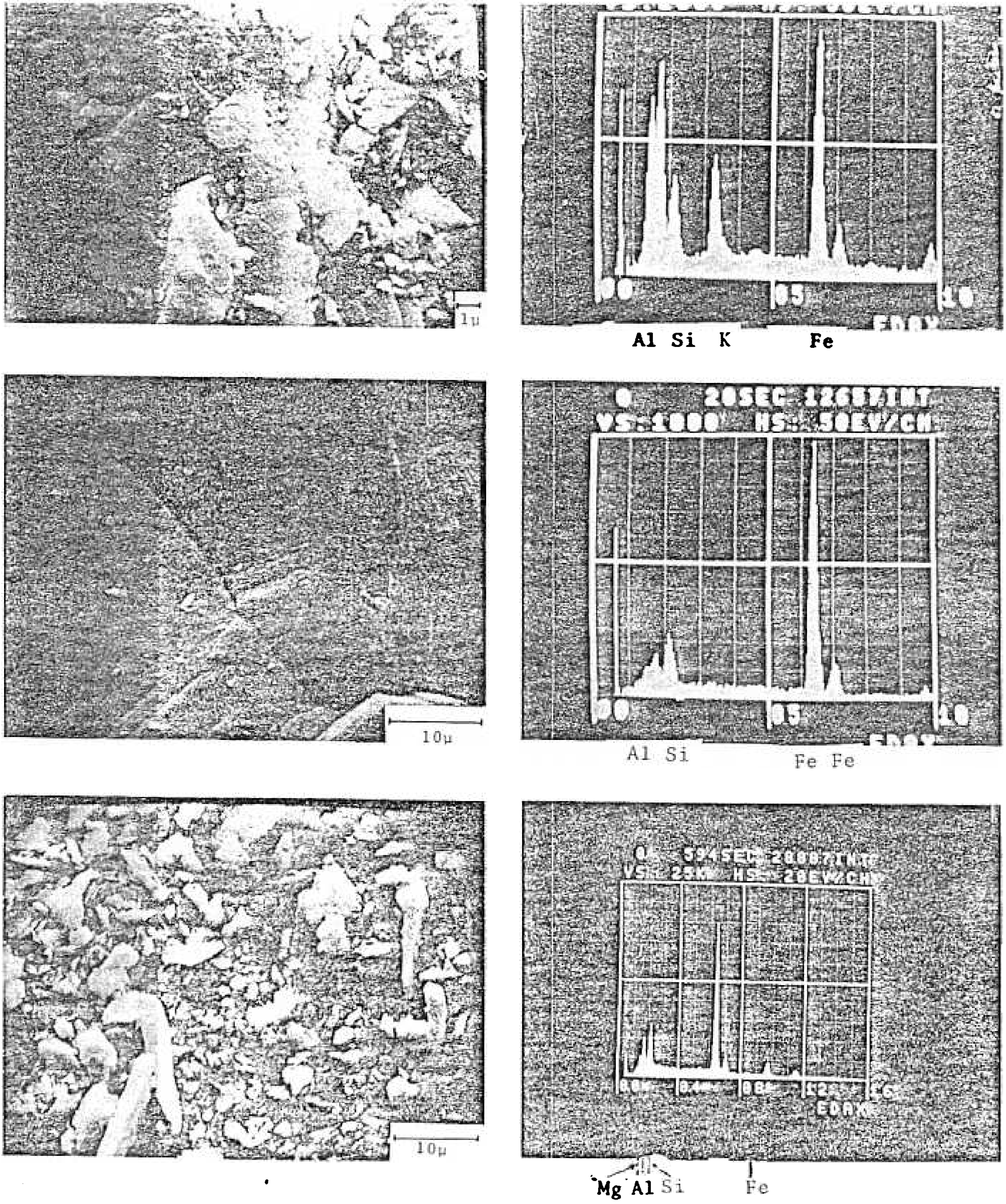

Fig. 3 Scanning electron photomicrographs and EDAX analysis of (*a*) (*top pair*) unwashed coarse hematite; (*b*) (*centre pair*) washed coarse hematite; and (*c*) (*bottom pair*) hematite slime obtained by washing

Rugosity of the surface or shape of the particles will affect the probability of adhesion to bubbles and, hence, the rate of flotation. An angular particle can be expected to cause rupture of the intervening liquid film between the bubble and the particle much more easily than a spherical particle.

Similarly, detachment might also occur much more easily with the spherical particle than with an angular particle. Anfruns and Kitchener[12] have confirmed a decrease in recovery for both the irregularly shaped silica fractions and spherical polystyrene spheres down to sub-sieve size range. The efficiency of collection has been of 600- and 1000-μm diameter—in general agreement with the estimated exponential dependence of flotation efficiency on particle size.

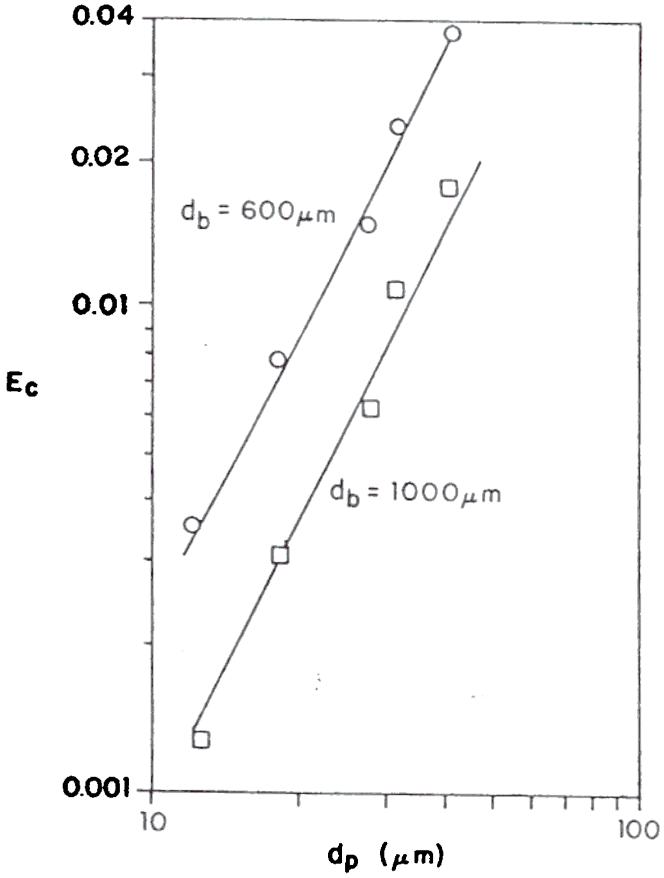

Fig. 4 Collection efficiencies, E_C, of quartz particles as a function of size for two bubble sizes. Data of Anfruns and Kitchener[12] as treated by Arbiter[2]

The exponent has been calculated to be 1,[12] or, more rigorously, 1.5 to 2.[13] The corresponding value for latex particles is 0.4.[14] The experimental and theoretical estimates thus clearly show a decrease in flotation with fineness. Similar dependence on particle size was obtained also by Gaudin *et al.* for galena flotation with xanthates.[15] Below a particle size of about 4 μm flotation rate remained constant, this being attributed to the flocculation. If the decrease in flotation with size is intrinsic with the current flotation systems that are dependent on collision between particles and bubbles, the remedy lies evidently in developing such techniques as vacuum flotation and dissolved air flotation, where the bubbles are generated on the particles selectively or in pre-aggregating the desired particles before flotation. To the author's knowledge there has, however, been no detailed study of the potential of either vacuum flotation or dissolved air flotation for the beneficiation of sulphide fines. There have been a few laboratory-scale studies of selective aggregation of sulphides, and this topic is discussed later.

Liberation and oxidation problems

Any such technique as vacuum flotation can, indeed, become useful only if the fines can be made hydrophobic fines. With certain sedimentary phosphates, for example the mineralogy is different in the sub-sieve size range, aluminium and iron phosphates being the predominant phosphate components. For sulphides an additional serious problem is the increased oxidation of fines. Oxidized portions of the sulphide ores are often concentrated in the sub-sieve fractions. Although some amount of oxidation is considered beneficial for the flotation of sulphides, fines that are heavily oxidized are not floated with conventional reagents.

Oxygen and native floatability

The role of oxygen and oxidation has been the subject of much controversy for decades. As early as the 1930s, although a number of scientists considered sulphides to be floatable without the use of collectors,[16] and therefore inherently floatable, others[17-21] contended that collectorless flotation resulted from the contamination of minerals, excessive oxidation during drying or collector action of frother components or impurities. Taggart and co-workers[17] observed that the galena, when leached free of oxidation products and tested in what they considered to be an oxygen-free atmosphere, did not float with xanthate, which suggests that sulphides are not actually naturally floatable. In contrast, Ravitz and Porter[22] and, more recently, Fuerstenau and Misra[23] observed that cleaned galena samples are indeed floated without collector under oxygen-free conditions. Fuerstenau and Misra observed similar flotation for pyrite and chalcopyrite and, to a lesser extent, for sphalerite. Although such observations and counter-observations continued without resolution of the actual problem, a noteworthy contribution came in 1977 from Heyes and Trahar,[24] who clearly showed that chalcopyrite was naturally floatable but not under reducing conditions. Whereas chalcopyrite in a glass mill under nitrogen exhibited natural floatability, the same mineral in an iron mill did not float, presumably because of the reducing conditions. Interestingly, chalcopyrite ground in such iron mills, but with oxygen or oxidizing agents such as NaOCl, exhibited floatability (Fig. 5).

Measurements of pulp potential under these conditions showed a clear correlation between the potential and

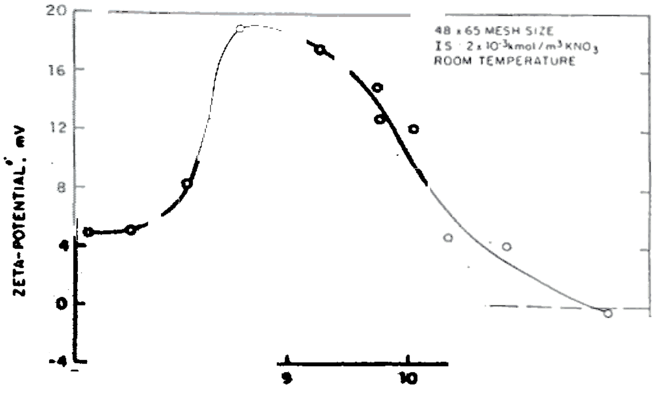

Fig. 5 Flotation of chalcopyrite ground under nitrogen in iron mill *before* and *after* conditioning with oxygen. After Trahar and Warren[4]

+100 mV and non-flotation below about −100 mV. Similar correlations between potential and flotation or contact angle have also been reported.[25,26]

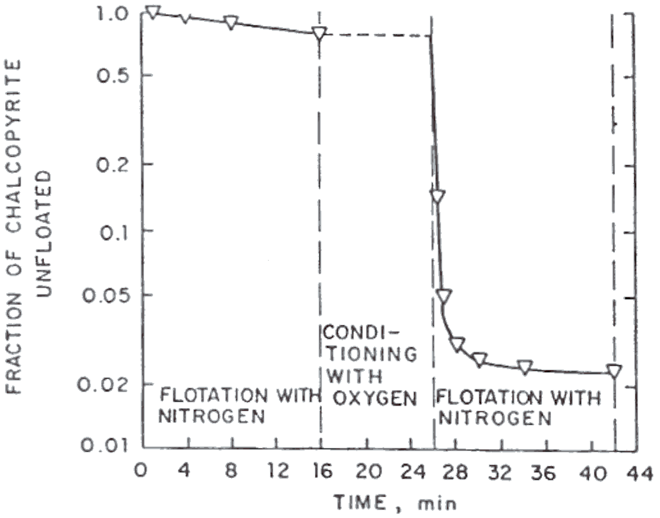

Fig. 6 Diagram illustrating dependence of flotation of chalcopyrite on potential. After Trahar and Warren[4]

Although a correlation has thus been shown between potential and flotation, the precise mechanism by which the electrochemical potential or oxidants and reductants control the flotation remains largely unclear. Suggested possibilities include oxidation of the sulphide to elemental sulphur or to various sulphoxide anions, oxidation of collectors such as xanthates (X^-) to dixanthogen (X_2), and chemisorption of xanthates.

$$PbS + 2X^- + \tfrac{1}{2}O_2 + 2H^+ \rightarrow PbX_2 + S + H_2O$$

or

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

or

$$PbS_{(s)} + NaX \rightarrow PbS_{(s)}X_{(adsorbed)} + Na^+ + S_xO_y^-$$

In addition to the above, major mechanisms considered for the flotation of sulphides with thiols have included adsorption of their neutral acids, precipitation of metal thiolates and adsorption of thiolates by ion exchange.[36] The observed dixanthogen formation on certain minerals—for example, galena—is now suspected to be the result of the analytical techniques used. Fractional coverages by chemisorbed heavy metal thiolate can be sufficient to impart hydrophobicity to the minerals. It is indeed possible that co-adsorption of neutral acid or dixanthogen can enhance the degree of hydrophobicity. In any case, minerals that have a potential in excess of thiol–disulphide reversible potential should be expected to have disulphide as a reaction product whether it is mainly responsible for flotation or not.

Role of elemental sulphur and dixanthogen

Gardner and Woods,[25] among others, have attributed the natural flotation to elemental sulphur formed on the

al.[27] have found no correlation of flotation with sulphur on the surface. Unfortunately, the technique used by these authors to detect sulphur on the surface or to remove it for analysis cannot be considered reliable for this purpose. First, it is not established whether attempts to leach the surface sulphur by acetone or pyridine are successful in removing it *completely*. Secondly, it is conceivable that sulphur might form or reform, even if previously leached, during subsequent flotation. Clifford and co-workers,[28] by use of the ESCA technique, have reportedly observed sulphur on sulphides ground in air. This technique also has the potential for similar complications, however, since the samples must be dried and subjected to high vacuum for the analysis. Granville and co-workers[29] had earlier speculated that the formation of sulphur on galena in the presence of dixanthogen was the reason for its flotation with xanthate, since they could not detect dixanthogen itself on xanthate-treated galena by use of infrared spectroscopy. Again, problems arising from the difficulty of using experimental techniques under *in-situ* conditions should be noted.

An additional complication in the above procedures results from our lack of knowledge of the amount of hydrophobic entity required on the surface for inducing flotation. Sulphur or dixanthogen in smaller amounts can conceivably be sufficient to cause bubble attachment, particularly if it is present on the surface in patches. Even though it must be obvious to workers, spectroscopic techniques with an inherent potential for introducing complications are still used to study mechanisms of interaction of minerals with reagents. These techniques do have their use, but their limitations have to be fully recognized lest misleading conclusions be disseminated. Identification of reaction products and the original reactant species on the minerals will remain an important task for the advance of flotation chemistry, but only if cautiously conducted. Any change in the environment or mechanical or chemical pretreatment that the minerals are usually subjected to during experimentation can affect the properties of minerals.

Pretreatment effects

Marked effects that grinding, leaching, drying, storage, etc., can produce have been discussed and emphasized by the author and his co-workers on several occasions.[10,30–33] Such effects have been considered particularly for the isoelectric point of both oxides[31,33,34] and sulphides.[35] The isoelectric point is a useful and popular interfacial parameter in flotation research, since it can be determined experimentally, at least with non-conducting minerals, and since the adsorption of various organic and inorganic ions on minerals under certain conditions will be governed by its location with respect to the concentration of potential-determining ions in solutions under consideration. It is to be recognized that this parameter can be altered significantly by various factors, such as pretreatment of the solid, extent of aging and storage, as well as pH and commonly used cleaning procedures, such as leaching in acidic or hot solution, can drastically affect the magnitude and sign of the zeta-potential.[33] In addition, Kulkarni and Somasundaran[10] have recently shown that the surface-chemical heterogeneities of these particles can also contribute significantly to wide alterations in zeta-potential. Although such effects have been considered in detail mainly only for oxides and silicates, Healy and Moignard[35] have shown sulphides to be similarly sensitive to these treatments. These authors found the isoelectric point of zinc sulphide to vary anywhere from pH 4 to 8, depending on the pH of equilibration, and, surprisingly, even on pulp density. They attributed the lower isoelectric point to the formation of elemental sulphur in acidic solutions and the high isoelectric points to that of zinc oxide–zinc hydroxide precipitate in basic solutions. The authors have not reported any direct evidence for the formation of sulphur or oxide on the mineral. Their suggestions result from the correlation of the changes in the isoelectric point of the sulphide to the isoelectric points of sulphur (pH$\sim$2) and zinc oxide–hydroxide (pH$\sim$8.5). An isoelectric point of pH 11.6 obtained[37] for pentlandite in the basic pH region and another indicated point below pH 7 are possibly the result of such surface alterations (Fig. 7). If sulphur or oxide is present on sulphides, depending on various solution conditions, it becomes important to identify the role of all solution properties altered intentionally or otherwise in surface reactions to conduct a realistic and useful study of sulphide flotation chemistry.

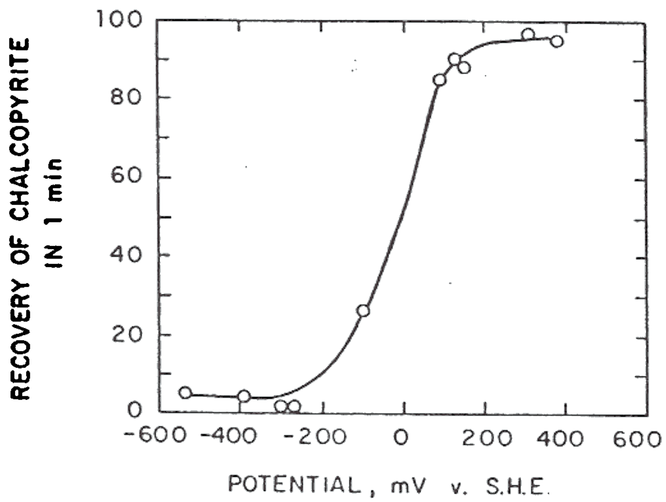

Fig. 7 Zeta-potential of pentlandite stored in triple-distilled water (not deaerated) as a function of pH[37]

Surface impurities and precipitates

In addition to oxides, the presence of various impurity elements on the sulphide surface is also of much consequence. This has been adequately illustrated by Finkelstein and Allison[38] for sphalerite flotation with ethyl xanthate. They cited the observation of Girczys and Laskowski[39] that the flotation of their sphalerite with ethyl xanthate without activation was due to the presence of iron in the sample, which dissolved to showed that there was no difference between the flotation response of sphalerite that contained 0.3% Fe and that of marmatite with 8.8% Fe. Finkelstein and Allison noted that this discrepancy could have resulted if the sphalerite used by Girczys and Laskowski had contained copper, which could activate it for flotation.

Similar confusion exists with the depression of sphalerite with zinc salts. Although there is considerable evidence that these salts act by the precipitation of zinc complexes similar to bulk $Zn(CN)_2$, $Zn(OH)_2$, $ZnCO_3$, etc., on the surface, it is not clear why such precipitates should adsorb in multilayers on the sphalerite to depress it, or why some of these complexes are better depressants than the others. In most studies $ZnSO_4$ and Na_2CO_3 are used in combination.

Again, the precise mechanism by which these reagents interact or the need for carbonate claimed by Vainshenker and co-workers[41] for depression is not established.

Float aids and flocculants for sulphide fines beneficiation

Identification of surface species has another important benefit, since such information can be used to develop new processing chemicals with sufficient selectivity in the ultrafine size range or to modify the currently used chemicals for similar ores.

Oxidized ores have been known to respond to flotation agents very poorly.[42] They also respond to depressants differently, as was shown by Shimoiizaka *et al.*[43] in their study of depression of galena with sulphite and chromate. It was observed by these authors that only oxidized galena could be depressed by sulphite or chromate (except at neutral pH with the latter), presumably because of the deposition of lead sulphite or lead chromate on the mineral surface. Comparison of

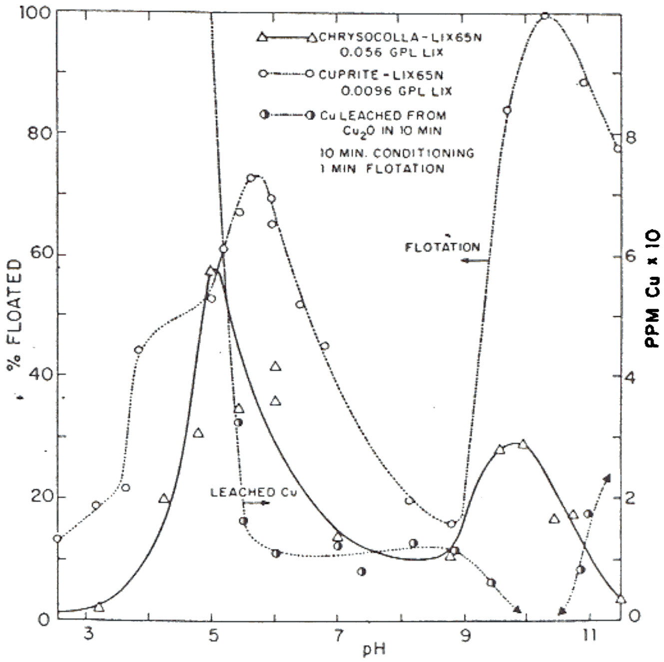

Fig. 8 Flotation of chrysocolla and cuprite with LIX 65N and correlation with solubility of cuprite[45]

Figs. 3 and 5 in Shimoizaka et al., for example), it is not possible to draw any definite conclusions on the reasons for the effect of oxidation on depression. Oxidized copper ores have been beneficiated successfully recently by use of reagents with oxime functional groups that chelate with copper.[44–47] Oxidized sulphide *fines* have also been beneficiated with these reagents in our laboratory. Flotation of chrysocolla and cuprite with LIX 65N is illustrated in Fig. 8. Flotation was found in these cases to have a correlation with the solubility of the mineral. Thus, an increase in their solubilities was found to correspond to a decrease in the flotation and vice versa. Similarly, increase in ionic strength (which enhances the solubility of the mineral), or addition of copper, decreased the flotation of both minerals. This is possibly due to the depletion of LIX in the bulk aqueous phase in the form of a Cu–LIX chelate, which may have no collecting property. As expected, the more refractory chrysocolla floated less than cuprite.

Specificity of groups towards metal ions can also be utilized for the beneficiation of sulfide fines by incorporating such groups into polymeric flocculants. A good example of this is the flocculation of chalcopyrite that can be obtained by the use of *xanthated* hydroxypropyl cellulose[48] (see Fig. 9); quartz was not adsorb on sulphides and the better performance of the cellulose xanthate on chalcopyrite than on quartz is due to similar adsorption of the xanthated polymer on the chalcopyrite particles. With ores, selective flocculation is often made difficult because of the interference from dissolved ions. Again, as in flotation, additives that can complex with such dissolved ions or adsorb on mineral particles selectively to modify them can be used to enhance the selectivity in such cases. Attia and Kitchener[49] have reported the possibility of the depressing flocculation of heavy minerals by xanthates with reagents of the type sodium sulphide, polyphosphate and polyacrylates. In contrast, an interesting example of activation of selective flocculation has been recently developed by Rubio and Kitchener.[50] Selective flocculation was obtained by these authors by use of hydrophobic polymers on minerals that are preconditioned with surfactants to produce a hydrophobic surface.

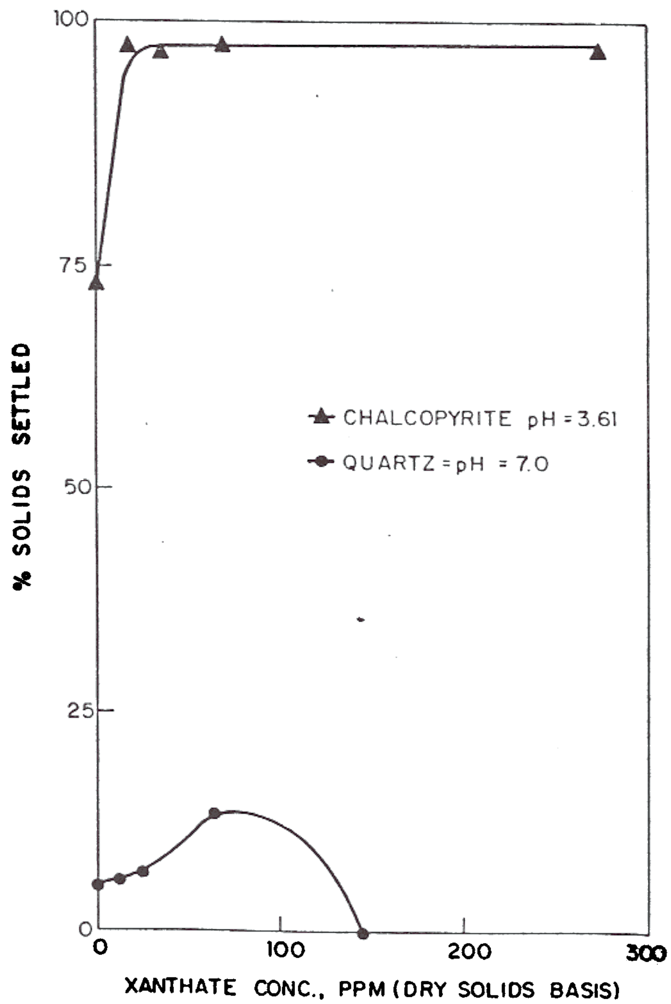

Fig. 9 Percentage of chalcopyrite fines and quartz fines settled as a function of concentration of hydroxypropyl cellulose xanthate: reagentizing time, 30 sec; settling time, 45 sec[67]

The principles that govern selective flocculation have been reviewed by the author recently.[6,7] Briefly, it is dependent on selective interaction between particles that are in a totally dispersed state. Major component events to be considered in selective flocculation are collision between particles, adhesion during collision and detachment.

Although collisions can be influenced to some extent for selective flocculation by agitation, as in the case of carrier flotation,[51,52] it is adhesion that can actually be manipulated to obtain the required selectivity. The probability of adhesion during collision will be determined by the size of the particles as well as the nature of the total interactions between them. Interactions to be considered include London–van der Waals attractive forces, electrical double-layer forces, steric forces that arise from the overlap of the adsorbed layers and bridging forces that result from the multi-particle adsorption of single polymer species. An analysis of available data suggests that, at least in principle, it should be possible to obtain selective aggregation of mineral fines by controlling the zeta-potential (ζ) of various mineral components ($1, 2, 3, \ldots n$) so that, say, $|\zeta_1| < \sim 15$ mV and $|\zeta_2|, \ldots |\zeta_n| > \sim 30$ mV and $\frac{\zeta_1}{\zeta_2} = +, \ldots \frac{\zeta_1}{\zeta_n} = +$, or by selective adsorption of coagulants or flocculants. In practice, selectivity is rarely achieved by the control of zeta-potential alone and it therefore becomes necessary to use polymers to obtain the required selectivity. In addition to bridging, polymers, when adsorbed on particles, also cause flocculation by shifting the zeta-potential so that the electrical nature of the interfaces that might not have been originally conducive to selective aggregation assumes a secondary role. Evidently, success with the use of polymers will depend on the selective adsorption on the mineral particles to be flocculated. Fundamentals of adsorption of polymers have been reviewed recently.[53]

Adsorption of polymers on minerals can take place due to hydrogen bonding, electrostatic bonding or covalent bonding of functional groups with mineral surface species. Adsorption of most non-ionic polymers

Selectivity of bulk flocculants can be enhanced by incorporating functional groups in the polymer structure and by altering the interfacial potential of the mineral to create the required electrostatic interactions between the mineral surface and the polymer. The role of electrostatic adsorption has been discussed by Yarar and Kitchener for the case of selective flocculation of galena from a mixture of it with other minerals.[54] They noted that galena flocculation with an anionic polyacrylamide can be promoted by the addition of lead nitrate and inhibited by that of lead sulphide. If the galena were dried in air, however, it did not undergo selective flocculation from quartz, presumably because of the reduction of zeta-potential of galena to close to zero by oxidized lead salts and consequent aggregation with quartz as well. Similarly, no selective flocculation could be obtained with a mixture of galena and calcite without an additive, since the zeta-potentials of these minerals were not sufficiently high for the required predispersion.

In general, although selective flocculation has been attempted on both the laboratory and industrial scales for a number of non-sulphide minerals,[55] investigations of its use for systems that contain sulphides has been limited to a few laboratory studies.[49,54,56,57] Usoni *et al.*[56] were among the first to study the separation of a number of metal sulphides, such as galena and sphalerite, from associated quartz with both non-ionic and anionic polymers as flocculants. Interestingly, their results showed the prediction of selective flocculation on the basis of the results from single mineral tests to agree with the results obtained for pyrite–quartz and sphalerite–quartz mixtures with a non-ionic polymer (Separan), but to fail for mixtures of galena–quartz and sphalerite–quartz with anionic Aerofloc or Hercules CMC and for the mixtures of smithsonite–quartz even with Separan, which had worked for all other mixtures. The reason for this discrepancy is not known.

As was discussed earlier, an obvious way to generate selectivity is by incorporating complexing or chelating agents into the polymer. Attia and Kitchener[49] have discussed the possibility of synthesizing such flocculants with chelating groups specific to each metal. Inasmuch as xanthates are used to *selectively* float sulphide minerals, xanthated polymers should be expected to act as selective flocculants for sulphides. Our initial work has, however, been limited to the separation of a sulphide from its mixture with a non-sulphide. Since xanthated hydroxypropyl cellulose was found to flocculate chalcopyrite but not quartz, it was tested as a selective flocculant for a mixture of these minerals. Both grade and recovery of chalcopyrite in the sediment portion were observed to improve with increase in polymer concentration (Fig. 10). At high concentrations of polymer, however, entrapment of the quartz by the bulky chalcopyrite flocs caused a lowering of the assay, and, as shown in Fig. 10, cleaning of the product improved the grade of the sediment.

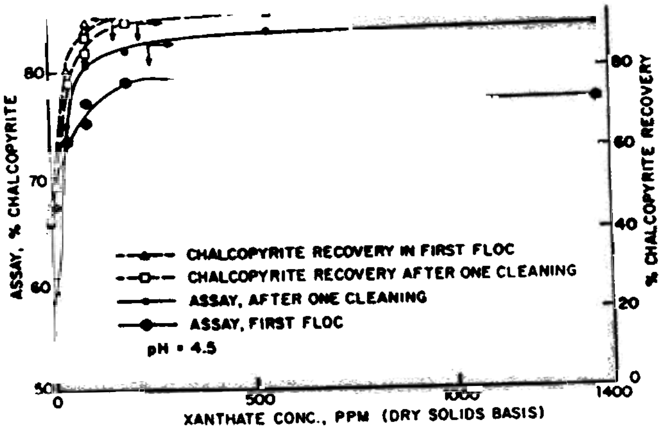

Fig. 10 Recovery and grade (chalcopyrite) of concentrate from selective flocculation of chalcopyrite–quartz mixture as a function of concentration of hydroxypropyl cellulose xanthate; reagentizing time, 30 sec; settling time, 45 sec[53]

Polymers of the above type have a potential for the beneficiation of sulphide fines; it is, however, also necessary to understand possible ways in which they can influence various downstream operations before they can be widely developed for commercial use. Usoni *et al.*,[56] for example, found that the flotation of sphalerite was enhanced by Separan NP10, Aerofloc R550 and Nalco 600 up to certain concentrations, and was depressed above them. This effect was higher at pH 9 than at pH 7. Possibly the increase at low concentrations is due to a fractional surface coverage and consequent flocculation. A more complete coverage at higher concentrations can be expected to retard flocculation, and possibly collector adsorption and, thereby, flotation The reasons for the activating effect at low concentrations and the depressing effect at higher concentrations have not, however, been established and the problem warrants a systematic study.

Concluding remarks

Sulphides were the first major minerals to be floated and have been subjected to the most extensive research during the past 50 years. Yet it is the surface chemistry of sulphides and their interactions with reagents that are least established with any degree of certainty. The past work has taught us much concerning the difficulties and the pitfalls in research and the dangers of using techniques indiscriminately. The path now appears clearer than ever before. With the increased need to treat sulphide fines it is essential that detailed carefully planned work be conducted as a function of relevant variables, such as particle size, pretreatments, dissolved ions, gases, etc., to elucidate the governing mechanisms. Major research tasks in this area include the following.

(1) Identification of investigative techniques and their limitations; standardization of experimentation with respect to sample history, storage conditions, aging and equilibration conditions, including pH, dissolved ions, oxygen content of the solution, and pulp density.

(2) Study of the role of mineralogical heterogeneity and its dependence on particle size.

(3) Identification of the surface species on the minerals

(4) Identification of reaction products of the mineral with the flotation agents and correlation of the presence of various products with flotation.

(5) Elucidation of the direct and synergistic roles of various collector, activator, depressant and flocculant reaction products in flotation.

(6) Identification of the role of the potential and the semiconducting properties of the sulphides in determining adsorption, flotation and flocculation.

(7) Confirmation of activation and depression of various sulphides by dissolved species as well as other mineral components of the ore, including other sulphides.

(8) Understanding of the role of agitation intensity and uniformity and other physico-chemical parameters, such as reagentizing temperature, in controlling adsorption, flotation, aggregation, mechanical entrapment of fines and selective aggregation.

Acknowledgment

The partial support of the Division of Applied Research of the National Science Foundation (DAR-79-09295) and of the International Nickel Company are gratefully acknowledged.

References

1. Duggan E. J. Fine grinding and concentration at Climax. *Min. Metall.*, 27, 1946, 323–9.

2. Arbiter N. Problems in sulfide ore processing. In *Beneficiation of mineral fines* Somasundaran P. and Arbiter N. eds (New York: AIME, 1979), 139–52.

3. Agar G. E. Personal communication.

4. Trahar W. J. and Warren L. J. The floatability of very fine particles—a review. *Int. J. Mineral Process.*, 3, 1976, 103–31.

5. Somasundaran P. Fine particles treatment. In *Research needs in mineral processing* Somasundaran P. and Fuerstenau D. W. eds (New York: Columbia University, 1976), 125–33.

6. Somasundaran P. Principles of selective aggregation. Reference 2, 183–96.

7. Somasundaran P. Principles of flocculation, dispersion, and selective flocculation. In *Fine particles processing* Somasundaran P. ed. (New York: AIME, 1980), vol. 2, 947–76.

8. Somasundaran P. Foam separation methods. In *Separation and purification methods* (New York: Marcel Dekker, 1972), vol. 1, 117–98.

9. Somasundaran P. Separation using foam techniques. In *New developments in separation methods* Grushka E. ed. (New York: Marcel Dekker, 1976), 117–34.

10. Kulkarni R. D. and Somasundaran P. Mineralogical heterogeneity of ore particles and its effects on their interfacial properties. *Powder Technol.*, 14, 1976, 451–61.

11. Finch J. A. and Smith G. W. Contact angle and wetting. *Minerals Sci. Engng*, 11, 1979, 36–63.

12. Anfruns J. P. and Kitchener J. A. The absolute rate of capture of single particles by single bubbles. In *Flotation: A. M. Gaudin memorial volume* Fuerstenau M. C. ed. (New York: AIME, 1976), vol. 2, 625–37.

13. Flint C. H. and Howarth W. J. *Chem. Engng News*, 26, 1971, 1155–61.

14. Reay D. and Ratcliff G. A. Removal of fine particles from water by dispersed air flotation: effects of bubble size and particle size on collection efficiency. *Can. J. chem. Engng*, 51, 1973, 178–85.

15. Gaudin A. M. *Flotation, 2nd edn* (New York: McGraw-Hill, 1957), 374–8.

16. Sulman H. L. The concentration of ores by flotation. *Trans. Instn Min. Metall.*, 39, 1929–30, 548–87.

112, 1934, 348–81.

18. Wark I. W. *Principles of flotation* (Melbourne: Australas. Inst. Min. Metall., 1938), 127.

19. Wark I. W. and Cox A. B. Principles of flotation 1.—an experimental study of the effect of xanthates on contact angles at mineral surfaces. *Trans. Am. Inst. Min. Engrs*, 112, 1934, 189–232.

20. Wark I. W. Methods of separation based on surface properties. *J. Proc. R. Aust. chem. Inst.*, 16, 1949, 387–404.

21. Sutherland K. L. and Wark I. W. *Principles of flotation* (Melbourne: Australas. Inst. Min. Metall., 1955), 489 p.

22. Ravitz S. F. and Porter R. R. Oxygen-free flotation. *Tech. Publ. Am. Inst. Min. Engrs* no. 513, 1933, 17 p.

23. Fuerstenau M. C. and Misra M. Sulfide flotation in the absence and presence of oxygen. Paper presented at 106th AIME annual meeting, Atlanta, March 1977.

24. Heyes G. W. and Trahar W. J. The natural floatability of chalcopyrite. *Int. J. Mineral Process.*, 4, 1977, 317–44.

25. Gardner J. R. and Woods R. The use of a particulate bed electrode for the electrochemical investigation of metal and sulphide flotation. *Austr. J. Chem.*, 26, 1973, 1635–44.

26. Chander S. and Fuerstenau D. W. The effect of potassium diethyldithiophosphate on the electrochemical properties of platinum, copper and copper sulfide in aqueous solutions. *Electroanalyt. Chem. Interfacial Electrochem.*, 56, 1974, 217–47.

27. Finkelstein N. P. *et al.* Natural and induced hydrophobicity in sulfide mineral systems. In *Advances in interfacial phenomena of particulate/solution/gas systems; applications to flotation research* Somasundaran P. and Grieves R. B. eds (New York: American Institute of Chemical Engineers, 1975), 165–75. (*AIChE Symp. Series* no. 150, vol. 71)

28. Clifford R. K. Purdy K. L. and Miller J. D. Characterization of sulfide mineral surfaces in froth flotation systems using electron spectroscopy for chemical analysis. Reference 27, 138–47.

29. Granville A. Finkelstein N. P. and Allison S. A. Review of reactions in the flotation system galena–xanthate–oxygen. *Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.)*, 81, 1972, C1–30.

30. Somasundaran P. Pretreatment of mineral surfaces and its effect on their properties. In *Clean surfaces, their preparation and characterization for interfacial studies* Goldfinger G. ed. (New York: Dekker, 1970), 285–306.

31. Kulkarni R. D. and Somasundaran P. The effect of aging on the electrokinetic properties of quartz in aqueous solutions. In *Oxide–electrolyte interfaces* Alwitt R. S. ed. (Princeton: American Electrochemical Society, 1972), 31–44.

32. Lin I. J. and Somasundaran P. Effect of the nature of environment on comminution processes. *Powder Technol.*, 6, 1972, 171–80.

33. Kulkarni R. D. and Somasundaran P. Effect of pretreatment on the electrokinetic properties of quartz. *Int. J. Mineral Process.*, 4, 1977, 89–98.

34. Smith R. W. and Trivedi N. Variation of point of zero charge of oxide minerals as a function of aging time in water. *Trans. Am. Inst. Min. Engrs*, 256, 1974, 69–74.

35. Healy T. W. and Moignard M. S. A review of electrokinetic studies of metal sulfides. Reference 12, vol. 1, 275–97.

36. Poling G. W. Reactions between thiol reagents and sulphide minerals. Reference 12, vol. 1, 334–57.

37. Ramachandran S. and Somasundaran P. Electrokinetic and flotation properties of pentlandite and pyrrhotite. Paper in preparation.

38. Finkelstein N. P. and Allison S. A. The chemistry of activation, deactivation and depression in the flotation of zinc sulfide: a review. Reference 12, vol. 1, 414–57.

39. Girczys J. and Laskowski J. Mechanism of flotation of unactivated sphalerite with xanthates. *Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.)*, 81, 1972, C118–9.

40. Clifford K. L. Mechanism of the flotation of natural sphalerite with xanthates. Ph.D. thesis, University of Utah, 1971.

41. Vainshenker I. A. Grosman L. I. and Khadzhiev P. G. Depressing of sphalerite flotation by ppts. *Zap. Leningrad Govn. Inst.*, 46, no. 3, 1966, 22–6; *Chem. Abstr.*, 67, 84082x.

42. Formanek V. *et al.* Coarse middlings flotation: application to the beneficiation of Soldado copper ore (Chile). In *Proceedings 11th*

43. Shimoiizaka J. *et al.* Depression of galena flotation by sulfite or chromate ion. Reference 12, vol. 1, 393–413.

44. Nagaraj D. R. and Somasundaran P. U.S. Patent 4 130 415, 1979.

45. Nagaraj D. R. and Somasundaran P. Commercial chelating extractants as collectors: flotation of copper minerals using 'LIX' reagents. *Trans. Am. Inst. Min. Engrs*, in press.

46. Nagaraj D. R. and Somasundaran P. Chelating agents as flotaids: LIX–copper minerals system. In *Recent developments in separation science* Li N. N. *et al.* eds (West Palm Beach, Florida: CRC Press, 1979), 5, 81–93.

47. Nagaraj D. R. and Somasundaran P. Chelating agents as collectors in flotation: oximes–copper minerals systems. Accepted for publication in *Trans. Am. Inst. Min. Engrs*, presented at the 1979 AIME Annual Meeting, New Orleans, preprint no. 79-76.

48. Somasundaran P. Selective flocculation of fines. In *Physical chemistry of mineral–reagent interactions in sulfide flotation. Inf. Circ. U.S. Bur. Mines* 8818, 1980, in press.

49. Attia Y. and Kitchener J. A. Development of complexing polymers for the selective flocculation of copper minerals. Reference 42, 1233–48.

50. Rubio J. and Kitchener J. A. New basis for selective flocculation of mineral slimes. *Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.)*, 86, 1977, C97–100.

51. Wang Y. C. and Somasundaran P. A study of carrier flotation of clay. Reference 7, 1112–28.

52. Wang Y. C. and Somasundaran P. Unpublished results.

53. Sresty G. C. Raja A. and Somasundaran P. Selective flocculation of mineral slimes using polymers. In *Recent advances in separation science* (New York: CRC Press, 1978), 4, 93–105.

54. Yarar B. and Kitchener J. A. Selective flocculation of minerals: 1—basic principles; 2—experimental investigation of quartz, calcite and galena. *Trans. Instn Min. Metall. (Sect. C: Mineral Process. Extr. Metall.)*, 79, 1970, C23–33.

55. Somasundaran P. ed. *Fine particles processing* (New York: AIME, 1980), vol. 2, section 6.

56. Usoni L. *et al.* Selective properties of flocculants and possibilities of their use in flotation of fine minerals. In *Eighth international mineral processing congress, Leningrad, 1968* (Leningrad: Institut Mekhanobr., 1969), vol. 1, 514–32. (Russian text); Paper D13, 14 p. (English text).

57. Sresty G. C. and Somasundaran P. Beneficiation of mineral slimes using modified polymers as selective flocculants. *XIIth Int. Mineral Process. Congr., Sao Paolo, 1977, special publ.*, vol. 1, 1977, 160.