programs. Indeed the use of such computer programs occasionally requires more knowledge of the analyst than if his own programs are utilized. The use of such programs should not be feared or shunned, nor on the other hand viewed with any blind belief in the magical accuracy of the results. Proper utilization will allow the analyst not only access to quick analyses, but also the luxury of materials and design optimization if he so desires. It will also allow fast input into materials cost optimization in the preliminary design phase of a program. Improper or careless use, however, will at best be reflected in very uneconomical computer bills, and at worst provide results which will require more time to be frustratingly spent in debugging and error hunting than in the exercise of engineering judgement and design.

References

[1]Bushnell, D., "A Computerized Information Retrieval System," *Structural Mechanics Computer Programs, Surveys, Assessments and Availability*, W. Pilkey, K. Saczalski, and H. Shaeffer, eds., University Press of Virginia, 1974.

[2]Svalbonas, V., and Ferdie, R., "Use of STARS Numerical Integration Codes for the Solution of Complex Shell Problems," *Proceedings*, IKOSS FEM Kongres 74, 1974.

[3]Svalbonas, V., "Numerical Analysis of Stiffened Shells of Revolution," NASA CR2273, 1973.

[4]Svalbonas, V., and Levine, H., "Numerical Nonlinear Inelastic Analysis of Stiffened Shells of Revolution," NASA CR2559, 1975.

[5]Bushnell, D., "Analysis of Ring-Stiffened Shells of Revolution under Combined Thermal and Mechanical Loading," *AIAA Journal*, Vol. 9, No. 3, March 1971.

[6]Guerguerian, R., "Structural Considerations Affecting Selection of Major Components in Grinding Mill Design," 80th Annual General Meeting, Canadian Institute of Mining & Metallurgy, April 1978.

[7]Dowling, N., "Fatigue at Notches and the Local Strain and Fracture Mechanics Approaches," 11th National Symposium on Fracture Mechanics, June 1978.

Chemistry of Oleate and Amine Solutions in Relation to Flotation

K. Ananthpadmanabhan, P. Somasundaran, and T.W. Healy

Abstract—*Hydrolyzable surfactants such as fatty acids and amines undergo, in addition to micellisation and precipitation, various associative interactions in aqueous solutions to form ionomolecular complexes such as acid-soap, dimers, etc., depending upon the solution conditions such as pH. The interaction of these collector species with the mineral surface and with other dissolved species in solution will play a significant role in determining the interfacial processes such as adsorption and flotation. Marked differences in the hydrophobicity imparted to the mineral surface depending upon the solution conditions such as pH can be attributed to possible differences in surface activities of the foregoing complexes. This aspect of solution chemistry of flotation systems is discussed here for two widely used collectors, namely, oleic acid and dodecylamine. Equilibrium species distribution diagrams, based on the available literature data and on estimates of energy of interactions between molecules, have been obtained for oleic acid and dodecylamine solutions.*

Introduction

Flotation of oxide minerals such as hematite is markedly dependent on solution conditions such as pH, particularly when a hydrolyzable collector is used. This was attributed in the past to the dependence on pH of properties of the mineral or its dissolved species, which can influence the adsorption of the surfactant on the mineral. The analysis of the dependence of flotation on the nature and form of collector species as a function of pH has been limited to the considerations of surfactant hydrolysis and their precipitation in the bulk or on the mineral surface. There is adequate indication in the literature that these species can undergo various associative interactions in bulk with themselves[1-12] and with others. Surface active complexes resulting from such interactions can have a significant role in governing interfacial phenomena. In this paper, the solution chemistry of two widely used collectors, namely, oleic acid and dodecylamine, is quantitatively examined and its importance to froth flotation of minerals is discussed.

Associative Interactions in Surfactant Solutions

In the past, surfactants were generally believed to exist as monomers up to a particular concentration and above which they aggregated to form a micelle or a precipitate. However, a number of investigations in the area of colloid chemistry suggested surfactant aggregation even at premicellar concentrations,[1-12] although the exact nature of these aggregates was not established.

Evidence for premicellar associations was obtained from studies of solution properties such as conductivity,[7-10] partial molar volume,[13-15] osmotic coefficient,[10, 16-18] hydrolysis,[3, 4, 6, 12, 19, 20] partition between an organic phase and an aqueous phase, etc.[11, 20-23] For example, below critical micelle concentration (cmc), conductivity of surfactant solutions has been found in certain cases to exhibit positive deviations from the Debye-Hückel-Onsager relationship for 1:1 electrolytes.[7-10] Such deviations can be accounted for by considering the formation of doubly charged dimers and other multimers which will have higher electrophoretic mobility owing to their lower hydrodynamic volume as compared to that of an equivalent number of monomers.[7] There have been attempts to attribute deviations from other properties also to such aggregations in aqueous phase. However, some of the foregoing

K. Ananthpadmanabhan and P. Somasundaran, member SME, are with Henry Krumb School of Mines, Columbia University, New York. T.W. Healy is with Dept. of Physical Chemistry, University of Melbourne, Melbourne, Australia.

SME Preprint 78B67, AIME Annual Meeting, Denver, CO, February 1978. Manuscript, Dec. 30, 1977. Discussion of this paper must be submitted, in duplicate, prior to July 31, 1980.

deviations can also arise from possible artifacts that can exist under the experimental conditions used.[16, 24-25]

The major driving force for the associative interactions is possibly the "hydrophobic" bonding between the nonpolar parts of the surfactant species.[16, 24] Accepting the postulate that water molecules are more ordered near a hydrocarbon chain than in bulk,[26-31] association of monomers can certainly be expected to decrease the number of water molecules in such ordered state. This is because of the decrease in hydrocarbon interfacial area exposed to water owing to association of monomers.[26-31] Indeed, the resultant increase in entropy will favor formation of multimers, energetically. On the other hand, interactions of the polar and/or ionic heads can lead to a positive or negative contribution depending upon the nature of the species involved in association. For example, the formation of a doubly charged dimer will have energy contributions arising from charge/charge repulsion which will oppose the formation of the dimer.

The structure of a doubly charged dimer (e.g., that between two oleate ions) considered by Mukerjee involved intertwining of hydrocarbon chains with the ionic heads on opposite ends. This structure was considered to be more favorable because of maximum possible contact between the hydrocarbon chains and minimum charge/charge repulsion.

On the other hand, formation of an ionomolecular complex, such as an acid-soap dimer (e.g., between neutral oleic acid molecules and oleate ions) was considered energetically even more favorable than the oleate dimers, because of the absence of charge/charge repulsion, both when the heads of the two chains were located on opposite ends or on the same end. In the latter case the possible interaction between the ionic and polar heads through hydrogen bonding is an additional favorable factor.[11,24]

It must be noted here that the solution properties mentioned previously will be affected by the formation, if any, of higher multimers such as trimers or tetramers. It is difficult at this point to distinguish between the effects of various multimers on such properties. In fact, existence of higher multimers in any significant amount is questionable because of accentuated repulsion between the charged heads which must now be positioned[7-10, 24] closer to one another at both ends. All the deviations from ideality have, therefore, been attributed to the formation of dimers.

Based on the foregoing considerations and on the data available in the literature for relevant processes, the associative interactions that are likely to occur in solutions of potassium oleate and dodecylamine are considered in the following sections.

Oleate Solutions: Oleic acid being a weakly acidic compound exists predominantly in the molecular form below the neutral pH range and in ionized form above that. Under appropriate conditions, the molecular monomer (RCOOH) and the ionic monomer ($RCOO^-$) can undergo associative interactions to form various complexes such as an acid-soap dimer ($(RCOO)_2H^-$), soap dimer ($(RCOO)_2^{--}$), acid-soap salt ($(RCOO)_2HNa$), and possibly even an acid dimer ($(RCOOH)_2$). Interaction of oleic acid (RCOOH) with potassium oleate (RCOOK) to form a 1:1 complex of RCOOH. RCOOK was suggested by McBain as early as 1927.[32] Subsequent studies by McBain,[33-34] Ekwall,[3,4] Mukerjee,[11] Cook,[6] and Eagland and Franks[20] have further considered the formation of acid-soaps and dimers in the oleic acid system. Supporting evidence for the formation of acid-soap complexes in oleic acid and dodecylamine systems was provided by Goddard, et al.[35-37] from investigations using differential thermal analysis.

On the basis of the present understanding of these systems and on the equilibrium data available for the various oleate species, the following chemical equilibria are written:

$$RCOOH_{(s)} \rightleftarrows RCOOH_{(aq)} \qquad pK_{sol} = 7.6\ (25) \qquad (1)$$

$$RCOOH_{(aq)} \rightleftarrows H^+ + RCOO^- \qquad pK_a = 4.95\ (25) \qquad (2)$$

$$2RCOO^- \rightleftarrows (RCOO)_2^{--} \qquad pK_D = -4.3\ (25) \qquad (3)$$

$$RCOO^- + RCOOH \rightleftarrows (RCOO)_2H^- \qquad pK_{AD} = -3.35 \qquad (4)$$

$$(RCOO)_2H^- + Na^+ \rightleftarrows (RCOO)_2HNa \qquad pK_{SAS} = -9.35\ (25) \qquad (5)$$

$$n\,RCOOH \rightleftarrows (RCOOH)_n \qquad n > 1 \qquad (6)$$

In these equations only selected values for the constants are given.

The value chosen for pA of oleic acid in the present calculations is that obtained by Jung[25] by extrapolation of the pK_a values of short chain fatty acids of chain-length up to eight.

Dimerization constants for oleate species evaluated by various investigators have ranged over several orders of magnitude.[25] The value used here is that estimated by Jung assuming a linear relationship between the logarithm of solubility and the hydrocarbon chain length.

Mukerjee[11, 24] has estimated the formation constant (K_AD) for the oleic acid-oleate complex to be approximately 30 times that of the oleate dimer. This was on the basis of the higher stability of the former as discussed earlier. Mukerjee's calculation of ionic repulsion was based on a distance of 4 Å between the two charges in the dimer. A formation constant of 8.9×10^4 was obtained in the present calculations using a separation of 13.8 Å. The latter value was obtained by Bangs[16] using a geometrically scaled up molecular model for the dimer.

It must be pointed out here that the evaluation of charge/charge repulsion involves the dielectric constant of the medium surrounding the charges, which is expected to be lower than that of pure bulk water. However, in both the present treatment as well as the earlier one by Mukerjee a dielectric constant of 78 — that of pure bulk water — has been used. This aspect of the problem will be discussed elsewhere.

Logically, it is expected that the acid molecules form neutral multimers as shown in Eq. 6. However, it has not been possible to incorporate Eq. 6 in the present study because of the lack of equilibrium data for the formation of such multimers. Therefore, they, if any, have been treated as oleic acid monomers.

Using Eqs. 1 through 6 with the corresponding equilibrium constants, along with the mass balance:

$$C_T = [RCOOH] + [RCOO^-] + 2[(RCOO)_2^{--}] + 2[(RCOO)_2H^-] \qquad (7)$$

where C_T is total concentration of surfactant, it is possible to determine the activities of the individual species and their distribution in the aqueous phase.

Fig. 1 is a typical species distribution diagram as a function of pH calculated by solving Eqs. 1 through 7 at a total surfactant concentration of 3×10^{-5} moles/L which is below the precipitation limit for $(RCOO)_2HNa$.

It is to be noted from this diagram that (1) the concentration of acid-soap dimer is maximum at pH 7.8, (2) $RCOO^-$ and $(RCOO)_2^{--}$ species are present in maximum amounts above pH 7.8, and (3) oleic and precipitation takes place below the same pH. The significance of these observations to flotation is discussed in a later section.

Amine Solutions: Bases such as dodecylamine also can undergo hydrolysis and associative interactions resulting in several species as shown by the following reactions:

$$RNH_3^+ \rightleftarrows RNH_2 + H^+ \qquad pK_a = 10.3 \qquad (8)$$

$$2RNH_3^+ \rightleftarrows (RNH_3)_2^{++} \qquad pK_D = -2 \qquad (9)$$

$$RNH_3^+ + RNH_2 \rightleftarrows (RNH_3 \cdot RNH_2)^{++} \qquad pK_{AD} = -1 \qquad (10)$$

$$RNH_{2(s)} \rightleftarrows (RNH_2)_{(aq)} \qquad pK_{sp} = 3 \qquad (11)$$

Dimerization constant for dodecylamine hydrochloride treated here is assumed to be the same as that estimated by Mukerjee for dodecylamine thiosulfate.[10] K_AD was estimated in the present study in a manner similar to that described earlier for oleic acid. Total concentration of amine is given by

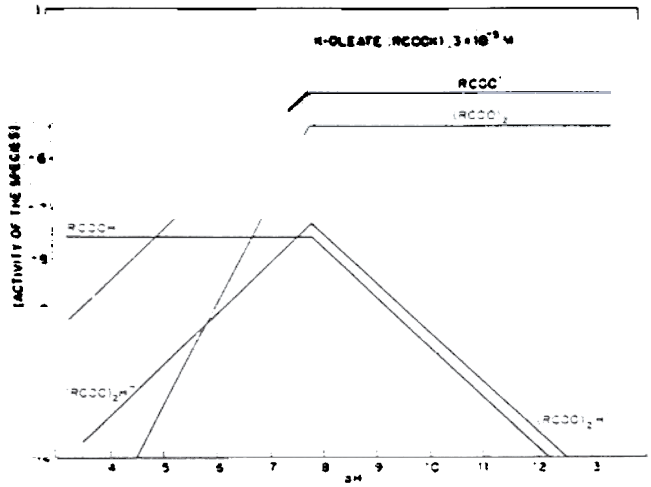

Fig. 1— Oleate species distribution diagram as a function of pH. Total oleate concentration = 3×10^{-5} moles/L.

$$C_{\frac{1}{2}}^{+} = [RNH_2] + 2(RNH_3)_2^{++} + 2[RNH_3 \cdot RNH_2]^{+} + [RNH_3^{+}] \quad (12)$$

As before, concentrations of various species in solution were calculated here for a total amine concentration of 10^{-4} mole/L and 10^{-5} mole/L. At 10^{-4} mole/L, precipitation of neutral amine occurs at pH 10 and above whereas at 10^{-5} mole/L, amine does not precipitate in solution. Thus, by choosing these concentrations, the effect of precipitation can be distinguished from that of the formation of complex ions in solution. It is to be noted that conditions under which precipitation commences often coincide with those of the formation of the complex species in maximum amounts. In the presence of precipitation it becomes, therefore, difficult to identify the governing parameters.

Surface Activities of Oleate and Amine Species in Solution

The surface activity of any of the various species mentioned can be expected to be different from that of the others owing to the differences in structure, charge, and the molecular size of the species. Thus the relatively larger molecular size and single charge can together make the acid-soap dimer more surface active than the oleate monomer or the dimer. Surface activity of the oleate dimer cannot be directly compared to that of the monomer due to the opposing effects on surface activity of the size of the hydrophobic part of the dimer and the presence of two ionic heads at the ends of the dimer. Similarly the surface activity of the acid-soap dimer also bears a complex relationship with that of the neutral monomer (RCOOH). These relationships have been evaluated on the basis of thermodynamically favorable models for the complexes and will be discussed separately.

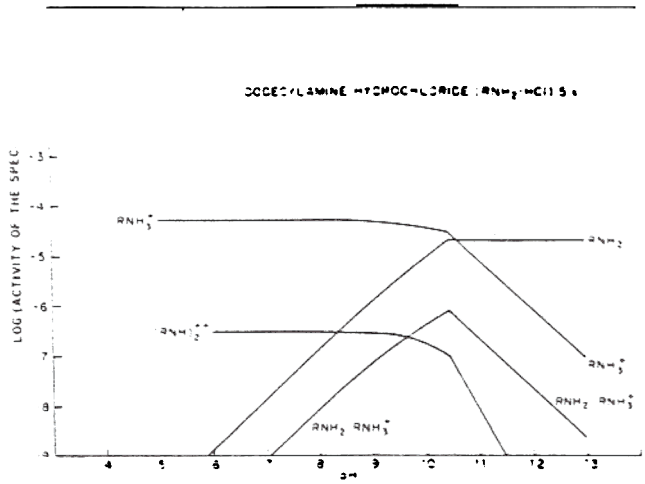

Fig. 2· Amine species distribution diagram as a function of pH. Total amine = 5×10^{-5} moles/L.

Owing to the variations in the concentrations of aqueous species of differing surface activities, solutions of hydolyzable surfactants such as amines and oleate can be expected to exhibit a change with pH in properties such as surface tension. Results obtained in the past[39, 40] for the surface tension dependence of oleate and amine solutions on pH are given in Fig. 4. It can be seen that at 3×10^{-5} mole/L the oleate solution exhibits a minimum in surface tension at pH 8.2 and the 4×10^{-4} mole/L amine solution exhibits a minimum at pH 10.2. It is to be noted that these are precisely the pH ranges in which maximum amounts of various dimers exist and precipitation of the neutral molecular form of the surfactant begins. These observations are in accord with the expected surface activities of various complexes and their activities in solution. Flotation behavior of typical minerals such as hematite and quartz using oleic acid and dodecylamine respectively will now be considered on the basis of the foregoing discussion.

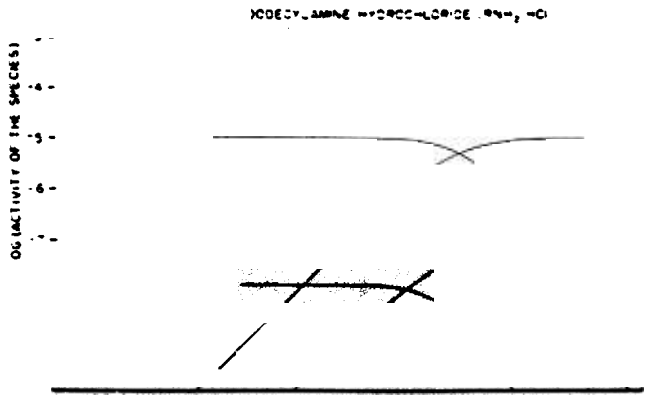

Fig. 3· Amine species distribution diagram as a function of pH. Total amine = 10^{-5} moles/L.

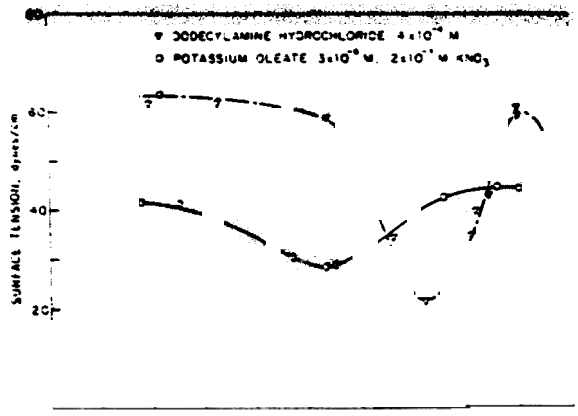

Fig. 4— Surface tension of potassium oleate and dodecylamine solutions as a function of pH. Total oleate = 3×10^{-5} moles/L. Total amine = 4×10^{-4} moles/L.

Flotation Using Oleate and Amine Solutions

Attachment of air bubbles to mineral particles is a complex process resulting from hydrophobic interactions between the two phases. These interactions depend upon the degree of hydrophobicity at the two interfacial regions. The hydrophobicity in turn is influenced by a number of factors such as the adsorption density of the surfactant, hydrophilic-lypophilic balance of the surfactant, orientation of the adsorbed species, and surface and bulk diffusion of the surfactant during rupture of the film between the bubble and the particle leading to attachment. These factors are to a large extent determined by the physical and chemical properties of the system which directly affect microprocesses such as adsorption at various interfaces. For example, adsorption of the surfactant on the mineral will be governed by the solution chemistry of the surfactant, aqueous chemistry of the mineral, interactions between surfactant species and dissolved mineral species, and other interfacial properties such as stern layer potential. The overall process of bubble attachment is further complicated by the fact that different combinations of these parameters could be important for different systems. In all cases involving naturally hydrophilic minerals, however, the solution chemistry can be expected to play a decisive role. It is the aim of the present study to analyze the role of solution chemistry of surfactant in determining flotation. A treatment of interactions between various collector species and dissolved mineral species requires a knowledge of equilibrium constants for various bulk and surface reactions. It is realized that lack of data for either the hematite-oleate or quartz-amine system limits a complete treatment at present.

Flotation Using Oleate: Typical data obtained previously[39] for the pH-dependence of the Hallimond cell flotation of hematite using oleate is given in Fig. 5. A sharp dependence on pH is observed with the maximum in flotation around pH 8. This has been attributed in the past to the chemisorption of oleate at the neutral surface hydroxyl sites which were proposed to be present in maximum amounts at the point of zero charge of hematite (pH ~ 8).[41, 42] It is not, however, clear as to why there should be increased chemisorption of oleate at a neutral hydroxyl site. Furthermore, on the basis of data available for activities of various iron-hydroxyl complexes[43] in bulk, it is questionable as to whether there will be any significant variation of surface hydroxyl concentration in the pH range of 5 to 11. On the other hand, there is, as shown in earlier sections, a strong dependence of oleate solution chemistry on pH.

A comparison of flotation data in Fig. 5 with that in Fig. 1, suggests, in fact, a correlation between flotation and the concentration of various oleate species in solution. Thus, the pH of maximum flotation is found to coincide with the pH of maximum acid-soap concentration (see Fig. 5). The observed maximum in flotation and surface tension lowering at the pH of maximum acid-soap concentration is consistent with the expected higher surface activity of the acid-soap. In addition, changes in concentration of other species, and in properties of the mineral such as the interfacial potential, can also cause accountable differences in the flotation behavior. Taking all such factors into consideration the following mechanism is proposed for the flotation of hematite using oleate. The role of various iron-oleate complexes can be incorporated into this scheme only when thermodynamic data for these complexes become available.

Increase in flotation with decrease in pH in the alkaline pH range is attributed to (1) increase in the acid-soap concentration with such pH decrease in this range and its consequent increase in adsorption by electrostatic interactions or hydrogen bonding, (2) increased adsorption of the acid-soap due to also the increase in the number of positive sites on the mineral, (3) possibly, increased adsorption of the negatively charged oleate monomer and the oleate dimer due to the increase in the number of positive sites on the mineral, and (4) any increased adsorption of neutral oleic acid due to hydrogen bonding with surface hydroxyl groups or coadsorption between the ionic species.

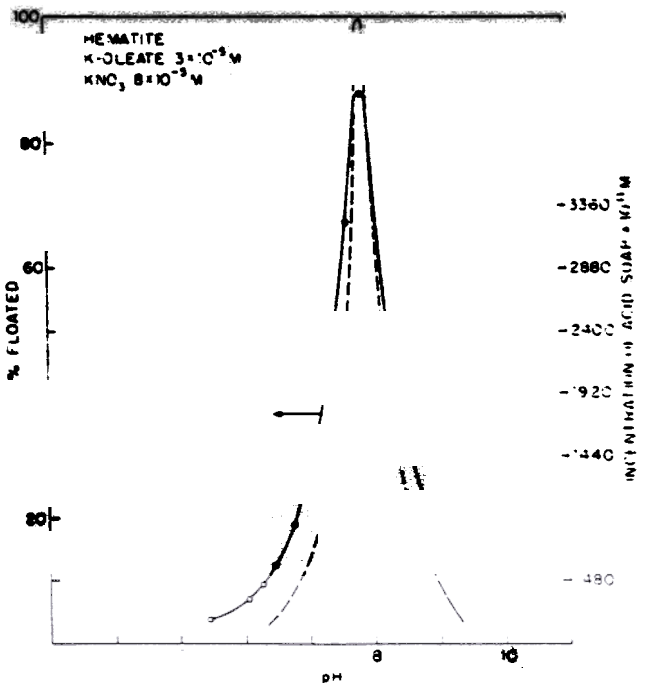

Fig. 5· Correlation of hematite flotation and concentration of acid-soap as a function of pH.

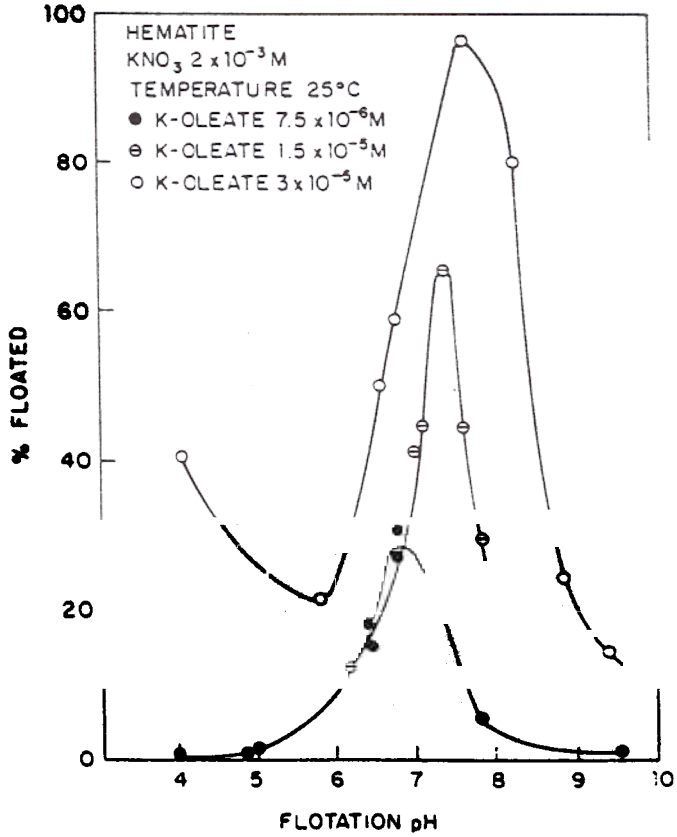

Fig. 6— Hematite flotation as a function of pH. Total oleate = 7.5 x 10^{-6} (•) moles/L, 1.5 x 10^{-5} moles/L (•) and 3 x 10^{-5} moles/L (•).

The decrease in flotation with decrease in pH below pH 8 is attributed in a similar manner to (1) a decrease in concentration of the acid-soap with decrease in pH in this pH range and consequent decrease in adsorption of it on hematite, and (2) the effects of decreases in concentrations of oleate monomers, oleate dimers, and the acid-soap dimer on their electrostatic adsorption. This effect should, however, be minimal since the logarithmic decrease in the concentration of the species with decrease in pH will be mostly offset by a similar increase in the concentration of the positive surface sites.

It is to be noted that the foregoing flotation mechanism based on the solution chemistry of oleate can also explain the dependence of pH of maximum flotation of hematite on the concentration of total oleate species in solution (see Fig. 6). The pH of maximum acid-soap formation and onset of oleic acid precipitation has been calculated at various oleate concentrations and are given in Table 1. It can be clearly seen that this parameter also follows the same trend with oleate concentration as the pH of maximum flotation giving further support to the proposed mechanism based on oleate solution chemistry.

It is the marked dependence of flotation of minerals on oleate chemistry that makes oleic acid a less specific collector compared to others. For example, results of Polkin and Najfonow[44] show the pH of maximum flotation of a number of different minerals to be around pH 7-8 (see Fig. 7) supporting the above contention.

Flotation Using Dodecyl Amine: Flotation using amines usually exhibits a maximum around pH 10-11. Typical results obtained for the flotation of quartz using 10^{-5} and 5×10^{-5} mole/L dodecyl amine solution using a Hallimond cell are given in Figs. 8 and 9. The pH of maximum flotation at 5×10^{-5} mole/L is found to correspond to the pH of formation of maximum amounts of aminium dimer and amine-aminium complex which also coincides with the pH of onset of amine precipitation. At 10^{-5} mole/L, however, there is no precipitation of dodecylamine and in this case the pH of maximum flotation corresponds simply to that of the pH of the ionomolecular complex formation. In this case, it is thus possible to distinguish between the role of the collector complexes and that of the neutral molecule precipitation. These observations fully support the proposed mechanism based on the formation of complexes between collector species.

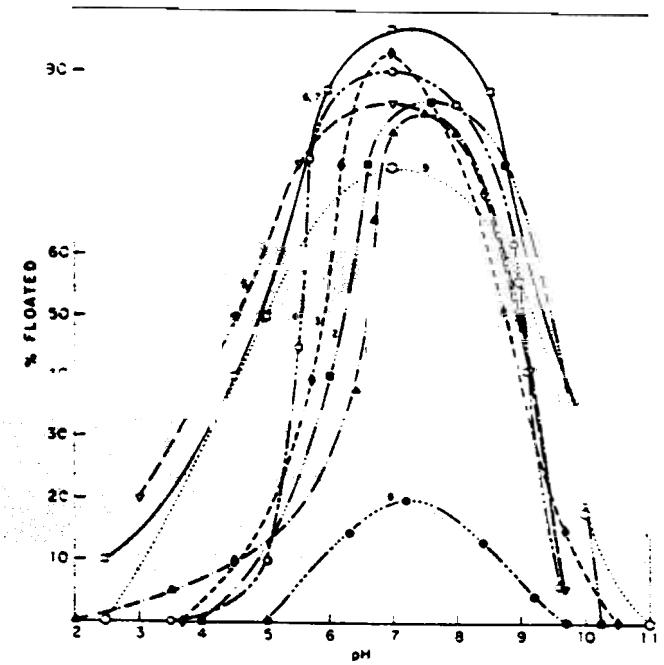

Fig. 7— Flotation recovery of minerals as a function of pH. Collector oleic acid (1000 g/t) (1) columbite, (2) zircon, (3) tantalite, (4) ilmenite, (5) rutile, (6) garnet, (7) tourmaline, (8) albite, (9) perovskite (from Ref. 44).

Table 1—pH of Maximum Acid-Soap Formation

C_T = Total Potassium Oleate in Solution	pH* = pH of maximum acid-soap complex formation (= pH of oleic acid precipitation)
3.5×10^{-5} M	7.78
1.5×10^{-5} M	7.53
7.5×10^{-6} M	7.37

The discussed mechanism is also in accord with the previous observations of Gaudin et al.[45] and Finch and Smith.[46] While the former authors investigated the contact angle hysteresis of benzene/water/quartz system, the latter studied the dynamic surface tension behavior of amine solutions and speculated the formation of dimers. In the present work, available thermodynamic data have been used to compute the activities of various possible complex collector species and thus to establish their role in determining interfacial processes such as flotation and surface tension.

Summary

Using equilibrium constants that are available in the literature, or reasonable estimates thereof, for the formation of various surfactant complexes, their activities have been computed as a function of pH for two common surfactant systems, namely, oleate and dodecylamine. Results show a good correlation between flotation and the formation of surfactant dimers as well as surface tension lowering. pH of maximum flotation is, in all cases, found to coincide with the pH of maximum concentration of ionomolecular dimers (which is also the pH of both the onset of precipitation of neutral surfactant molecules and of maximum concentration of ionic dimers). The correlation obtained strongly suggests the role of the hitherto ignored surfactant complexes in determining flotation of minerals using hydrolyzable collectors. Mechanisms involved in flotation of quartz using amine, and hematite using oleate, have been discussed taking into account the possible role of various surfactant species, including the dimers, and their interactions with mineral surface. Further refinement of these mechanisms will depend upon availability of data for the interaction between collector complexes and the mineral species at the surface as well as in the bulk.

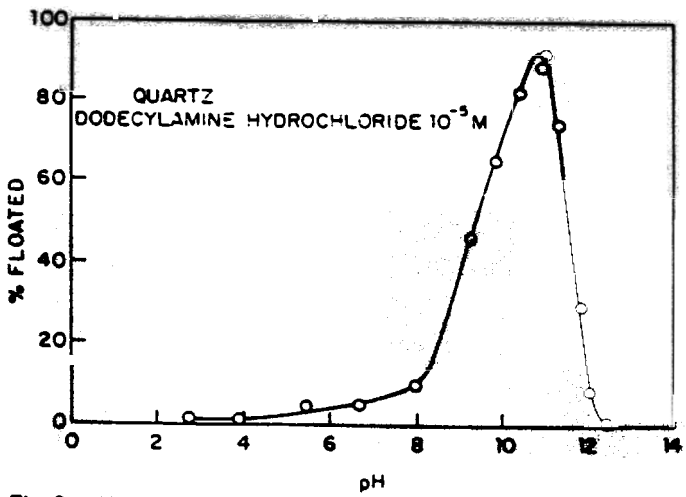

Fig. 8— Hallimond cell flotation of quartz as a function of pH. Dodecylamine hydrochloride 10^{-5} moles/L.

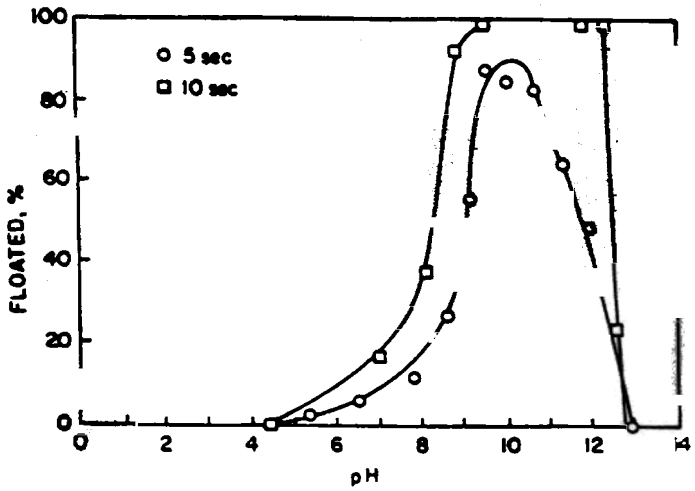

Fig. 9 Hallimond cell flotation of quartz as a function of pH. Dodecylamine hydrochloride 5 x 10^{-5} moles/L. Flotation time: 0-5 sec, □ -10 sec.

Acknowledgment

The authors wish to acknowledge the National Science Foundation, Div. of Engineering — Particulat and Multi-Phase Processes Program, for their support of the project (ENG-78-25213) under which this work was conducted.

References

[1]McBain, J.W., *Kolloid Zeitschrift*, Vol. 12, 1913, pp. 256-258.

[2]McBain, J.W., and McHan, H., "Soap Micelles that solubilize Dimethylphthalate, a Liquid Insoluble in Water and in Hydrocarbon," *Journal, American Chemical Society*, Vol. 70, 1948, pp. 3838-3840.

[3]Ekwall, P., "The Constitution of Dilute Soap Solutions. III. The Theory of Hydrolysis," *Kolloid Zeitschrift*, Vol. 92, 1940, pp. 141-157.

[4]Ekwall, P., and Lindblad, L.G., "Constitution of Dilute Soap Solutions. IV., OH Ion Activity of Solutions of Na-laurate," *Kolloid Zeitschrift*, Vol. 94, 1941, pp. 42-57.

[5]Stauff, J., "Equilibrium Between Molecular Dispersions and Colloidal Substances in Aqueous Soap Dispersions," *Zeitschrift fuer Phys. and Coll. Chem.*, Vol. 55, 183A, 1939, pp. 55-85.

[6]Cook, M.A., "Mechanism of Hydrolysis in Aqueous Soap Solutions," *Journal of Physical and Colloidal Chemistry*, Vol. 55, 1951, 383-402.

[7]Mukerjee, P., Mysels, K.J., and Dulin, C.I., "Dilute Solutions of Amphipathic Ions. 1. Conductivity of Strong Salts and Dimerization," *Journal of Physical Chemistry*, Vol. 62, 1958, pp. 1390-1397.

[8]Mukerjee, P., "Dilute Solutions of Amphipathic Ions. II. Transference of Lauryl Sulfate in Sodium Lauryl Sulfate," *Journal of Physical Chemistry*, Vol. 62, 1958, pp. 1397-1400.

[9]Mukerjee, P., and Mysels, K.J., "Dilute Solutions of Amphipathic Ions. III. Conductivity of Weak Salts," *Journal of Physical Chemistry*, Vol. 62, 1958, pp. 4100-4104.

[10]Mukerjee, P., "Dilute Solutions of Amphipathic Ions. IV. Some General Effects of Dimerization," *Journal of Physical Chemistry*, Vol. 62, 1958, pp. 1404-1408.

[11]Mukerjee, P., "Dimerization of Anions of Long-chain Fatty Acids in Aqueous Solutions and the Hydrophobic Properties of the Acids," *Journal of Physical Chemistry*, Vol. 69, 1965, pp. 2821-2827.

[12]Eagland, D., and Franks, F., "Association Equilibria in Dilute Aqueous Solutions of Carboxylic Acid Soaps," *Transactions*, Faraday Society, Vol. 61, 1965, pp. 2468-2477.

[13]Franks, F., and Smith, H.T., "Apparent Molal Volumes and Expansibilities of Electrolytes in Dilute Aqueous Solution," *Transactions*, Faraday Society, Vol. 63, 1967, pp. 2585-2598.

[14]Franks, F., and Smith, H.T., "The Association and Hydration of Sodium Dodecylsulfate in the Submicellar Concentration Range," *Journal of Physical Chemistry*, Vol. 68, 1964, pp. 3581-3584.

[15]Franks, F., Quickender, M.J., Ravenhill, J.R. and Smith, H.T., "Volumetric Behavior of Dilute Aqueous Solutions of Sodium Alkyl Sulfates," *Journal of Physical Chemistry*, Vol. 72, 1968, pp. 2668-2669.

[16]Bangs, L.B., "Surfactant Dimers and Their Adsorption," Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

[17]Walton, H.F., Heibert, E.N. and Scholtes, E.H., "Quaternary Ammonium Salts as Colloidal Electrolytes," *Journal of Colloidal Science*, Vol. 1, 1946, pp. 385-392.

[18]Robinson, R.A., and Stokes, R.H., *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1965.

[19]Eagland, D., and Franks, F., "pH of Soap Solutions," *Nature*, Vol. 191, 1961, pp. 1003-1004.

[20]Eagland, D., and Franks, F., "Preassociation and Thermodynamics of Hydrophobic Hydration in Dilute Solutions of Surfactants," *Proceedings*, 4th Inter. Congr. Surf. Active Substances, Vol. 2, Gordon and Breach, London, 1967, pp. 535-544.

[21]Goodman, D.S., "The Distribution of Fatty Acids Between n-Heptane and Aqueous Phosphate Buffer," *Journal, American Chemical Society*, Vol. 80, 1958, pp. 3887-3892.

[22]Proust, J., and Ter-Minassian, L.S., "Effect of the Structure of Water on the Dimerization by and on the Extraction of a Amphipathic Compound," *C.R. Acad. Sci.*, Paris, Vol. 270C, 1970, pp. 1354-1357 (French text).

[23]Smith, R., and Tanford, C., "Hydrophobicity of Long Chain N-alkyl Carboxylic Acids, as Measured by Their Distribution Between Heptane and Aqueous Solutions," *Proceedings, National Academy of Sciences*, Vol. 70, 1973, pp. 289-293.

[24]Mukerjee, P., "The Nature of Association Equilibria and Hydrophobic Bonding in Aqueous Solutions of Association Colloids," *Advances in Colloid and Interface Science*, Vol. 1, 1967, pp. 241-275.

[25]Jung, R.F., "Oleic Acid Adsorption at the Geothite Water Interface," M.S. Thesis, University of Melbourne, 1976.

[26]Frank, H.S., and Evans, M.W., "Free Volume and Entropy in Condensed Systems. III," *Journal of Chemistry and Physics*, Vol. 13, 1945, pp. 507-532.

[27]Frank, H.S., "The Structure of Ordinary Waters," *Science*, Vol. 169, 1970, pp. 635-641.

[28]Frank, H.S., and Wen, W.Y., "Ion-Solvent Interaction. Structural Aspects of Ion-solvent Interaction in Aqueous Solutions: A Suggested Picture of Water Structure," *Discussions*, Faraday Society, Vol. 24, 1957, pp. 133-140.

[29]Nemethy, G., and Scheraga, H.A., "The structure of Water and Hydrophobic Bonding in Proteins. III. The Thermodynamic Properties of Hydrophobic Bonds in Proteins," *Journal of Physical Chemistry*, Vol. 66, 1962, pp. 1773-1789.

[30]Nemethy, G., and Scheraga, H.A., "Structure of Water and Hydrophobic Bonding in Proteins. II. Model for the Thermodynamic Properties of Aqueous Solutions of Hydrocarbons," *Journal of Physical Chemistry*, Vol. 36, 1962, pp. 3401-3417.

[31]Nemethy, G., and Scheraga, H.A., "Structure of Water and Hydrophobic Bonding in Proteins. I. A Model for the Thermodynamic Properties of Liquid Water," *Journal of Physical Chemistry*, Vol. 36, 1962, pp. 3382-3401.

[32]McBain, J.W., and Stewart, A., "Acid-Soaps: A Crystalline Potassium Hydrogen Dioleate," *Journal, Chemical Society*, 1927, pp. 1392-1395.

[33]McBain, J.W., and Stewart, A., "Phase-rule Equilibria of Acid-soaps. Part III. Anhydrous Acid Potassium Oleate," *Journal, Chemical Society*, 1933, pp. 924-928.
[34]McBain, J.W., and Stewart, A., "Conductivity in Three Component System Oleic Acid-Potassium Oleate-Water," *Journal, Chemical Society*, 1933, pp. 928-932.
[35]Goddard, E.D., et al., "Molecular Association in Fatty Acid-Potassium Soap Systems," *Molecular Association in Biological and Related Systems*, Goddard, ed., American Chemical Society, 1968, pp. 67-77.
[36]Kung, H.C., and Goddard, E.D., "Molecular Association in Fatty Acid Potassium Soap Systems. II, *Journal of Colloid and Interface Science*, Vol. 29, No. 2, 1969, pp. 242-249.
[37]Kung, H.C., and Goddard, E.D., "Interaction of Amines and Amine Hydrochlorides," *Koll. Z. and Z. Polymere*, Vol. 232, No. 2, 1969, pp. 812-813.
[38]Smith, R.M., and Martell, A.E., "Amines," *Critical Stability Constants*, Vol. 2, Plenum Press, New York, 1975.
[39]Kulkarni, R.D., and Somasundaran, P., "Kinetics of Oleate Adsorption at the Liquid/Air Interface and Its Role in Hematite Flotation," *Advances in Interfacial Phenomena on Particulate/Solution/Gas Systems, Application to Flotation Research*, P. Somasundaran and R.B. Grieves, eds., AIChE Symp. Series, No. 150, 1975, pp. 124-133.
[40]Somasundaran, P., "The Role of Ionomolecular Surfactant Complexes in Flotation," *International Journal of Mineral Processing*, Vol. 3, 1976, pp. 35-40.
[41]Pope, M.I., and Sutton, D.I., "The Correlation Between Froth Flotation Response and Collector Adsorption from Aqueous Solution. I. Titanium Oxide and Ferric Oxide Conditioned in Oleate Solutions," *Powder Technology*, Vol. 7, No. 5, 1973, pp. 271-279.
[42]Pope, M.I., and Howe, T.M., "The Quantitative Determination of Flotation Agents Adsorbed on Mineral Powders, Using Differential Thermal Analysis," *Powder Technology*, Vol. 4, No. 6, 1970/71, pp. 338-344.
[43]DeBruyn, P.L., and Agar, G.E., "Surface Chemistry of Flotation," *Froth Flotation*, D.W. Fuerstenau, ed., AIME, NY, 1962, pp. 91-138.
[44]Polkin, S.I., and Najfonow, T.V., "Concerning the Mechanism of Collector and Regulator Interaction in the Flotation of Silicate and Oxide Minerals," in *Int. Min. Proc. Congr.*, Vol. 1, N. Arbiter, ed., Gordon and Breach Sci., 1965, pp. 307-318.
[45]Gaudin, A.M., Bangs, L.B. and Witt, A.F., "Hysteresis of Contact Angles in the System Benzene-Water-Quartz," *Proceedings*, International Mineral Processing Congress, Vol. 1, N. Arbiter, ed., Gordon and Breach, New York, 1965, pp. 321-328.
[46]Finch, J.A. and Smith, G.W., "Dynamic Surface Tension of Alkaline Dodecyl Amine Solutions," *Journal of Colloid and Interface Science*, Vol. 45, No. 1, 1973, pp. 81-91.

Forecasting Copper Production from Dump Leaching

Jonathan S. Jackson, W. Joseph Schlitt and Bayne B. McMillan

Abstract—*Various dump leach models have been developed by Kennecott, and these are reviewed with an eye toward production forecasting. Some of the models have been based on first principles, utilizing the chemistry and physics of dump leaching. While providing considerable insight into the leaching process, these have proved to be too cumbersome for use in estimating production. Other models have been based on a declining leach rate for a single block of waste. These permit good short-term projections of solution grades and production, but are inflexible with regard to changes in mining parameters because the trends are based only on historical data. Therefore, a simple and flexible computer model has been developed to aid in leach production forecasting and to provide a tool for assessing the impact of different mining plans on leaching. This program, LEACH, is based on annualized blocks of waste; input parameters are described and examples of its use are given.*

Introduction

For many years leaching of mine waste has been an important source of additional copper in US open-pit operations. At Kennecott, for example, dump leaching of low-grade sulfidic overburden has historically contributed about 20% of total copper output. In addition to providing a significant amount of copper, dump leaching also plays an important role in lowering unit production costs. This comes about because ore faces must be exposed by prior removal of waste whether or not this overburden is ever leached. Thus, waste haulage costs are generally assigned to pit operations while leach production is charged only for expenses associated with copper recovery and water distribution and collection.

This system of cost allocation can lead to problems since the tendency is to minimize haulage costs even when the resulting waste dump configuration is not conducive to maximum leach recovery. Integrated planning for optimum pit operations and leaching is one way to minimize this difficulty. However, even this concept is not without its problems. On the one hand, assays and metallurgical test work on drill cuttings from a given block of ore generally permit very accurate prediction of metal value recoveries in the resulting concentrate. On the other hand, forecasting leach production from the corresponding block of waste represents greater uncertainty.

The major challenges in leach production forecasting are estimating the rate and ultimate degree of copper recovery. Taken together, these two parameters represent the production level and depend on: (1) copper content and mineralogy of the waste, (2) dump configuration, (3) waste tonnage and fraction that can be contacted with leach solution, (4) availability of water, and (5) other factors that cannot be duplicated in column tests, as discussed by Roman.[1]

J.S. Jackson is project leader, dump leaching; W.J. Schlitt, member SME, is manager, hydrometallurgical dept.; and B.B. McMillan is associate scientist, Kennecott Minerals Co., Salt Lake City, UT. SME preprint 78AS397, SME Fall Meeting, Lake Buena Vista, FL, September 1978. Manuscript, Feb. 8, 1979. Discussion of this paper must be submitted, in duplicate, prior to July 31, 1980.

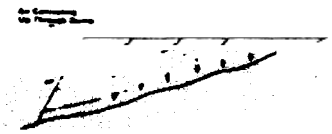

Fig. 1 Schematic representation of countercurrent flow of air and leach solution through dump.

Other considerations are the time lag between waste haulage and initial leaching and the fact that leach production from a block of waste may extend over several years. The latter will require discounting of the value of future years' production to give a net present value for each block of waste.

At Kennecott, dump leach production forecasting has been evolving for at least ten years. In all cases, the extreme complexity of the simultaneous chemical and physical processes occurring during leaching has prompted use of mathematical models to handle the computations involved. These models have ranged from physiochemical and empirical approaches to the present flexible system which permits feed forward inputs using expected operating parameters. The following sections review the different approaches, pointing out the advantages and disadvantages of each.

Physiochemical Model

Kennecott's physiochemical model was developed to satisfy two objectives:

1) To understand the interrelationships between the processes which occur during dump leaching.

2) To predict production coming from dump leaching.

As indicated in the following, only the first objective was fully realized.

The physiochemical model was first described by Cathles and Apps[2] in 1975, then updated and compared with available leach data by Cathles, Reese, and Murr in 1977.[3] Even more recently, Cathles[4] has reviewed these modeling efforts. Readers are referred to these papers for details.

Basically, the physiochemical model utilizes a finite difference approach to mathematically describe the dump leach process. The model starts with the chemistry of leaching both copper and noncopper-bearing minerals, then incorporates leach kinetics into the framework, and, finally, imposes various constraints on the system. These constraints include air convection, heat balance, temperature-dependent kinetics for leaching, and bacterial catalysis to oxidize ferrous iron in solution to the ferric state.

The mechanism of copper production requires that the sulfide minerals first be oxidized at least indirectly by air. Then copper from both sulfide and nonsulfide sources must be solubilized and periodically flushed from the dump by application of leach solution. This gives rise to countercurrent

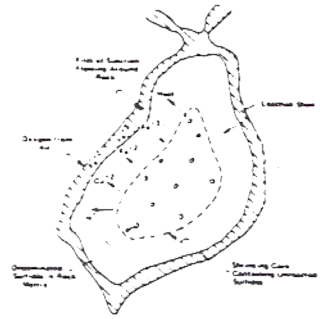

Fig. 2— Schematic representation of shrinking core concept for sulfide leaching.

flows of air and water through the dump. As shown schematically in Fig. 1, solution percolates down through the waste under the influence of gravity while air passes upward by convection. Since pyrite is generally the principal sulfide mineral in the waste (often 10 to 20 times more prevalent than the copper sulfides), its oxidation consumes much of the oxygen in the air. Pyrite oxidation is quite exothermic. The released heat warms the dump, accelerating leach kinetics. The heat also warms the air which, together with oxygen consumption, creates a density gradient in the gas within the dump. This gradient provides the driving force for natural air convection through the waste. Pyrite oxidation is also the primary source of iron in solution and generates the acid needed to prevent hydrolysis of both copper and iron, to leach nonsulfide copper, and to create a suitable environment for bacteria.

The physiochemical model provides for balances between the various phenomena occurring in the dump. Examples include buffering of leach solution acidity by reaction with various gangue constituents and removal of heat in air or leach solution leaving the dump. However, bacterial catalysis is the principal restraining influence. Although oxygen in the air is the source of oxidant for sulfide leaching, the actual lixiviant is ferric iron. At typical dump leach temperatures (ambient to 50° or 60°C), chemical conversion of ferrous iron to the ferric state is very slow. As a result, bacterial catalysis for ferric iron formation is needed to explain the high ferric iron concentrations and rapid copper leaching observed in practice. When a dump is first put under leach, the rate of bacterial activity increases causing the temperature and acidity to rise within the dump. However, as near optimum conditions for bacteria are established, bacterial activity also appears to reach a steady-state level. If the bacterial activity were not self limiting, then catalyzed oxidation would continue to accelerate until temperatures and acid levels were reached which would destroy the bacterial population.

One other aspect of the physiochemical model is the use of a standard "shrinking core" approach (see Levenspiel,[5] for example) to describe the declining rate of copper sulfide oxidation in the rock fragments. The shrinking core concept is

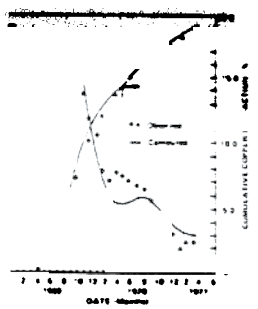

Fig. 3— Simulation of test dump performance using physiochemical model (Ref. 2).

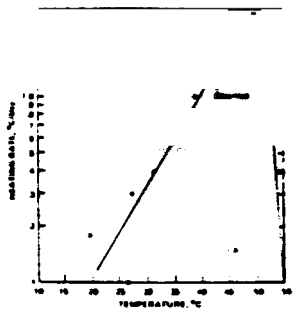

Fig. 4— Comparison of observed and predicted heating rate in large column leach test (Ref. 3).