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Bibliography

Bayes, Th., "An Essay Towards Solving a Problem in the Doctrine of Chances," *Philosophical Transactions*, London, 1763, pp. 376-399; Hafner Publishing Co., New York, 1963.

Brujewicz, S. W., "Oxidation-Reduction Potentials and pH of Sea Bottom Deposits," *Verh. der Internat. Vereinigung fuer theoretische und angewandte Limnologie*, Band 8, 1938, pp. 35-49.

Fisher, R. A., *The Design of Experiments*, 8th ed., Hafner Publishing Co., 1966, 248 pp.

Fisher, R. A., *Statistical Methods for Research Workers*, 13th ed., Hafner Publishing Co., New York, 1967, 356 pp.

Garrels, R. M., and Christ, C. L., *Solutions, Minerals, and Equilibria*, Harper and Row, New York, 1965, 450 pp.

Hagner, A. F., and Collins, L. G., "Magnetite Ore Formed During Regional Metamorphism, Ausable Magnetite District, New York," *Economic Geology*, Vol. 62, 1967, pp. 1034-1071.

Kendall, M. G., and Stuart, A., "Distribution Theory," *The Advanced Theory of Statistics*, 2nd ed., Vol. 1, Charles Griffin and Co., Ltd., London, 1963, 433 pp.

Klein, C., "Mineralogy and Petrology of the Metamorphosed Washbush Iron Formation, Southwestern Labrador," *Journal of Petrology*, Vol. 7, 1966, pp. 264-305.

Matala, N. C., and Reiber, B. J., "Some Comments on the Use of Factor Analysis," *Water Resources Research*, Vol. 3, No. 1, 1967, pp. 213-223.

Melton, M. A., "Correlation Structure of Morphometric Properties of Drainage Systems and Their Controlling Agents," *Journal of Geology*, Vol. 66, 1958, pp. 442-460.

Nichol, I., Garrett, R. G., and Wegg, J. S., "The Role of Some Statistical and Mathematical Methods in the Interpretation of Regional Geology," *Economic Geology*, Vol. 64, No. 2, 1969, pp. 204-220.

Saager, R., and Esselaar, P. A., "Factor Analysis of Geochemical Data from the Basal Reef, Orange Free State Goldfields, South Africa," *Economic Geology*, Vol. 64, No. 3, 1969, pp. 445-451.

Tyler, S. A., "Development of Lake Superior Soft Iron Ores From Metamorphosed Iron Formation," *Bulletin*, Geological Society of America, Vol. 60, 1949, pp. 1101-1124.

Vincent, D. F., "The Origin and Development of Factor Analysis," *Applied Statistics*, Vol. 2, 1952, pp. 107-117.

Zodrow, E. L., "Relationship of Olivine Gabbro and Amphibolite Schist at Carol West, Labrador Geosyncline," *Geologische Rundschau*.

Zodrow, E. L., "Contribution to the Theory of Geological Mineral Sample," Part 1, PhD Dissertation (in progress).

Hydroxamate vs. Fatty Acid Flotation of Iron Oxide

by M. C. Fuerstenau, R. W. Harper, and J. D. Miller

Data were obtained with hematite with octyl hydroxamate and oleate as collectors to determine the mechanism of collector adsorption and also to establish the roles that conditioning time and temperature assume in this system. The presence of hydroxy complexes of iron are apparently necessary for chemisorption of collector to occur, and it appears as if extended conditioning times and elevated temperature promote greater dissolution of the mineral and hence greater concentrations of hydroxy complexes. Data were also collected with two natural hematitic ores. With one ore that was ground to 70% - 15 μ , an addition of 0.4 lb per ton hydroxamate resulted in a final concentrate recovery of 86% at a grade of 64% iron. Satisfactory concentrate grade could not be obtained with fatty acid under these conditions. The effect of conditioning time prior to the addition of collector was also examined with another ore. When the ore was conditioned for 3 min, 19% of the iron was recovered in the concentrate at a grade of 67% Fe. With a conditioning time of 7 min, 73% of the iron reported to the concentrate at a grade of 62% Fe. These products were obtained with an addition of 0.2 lb per ton hydroxamate. This ore also responded well to flotation with fatty acid.

The use of potassium octyl hydroxamate as a collector for iron oxide has been the subject of an earlier study.¹ From this initial study, it was suspected that hydrolysis of surface ferric iron was involved in collector adsorption. More recent work in other systems has shown that slight mineral dissolution, followed by hydrolysis of cations common to the mineral lattice, is apparently necessary, and that adsorption of these hydroxy com-

plexes probably occurs prior to the adsorption of collector.

In view of these facts, work has been continued on the hydroxamate-hematite and oleate-hematite systems to gain better insight into the mechanisms of collector adsorption on iron oxide. Microflotation experiments in conjunction with infrared analysis were used in this regard. In addition it was felt necessary to establish more clearly the responses that can be obtained from natural ores when hydroxamate is used as collector as compared to those obtained when fatty acid is used.

Experimental Materials and Techniques

Pure potassium oleate, potassium octyl hydroxamate, synthesized from hydroxylamine hydrochloride and methyl octanoate,² and a distilled Tall Oil were employed as collectors. Conductivity water was used in the

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microflotation experiments, while tap water was used in the experiments with the natural ores.

A natural sample of red crystalline hematite was used in the microflotation and infrared experiments. For flotation in the Hallimond cell, the mineral was ground dry and sized to 65×100 mesh. A 1-g charge was delimed and then added to a solution containing the desired reagents. The system was conditioned for a predetermined period of time and then floated for 45 sec. Reagent-grade HCl or KOH was used for pH adjustments.

Infrared spectra of potassium octyl hydroxamate, precipitated ferric hydroxamate, hematite, and hematite contacted with octyl hydroxamate were determined, utilizing the KBr pellet technique.

Two natural ores were used in this study; the one ore, termed ore I, contained 42% Fe, present mainly as specular hematite with a minor amount of magnetite in a chert gangue. Prior to flotation in a Fagergren cell, 500 g of this material were ground for 10 min at 60% solids by weight in order to achieve liberation. The product obtained had the following size distribution as determined by wet screening:

Ore I

Size (μ)	Cumulative % Finer
105	99
74	96
44	71

The second ore, which contained 45% Fe iron in the form of red hematite, was finely disseminated and was ground for 50 min at 60% solids to effect liberation. The distribution of products was:

Ore II

Size (μ)	Cumulative % Finer
42	99
32	98
23	96
15	70
11	53

The size distribution of ore II, based on the settling characteristics of pure quartz, was determined with a Warman Cyclosizer. Because of the density difference between hematite and quartz, the actual size of the particles will be somewhat smaller than these values.

Experimentally, the procedures were somewhat different when hydroxamate was used as collector as opposed to the Tall Oil fatty acid. In the case of hydroxamate, the charge was ground at 60% solids, diluted to 20% solids, and conditioned for a predetermined length of time in a Fagergren flotation cell in the absence and/or in the presence of collector. MIBC (0.15 lb per ton) was added as frother, and flotation was effected for 5 min. The rougher concentrate was cleaned with an addition of 0.08 lb per ton frother with a conditioning time of $\frac{1}{2}$ min before refloating. All of the recoveries and grades reported in Figs. 7-10 refer to the final cleaner flotation concentrate.

When fatty acid was used with ore I, the collector was added to the rod mill containing ore at 70% solids by weight. The ground product was diluted to 20% solids; the frother was added, and flotation was effected as described previously. There was no conditioning in the flotation cell prior to the rougher flotation. Again,

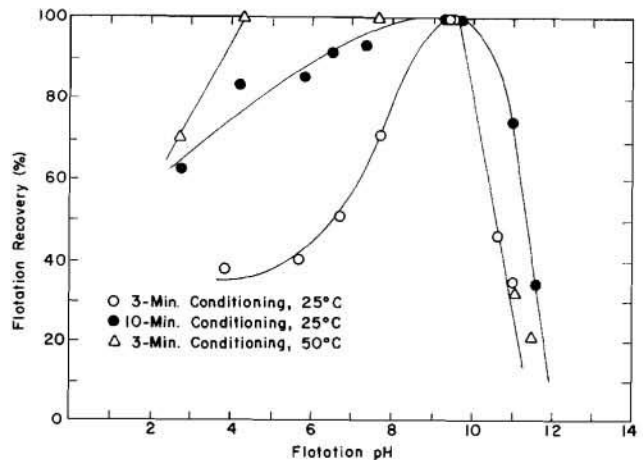


Fig. 1—Relationship between flotation recovery of hematite and pH with 5×10^{-4} mole per l octyl hydroxamate with various periods of conditioning and temperatures.

a conditioning time of $\frac{1}{2}$ min was used before cleaner flotation was effected.

All of the flotation products were analyzed for iron by X-ray fluorescence.

Experimental Results

The first series of experiments involved determining the flotation response of hematite as a function of conditioning time and temperature in the presence of hydroxamate; see Fig. 1. When the system was conditioned for 3 min at room temperature, moderate flotation was effected at pH 4, whereas complete flotation was obtained at pH 9.5. Increasing the conditioning time or increasing the temperature under these same conditions improved the flotation response and extended the pH range in which favorable flotation was obtained.

The phenomena occurring during conditioning were examined further both in the absence and presence of collector. As shown in Fig. 2, conditioning the solids in the absence of collector results in improved response; but when longer conditioning times are used in the presence of collector, even higher recoveries are obtained. The collector addition was reduced to 2×10^{-4} mole per l hydroxamate to show these effects more clearly.

Potassium oleate was also used as collector, and the flotation responses obtained with an addition of 1×10^{-4} mole per l for two periods of conditioning are shown in

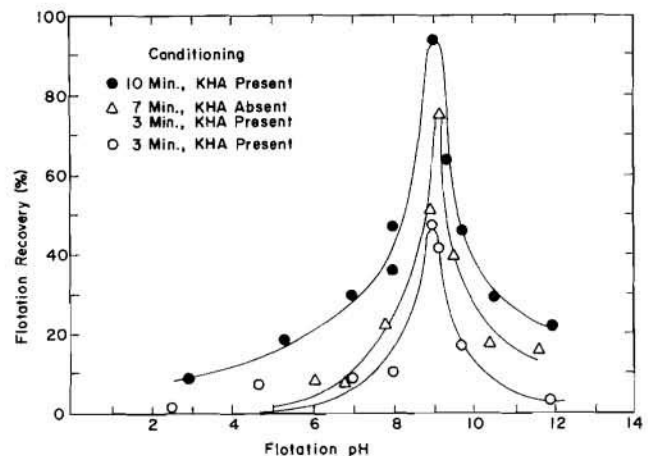


Fig. 2—Relationship between flotation recovery of hematite and pH with 2×10^{-4} mole per l octyl hydroxamate with various periods of conditioning at 25°C.

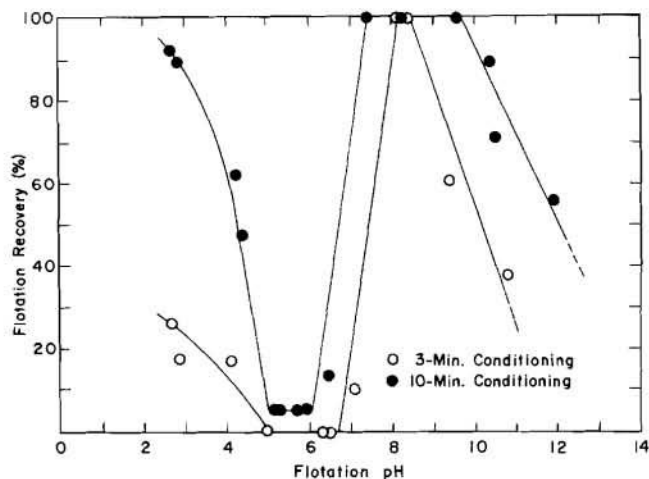


Fig. 3—Relationship between flotation recovery of hematite and pH with 1×10^{-4} mole per l potassium oleate with two periods of conditioning at 25°C.

Fig. 3. In these cases, the collector was present for the complete time of conditioning. Optimum flotation was effected in the vicinity of pH 8 to 8.5, and, interestingly, a region of depression can be noted from about pH 5 to 6.5.

Infrared patterns were obtained for hematite in the absence and presence of hydroxamate. The spectrum of hematite is presented in Fig. 4, and the presence of adsorbed water at 1620 and 3430 cm^{-1} can be noted. This agrees well with another published spectrum.³

The principal absorption band of potassium octyl hydroxamate occurs at 1625 cm^{-1} . Other important bands can be found at 1550, 1465, 1330, 1300, and 1120 cm^{-1} in Fig. 5.

Two principal absorption bands of basic ferric hydroxamate, precipitated at pH 3.0, are at 1518 and 1583 cm^{-1} ; see Fig. 6. The pH was maintained at this low value to prevent simultaneous precipitation of ferric hydroxide and contamination of the product.

The spectrum of hematite conditioned at pH 9.0 in the presence of hydroxamate is also shown in Fig. 6. Expanded scale (20X) was required, and only the region between 1500 and 1700 cm^{-1} is presented. Two absorption bands are present, and these are located at 1518 and 1580 cm^{-1} .

The effect of conditioning time on the flotation responses of natural ores was also investigated. Ore I was floated with 0.2 lb per ton hydroxamate at pH 8.5. Conditioning periods of 3, 5, 7, and 10 min in the flotation cell were used prior to introduction of collector into the system. After hydroxamate was added, the system was conditioned for another 3 min. As shown in Fig. 7

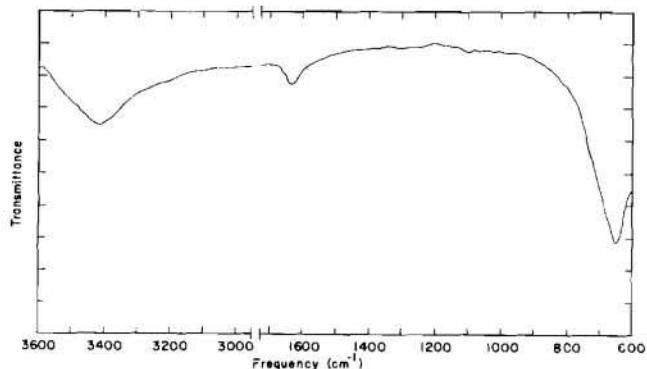


Fig. 4—Infrared spectrum of hematite.

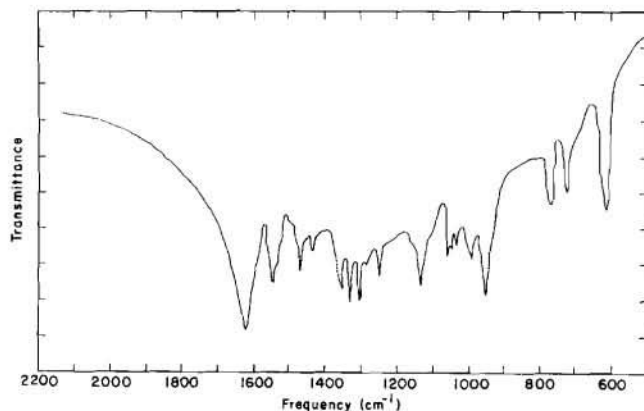


Fig. 5—Infrared spectrum of potassium octyl hydroxamate.

when the ore was conditioned for 3 min prior to collector addition, 19% of iron reported to the concentrate at a grade of 67% Fe. When the time was increased to 7 min prior to collector addition, the concentrate contained 73% of the original iron at a grade of 62%. A conditioning time of 10 min did not result in any improvement in recovery over that obtained with 7 min. Three stages of cleaner flotation were used in these experiments.

Iron recovery from this ore and concentrate grade are shown as a function of hydroxamate addition in Fig. 8. The ore was conditioned in the Fagergren cell for 10 min prior to collector addition and for 3 min after collector addition. Recoveries of 32, 71, and 82% were effected with collector additions of 0.15, 0.20, and 0.30 lb per ton, respectively. Concentrate grades were 61, 62, and 57% with three cleaner flotation steps.

When 0.6, 1.0, and 1.25 lb per ton fatty acid were used as collector, recoveries of 35, 73, and 82% were obtained at concentrate grades of 63, 59, and 59%, respectively; see Fig. 9. Four cleaning stages were employed to effect these grades. In these cases, grinding and conditioning for 10 min in the presence of collector were achieved at the same time in the rod mill.

The results obtained with ore II with hydroxamate are presented in Fig. 10. The ore was conditioned in the Fagergren cell for 10 min prior to collector addition and for 3 min after collector addition. Additions of 0.4 and 0.5 lb per ton resulted in recoveries of 86 and 87% with concentrate grades of 64 and 68% Fe. The concentrate was cleaned four times when 0.5 lb per ton was added and two times with 0.2 and 0.4 lb per ton.

Similar additions of fatty acid were made to this system. Satisfactory concentrate grades could not be

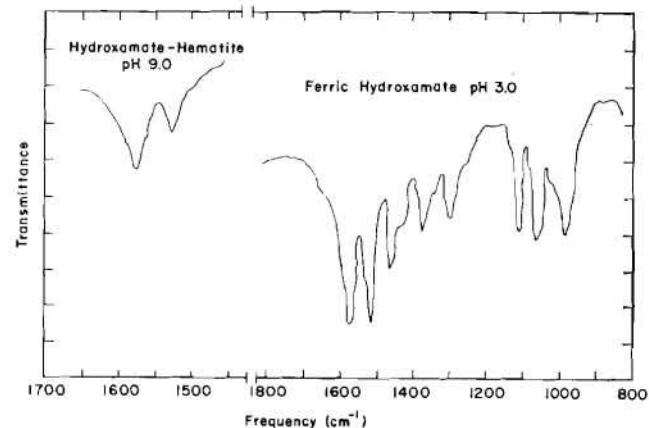
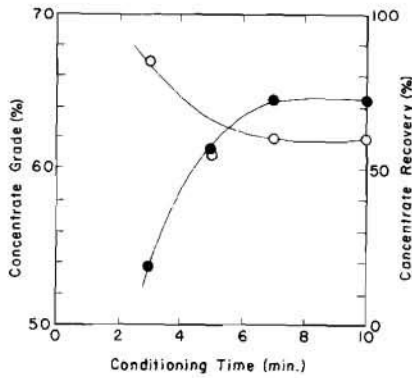


Fig. 6—Infrared spectra of ferric hydroxamate precipitated at pH 3.0 and of hematite contacted with hydroxamate at pH 9.0.

Fig. 7—Relationship between concentrate grade and concentrate recovery from ore I and conditioning time in the absence of collector. After each of these conditioning periods, the system was conditioned for 3 min in the presence of 0.2 lb per ton hydroxamate at pH 8.5 and 25°C. Open circles, grade; filled circles, recovery.



obtained when MIBC was used as frother, since the pulp was essentially one column of foam. As a result, pine oil (0.6 lb per ton) was added instead, and concentrate grades of 61, 64, and 49% were obtained with concentrate recoveries of 58, 53, and 80%, respectively. In each of these cases, the concentrate was given four stages of cleaning with no frother addition.

Discussion of Results

The optimum values of pH for flotation with oleate and hydroxamate are pH 8 and 9, respectively. Since the zpc of natural iron oxide is pH 6.7,⁴ it can be concluded that both of these collectors are adsorbing chemically under these conditions. The infrared results of oleate adsorption on hematite³ and those of the system hydroxamate-hematite (Figs. 4-6) confirm this premise. In the case of hydroxamate adsorption on hematite, the principal absorption bands occur at 1518 and 1583 cm^{-1} . These two bands correspond exactly to those present in basic ferric hydroxamate precipitated at pH 3.0. Further, a color change of hematite occurs after hydroxamate adsorption. These facts suggest that the collector is present on the surface in multilayers of basic ferric hydroxamate.

The region of depression noted about pH 5 to 6.5 when oleate was used as collector has also been observed by others.⁵ Flotation below about pH 5 can probably be attributed to electrostatic attraction of oleate ions to the positively charged surface.

In this system and others,^{2,5-7} mineral dissolution has been shown to be involved in the chemisorption of collectors. In addition, flotation occurs in a pH range in which the cations common to the lattice hydrolyze. The hydroxy complexes of ferric iron that will be present in solution as a function of pH are presented in Fig. 11. As shown, the species that is present in the most significant concentration at pH 9 is $\text{Fe}(\text{OH})_{3(aq)}$. Other species such as $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}(\text{OH})_4^-$ will also be present but at lower concentrations. These phenomena would seem

Fig. 8—Relationship between concentrate grade and concentrate recovery from ore I and hydroxamate addition at pH 8.5 and 25°C. Conditioning time was 10 min prior to hydroxamate addition, 3 min after hydroxamate addition. Open circles, grade; filled circles, recovery.

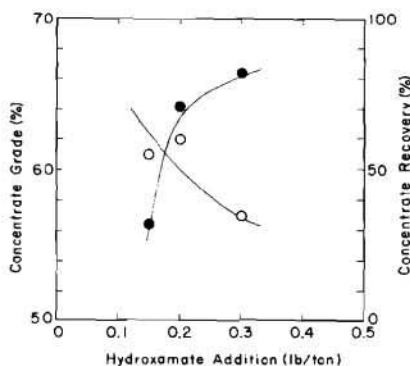
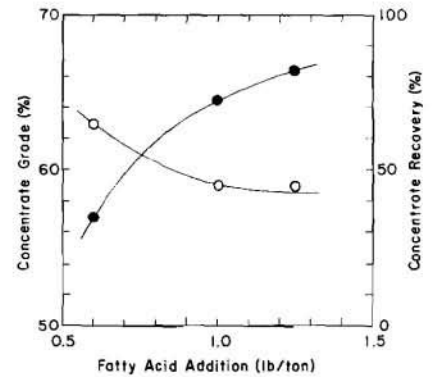


Fig. 9—Relationship between concentrate grade and concentrate recovery from ore I and fatty acid addition at pH 8.5 and 25°C. A conditioning time of 10 min was effected in the rod mill during grinding. Open circles, grade; filled circles, recovery.



to indicate that basic salts of metal collector are involved in the chemisorption process. In support of this premise, only the basic salt of ferric hydroxamate is insoluble. Ferric hydroxamate is a colored soluble complex. The interaction of hydroxy complexes with the mineral surface and with collector has yet to be established, however. Detailed infrared and analytical work are required before an understanding will be achieved.

These concepts are supported additionally by the fact that flotation is enhanced when the solids are conditioned for longer periods of time in the absence of collector (Figs. 2 and 7). Longer conditioning times enable more iron to dissolve from the mineral. As expected, there is a maximum effect produced with conditioning. In the case of ore I, this turned out to be 7 min. Part of the effect of elevating the temperature in these systems is also probably related to this phenomenon; that is, greater dissolution of hematite will be obtained at higher temperatures with the result that more of the hydrolyzed species will be ultimately available for adsorption.

Fig. 10—Relationship between concentrate grade and concentrate recovery from ore II and hydroxamate addition at pH 8.5 and 25°C. Conditioning time was 10 min prior to hydroxamate addition, 3 min after hydroxamate addition. Open circles, grade; filled circles, recovery.

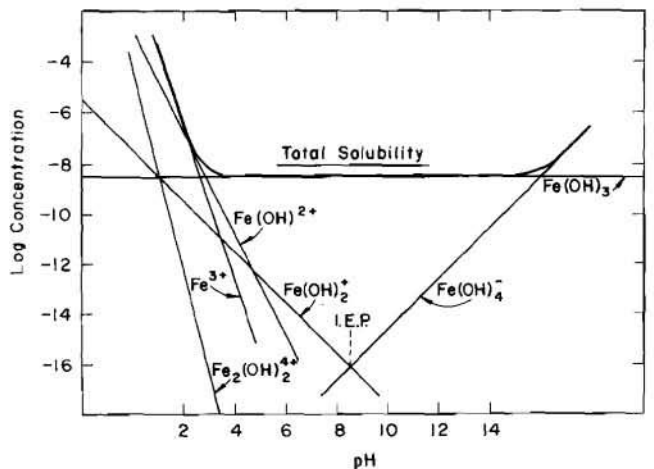
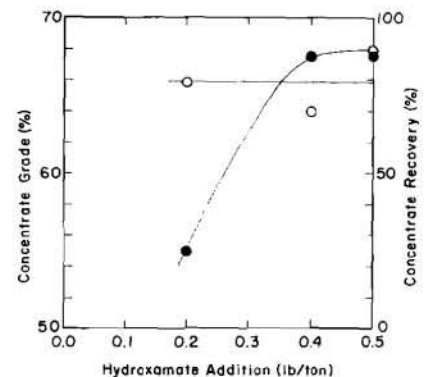


Fig. 11—Concentration of iron (III)-bearing species in equilibrium with solid hematite as a function of pH.⁸

Essentially no difference was found between the results obtained with hydroxamate or fatty acid with ore I, although higher collector additions and high pulp density conditioning were required in the case of fatty acid. The high solids conditioning step may reflect the difference in solubility products of ferric hydroxamate and ferric oleate. Although difficult to determine, it would be most useful to know these solubility products.

From a practical standpoint, hydroxamate can probably be produced for approximately 60¢ per lb, while this particular fatty acid can be purchased for about 10¢ per lb. Very nearly the same products were obtained when 0.2 lb per ton hydroxamate or 1 lb per ton fatty acid were involved with this ore.

On the other hand, with an ore that had to be ground to a very fine size (ore II), good product grade and recovery were obtained with relatively small additions

of hydroxamate, whereas almost no enrichment was effected with fatty acid when MIBC was used as frother. When pine oil was substituted for MIBC, acceptable concentrate grade was made, but only approximately 50% of the iron reported to the concentrate.

References

- ¹ Fuerstenau, M. C., Miller, J. D., and Gutierrez, *Trans. SME/AIME*, Vol. 238, 1967, p. 200.
- ² Peterson, H. D., Fuerstenau, M. C., Rickard, R. S., and Miller, J. D., *Trans. SME/AIME*, Vol. 232, 1965, p. 389.
- ³ Peck, A. S., Raby, L. H., and Wadsworth, M. E., *Trans. SME/AIME*, Vol. 235, 1966, p. 301.
- ⁴ Iwasaki, I., Cooke, S. R. B., and Choi, H. S., *Trans. SME/AIME*, Vol. 217, 1960, p. 237.
- ⁵ Fuerstenau, M. C., and Rice, D. A., *Trans. SME/AIME*, Vol. 241, 1968, p. 453.
- ⁶ Rice, D. A., "Some Mechanisms of Collector Adsorption on Tourmaline as Related to Other Silicates," D.Sc. Thesis, Colorado School of Mines, Golden, Aug. 1968.
- ⁷ Zambrana, G. Z., "Flotation Behavior of Cassiterite in a Pure System," M.Sc. Thesis, Colorado School of Mines, Golden, Aug. 1968.
- ⁸ deBruyn, P. L., and Agar, G. E., *Froth Flotation*, D. W. Fuerstenau, ed., Chap. 5, AIME, New York, 1962, p. 101.

Chlorination of Manganiferous Iron Ores

by Y. Okahara and I. Iwasaki

Chlorination behaviors of pure iron and manganese oxides were investigated by combining a thermogravimetric analysis (TGA) technique with batch-boat roasting followed by leaching. Ferrous and manganous oxides could be chlorinated readily, but, in the absence of a reductant, the higher oxides of both iron and manganese were difficult to chlorinate. Thermogravimetric analysis curves were drawn to illustrate the complexities of the reactions, and the possible mechanisms were discussed. Then three manganiferous materials from the Cuyuna Range of Minnesota were treated by a process involving the selective chlorination of manganese followed by leaching. The results were interpreted in the light of the chlorination mechanisms observed on the pure iron and manganese oxides.

One of the unsolved problems challenging Minnesota's mining industry is the development of an economic process to utilize the manganiferous iron ores of the Cuyuna Range. Although these ores constitute one of the major domestic reserves of manganese (estimated at 432 million tons¹), their grade is too low for them to be mined solely for manganese. The nearly exclusive dependence of the U.S. steelmaking industry on foreign manganese ores has stimulated research over the years in treating the low-grade Cuyuna ores. As a result, a

number of processes have been proposed.²⁻⁴ Among these processes is chlorination.

Chlorination is the high-temperature conversion of metallic oxides to chlorides by either chlorine or hydrogen chloride gas, or by solid chlorides of sodium, calcium, or magnesium. The metallic chlorides are then recovered by either vaporization or leaching. Although chlorination is an old art, it has become popular in recent years for the recovery of such new metals as titanium, zirconium, and niobium; for the removal of impurities like copper, lead, and zinc from pyrite cinder for ironmaking raw materials;⁵ and for the segregation roasting of copper⁶ and nickel⁷ ores.

The chlorination processes proposed for manganiferous iron ores have been relatively few (hydrogen chloride chloridization-leaching, hydrogen chloride and calcium chloride chloridization-volatilization,⁴ and chlorination-selective condensation⁸), due presumably to the economics and to the corrosion problems involved. However, the successful application of chlorination processes to other ores will undoubtedly contribute to technological advancements in the chlorination of man-

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