

Chapter 17

FLOTATION BEHAVIOR OF CHROMIUM AND MANGANESE MINERALS

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ABSTRACT

Flotation behavior of chromite and manganese-bearing minerals has been reviewed. Flotation of these minerals and ores with fatty acids, amines, sulfates, sulfonates and hydroxamates has been presented and is discussed in terms of surface charge and chemical interaction between the mineral surface and collectors. The role of metal hydroxy complexes such as FeOH^+ , CrOH^{++} , MgOH^+ and MnOH^+ is also discussed.

INTRODUCTION

Manganese and chromium are essential components in steelmaking. As far as the United States is concerned, presently 98 percent of the manganese and 90 percent of the chromium consumed are being imported (Kilgore and Thomas, 1982; Lemons et al., 1982). Annual domestic consumption of chromite in the United States in 1979 was 441,000 metric tons (Lemons et al., 1982). It has been reported that 4.6 million metric tons of Cr_2O_3 in chromite ores are potentially recoverable from U.S. deposits (Lemons et al., 1982).

Current demand in the United States for manganese is about 1.4 million metric tons per year (Kilgore and Thomas, 1982). A recent U.S. Bureau of Mines report indicates that there are eight known domestic deposits of manganese with estimated reserves of 420 million metric tons (Kilgore and Thomas, 1982). Average grade of these deposits is about 10 percent manganese. The estimated cost for processing these deposits ranges from \$8 to \$35 per long ton unit compared with the market price of \$1.70 per long ton unit (Kilgore and Thomas, 1982).

Sources of chromite for the U.S. are South Africa, Turkey and Russia. Beneficiation of ores is usually accomplished with magnetic and gravity concentration techniques.

In the case of manganese, principal sources are Brazil, Gabon and Australia. These ores are received without major beneficiation.

As lower grade materials are processed, techniques must be developed to concentrate these valuable minerals. Flotation is a promising technique, and research has been conducted to establish the fundamentals of chromite and manganese oxide flotation as well as the practical separations that can be obtained. A review of these principles and separations is presented in this paper.

Ores

Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) is the most common source of chromium. The mineral has a density of about 4.6 g/cm^3 , and the theoretical content of Cr_2O_3 is 68% by weight. Because of its frequent association with peridotite rocks and serpentine, beneficiation of chromite almost always involves these rocks (Nafziger, 1982). The mineral frequently occurs in nature as an impure spinel-structured entity with Mg^{+2} being commonly substituted for Fe^{++} and Fe^{+3} and Al^{+3} being substituted for Cr^{+3} . Therefore, it is important to understand the effect of these metal ions on the surface behavior of chromite for effective flotation.

The source minerals of manganese include pyrolusite, psilomelane, wad, manganite, rhodonite and rhodochrosite. These minerals are frequently associated with silica and aluminum silicates.

FLOTATION BEHAVIOR

Chromite

Taggart and Arbiter (1943) used contact angle as a measure of floatability of various oxides with oleic acid; large contact angles were obtained from pH 3-7 for chromite. Fatty acids have been used extensively in the flotation of chromite ores (Taggart and Arbiter, 1943; Morawietz, 1959; Sagheer, 1966; Havens, 1946; Sommerlatte, 1962; Sobieraj and Laskowski, 1973; Sullivan and Wodkentine, 1964; Sullivan and Stickney, 1960), and selective flotation is usually achieved in the acidic pH range, pH 1.5-6. Oil emulsion flotation with 4 lb/ton oleic acid and 40 lb/ton diesel oil was also conducted at pH 4 (Huiatt, 1985). CMC/tall oil mixtures consisting of 2.5 lb/ton tall oil, 0.5 lb/ton CMC and 1 lb/ton dispersant were successfully used at pH 11.3 (Sher et al., 1968).

To improve selectivity, various depressants have been used. These include sodium fluoride (Sullivan and Wodkentine, 1964; Sullivan and Stickney, 1960) and sodium fluosilicate (Morawietz, 1959). Havens (1946) suggested use of oleic acid with hydrofluoric acid for selective flotation of chromite. However, Abido (1971) discounts the notion that fluoride is an activator for soap flotation. In fact, it is reported that hydrofluoric acid is detrimental to soap flotation but is quite effective for selective amine flotation of chromite at pH 3.5-4.5 as shown in Figure 1. Other investigators (Morawietz, 1959; Sobieraj and Laskowski, 1973; Hunter and Sullivan, 1960; Smith et al., 1981) also used amine, and good selectivity was achieved in acidic solutions.

The important effect that ions such as Mg^{++} , Ca^{++} and Fe^{+3} exhibit in the flotation of chromite has been observed by numerous investigators (Sobieraj and Laskowski, 1973; Smith et al., 1981; Smith and Allard, 1983). Some authors (Sobieraj and Laskowski, 1973; Smith and Allard, 1983) have pointed out that aging and pre-treatment of chromite ores are also very important in governing flotation response.

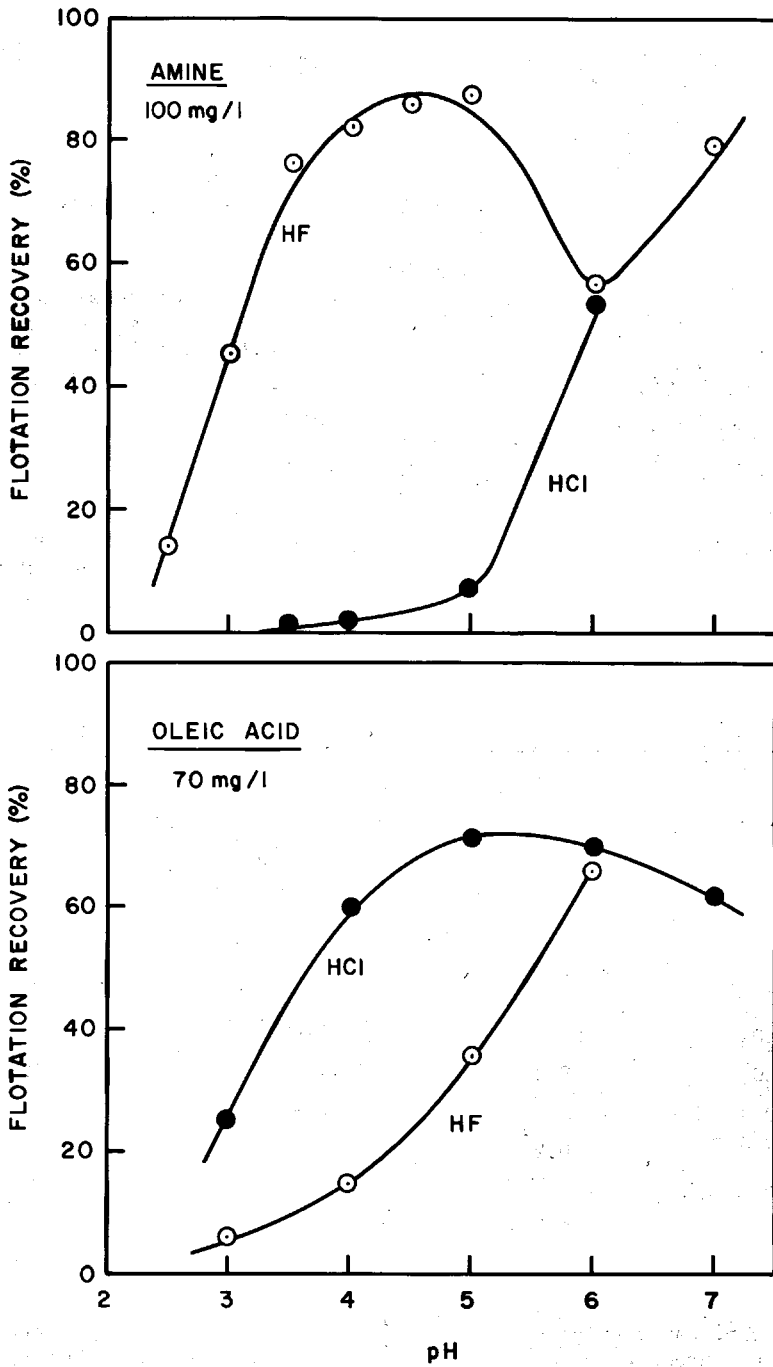


Figure 1. Flotation recovery of chromite with dodecylammonium chloride and oleic acid as a function of pH adjusted with HCl or HF (Abido, 1971).

Table I presents the point-of-zero-charge (pzc) of chromite and manganese-bearing minerals. The chemical compositions of three chromites whose flotation results will be reviewed in detail are listed in Table II.

Table I. The point-of-zero-charge of some chromium and manganese minerals.

Mineral	pzc (pH)	Reference
Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$)	5.0, 3.5-5.4 4.4-9.2	Sobieraj and Laskowski (1973), Smith and Allard (1983), Palmer et al. (1975b), Palmer (1972)
Rhodonite (MnSiO_3)	2.8	Palmer et al. (1975a)
Pyrolusite (MnO_2)	7.4	Fuerstenau and Rice (1968)
α - MnO_2	4.5	Healy et al. (1966)
β - MnO_2	7.3	Healy et al. (1966)
γ - MnO_2	5.5	Healy et al. (1966) Natarajan and Fuerstenau (1983)
δ - MnO_2	1.5	Healy et al. (1966)
Mn(II)-manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$)	1.8	Healy et al. (1966)

Table II. Composition of chromite samples.

	Chromite I	Wt. % Chromite II	Chromite III
Cr_2O_3	61.0	57.2	42.8
FeO	9.1	13.7	22.1
Fe_2O_3	10.7	3.0	11.7
Al_2O_3	8.0	12.0	13.4
MgO	14.8	13.5	9.7
CaO	0.2	-	<0.1
SiO_2	0.7	0.4	-
TiO_2	0.1	-	-

Palmer, Fuerstenau and Aplan (1975) studied the flotation characteristics of three different chromites. The response of one of these samples, Chromite I, using oleic acid as collector is provided in Figure 2. It should be noted that the point-of-zero-charge of this particular chromite was pH 7.2 (Figure 3). The maximum recovery in acidic media, pH 3-5, is believed to be due to physical adsorption of oleic acid onto the positively-charged surface. The two maxima in the alkaline region, namely at pH 8.5 and 11, coincide with the maximum concentration of

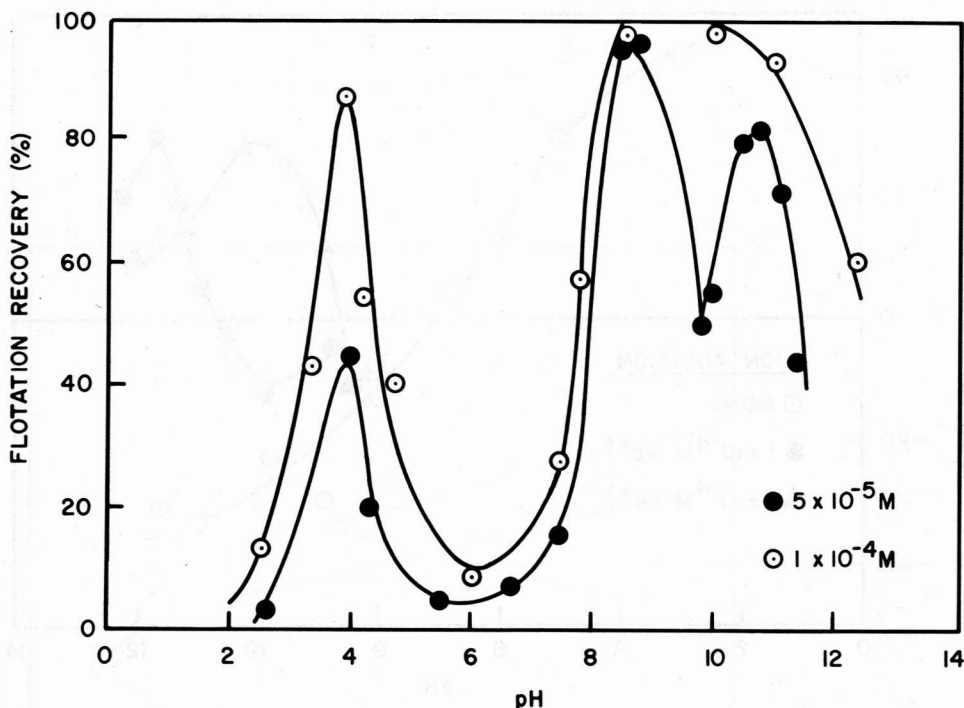
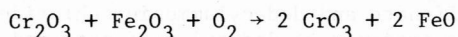


Figure 2. Flotation recovery of chromite I as a function of pH in the presence of oleic acid (Palmer, Fuerstenau and Aplan, 1975).

hydrolyzed species of Fe^{++} and Mg^{++} at these pH values as shown in Figure 4. In Figure 3, the effect of these ions on the zeta potential of chromite demonstrates clearly the remarkable influence of these hydroxy complexes and metal hydroxides. Chemisorption of high molecular weight collectors on oxides and silicates in the presence of hydroxy complexes at the solid surface has been well recognized and documented (Fuerstenau et al., 1985).

Sobieraj and Laskowski (1973) have floated synthetic and natural chromites with sodium laurate and found that there is no flotation maximum in the alkaline pH range with synthetic chromite, while a maximum recovery peak at pH 11 is noted with the natural chromite, Chromite II (Figure 5). The maximum recovery peak at pH 11 disappears when the natural chromite is washed with HCl solution and floated with fresh solution containing sodium laurate. Similar work was performed by Smith and Allard (1983) with chromite washed in concentrated HCl for one week. Flotation was performed on this washed mineral, Chromite III, with 10^{-4} M dodecylamine chloride and 10^{-4} sodium dodecyl sulfate. See Figure 6.

Several studies (Sobieraj et al., 1972; Laskowski, 1981; Smith, 1981; Sobieraj and Laskowski, 1973; Smith and Allard, 1983) have shown that heat treating chromite alters the subsequent flotation response with both anionic and cationic collectors in a rather complex manner. Chromium ion (Cr^{+3}) in chromite is easily oxidized to Cr^{+6} by the following reaction:



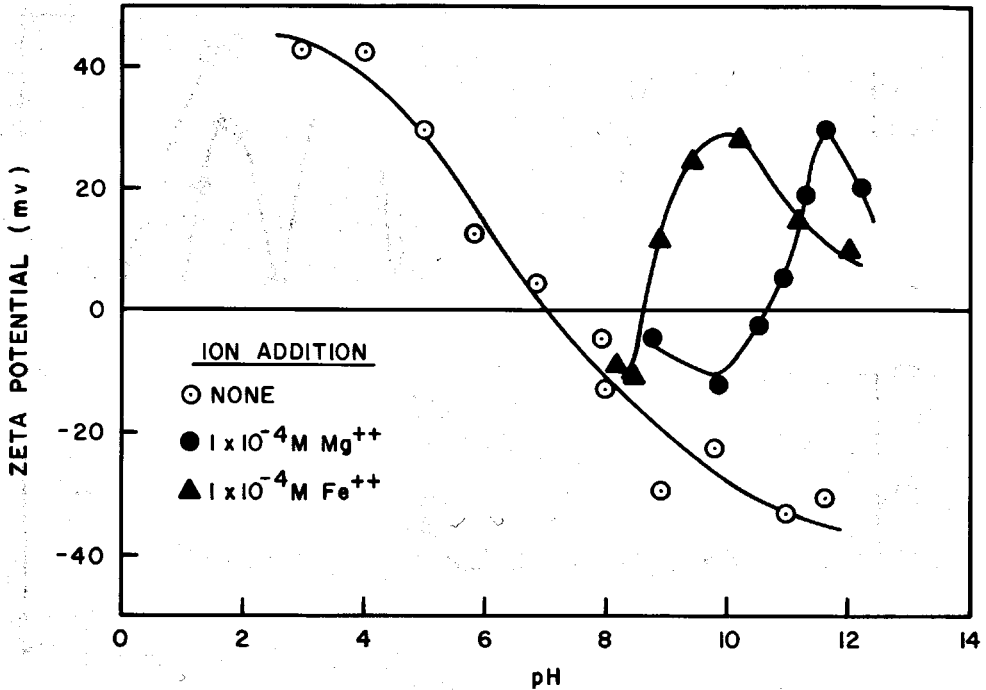


Figure 3. Zeta potential of chromite I in the absence and presence of Mg^{+2} and Fe^{+2} (Palmer, Fuerstenau and Aplan, 1975).

Consequently, flotation behavior of chromite changes with oxidation. Figure 7 presents the results of flotation before and after heat treatment in the presence of oxygen. These experiments were performed with 10^{-4} M sodium dodecyl sulfate. It is interesting to note that this sample of chromite did not respond well to flotation in alkaline medium before heat treatment. After heat treatment, however, chromite showed three distinctive peaks at pH 4, 8 and 10. It can be also noted that these peaks coincide well with the three maximal concentration peaks of CrOH^{++} , FeOH^+ , and MgOH^+ as seen in Figure 4. Smith and Allard feel that the heat treatment increases the solubility of chromite which then results in the release of these metal ions into solution. Extended heat treatment also leads to the oxidation of iron from Fe(II) to Fe(III) and strong laurate adsorption (Laskowski, 1981).

Typical flotation results of chromite ores found in the United States are presented in Tables III-VI.

Manganese Minerals

The points-of-zero-charge of some manganese-bearing minerals are listed in Table I. As noted by Healy, Herring and Fuerstenau (1966), the pzc for MnO_2 decreases with increase in the oxygen content of the oxide (Table I).

Fuerstenau and Rice (1968) studied the electrokinetic and flotation behavior of pyrolusite. The pzc was determined to be pH 7.4. Flotation response with sodium oleate, sodium dodecyl sulfonate and dodecylammonium chloride is given in Figures 8 and 9. Flotation in the presence of dodecyl sulfonate and dodecylamine is due to electrostatic interaction between oxide and collectors (Figure 8). The flotation

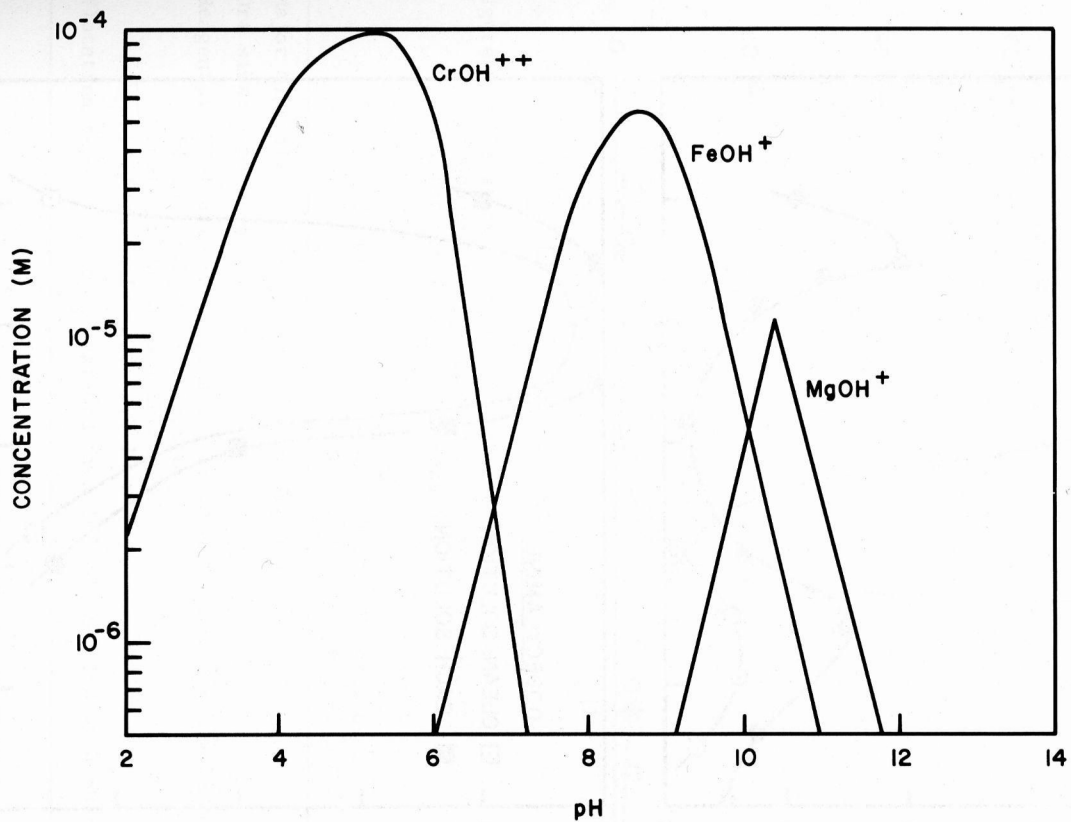


Figure 4. Logarithmic concentration diagram for 1×10^{-4} M Cr^{+3} , 1×10^{-4} M Fe^{+2} and 1×10^{-4} M Mg^{+2} (Palmer, Fuerstenau and Aplan, 1975).

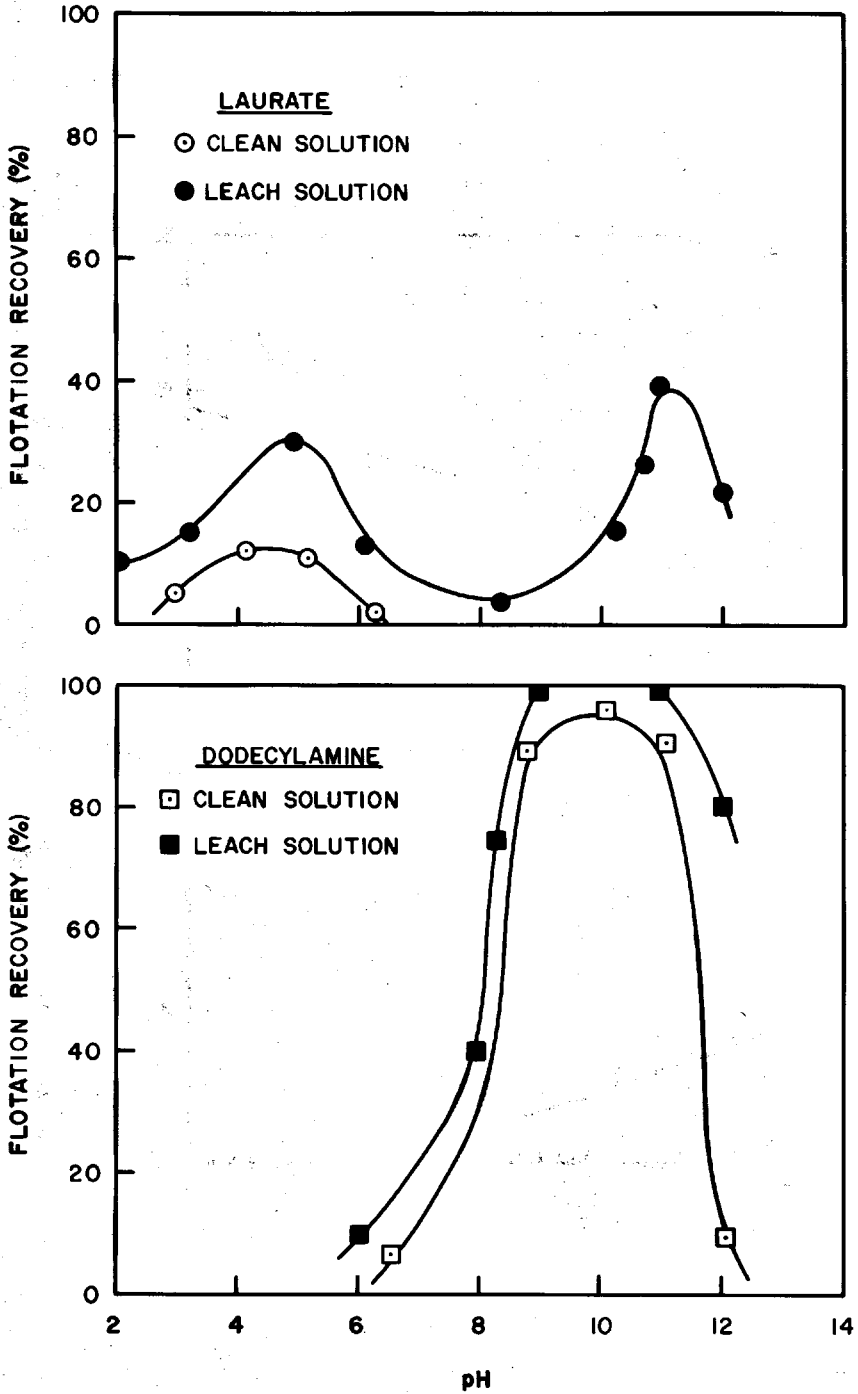


Figure 5. Flotation recovery of chromite II as a function of pH in the presence of laurate and dodecylamine (Sobieraj and Laskowski, 1973).

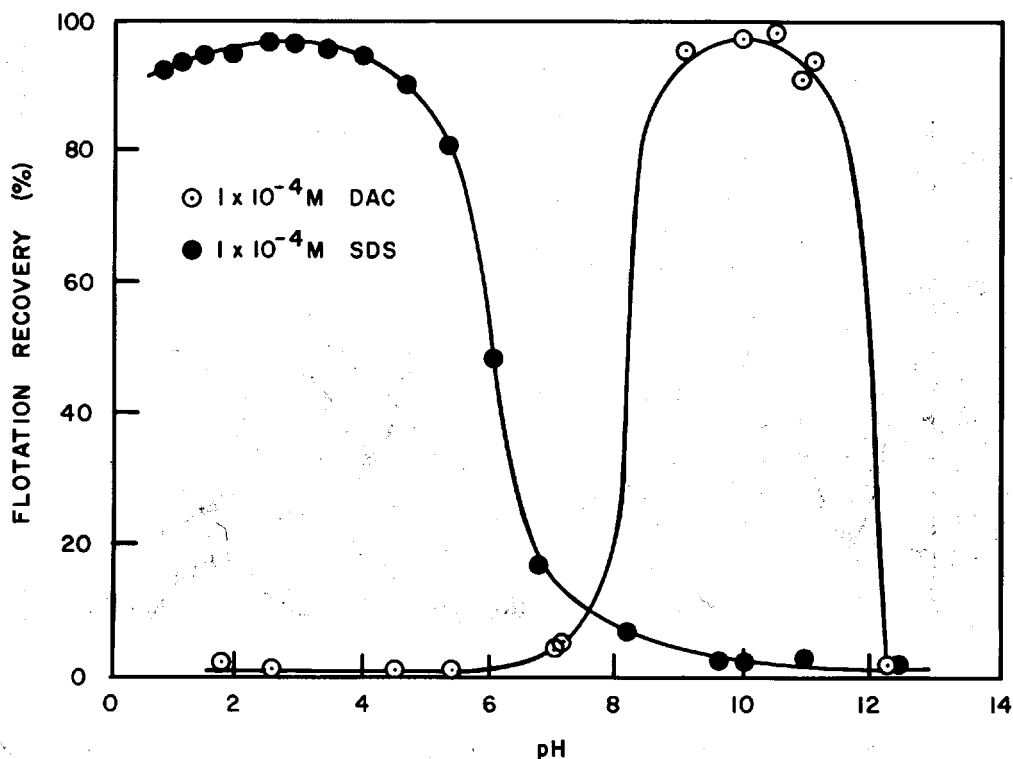


Figure 6. Flotation recovery of chromite as a function of pH in the presence of dodecylamine and dodecyl sulfate. Sample washed in concentrated HCl for one week (Smith and Allard, 1983).

Table III. Flotation of Mouat, Montana ore.
(Sullivan and Wodkentine, 1964)

Major minerals: chromite, olivine and orthopyroxene

Ore size: -65 mesh

Reagents: Fuel oil, tall oil and petroleum sulfonate - 7.5-25 lb/ton ore

Sodium silicate - 1 lb/ton

Sodium fluoride - 4 lb/ton

Sulfuric acid - 10-15.5 lb/ton

Flotation results: Cr_2O_3 upgraded from 10% to 22-33.5% with 80-86% recovery

behavior of pyrolusite with sodium oleate is more complex. As can be seen in Figure 8, there are two flotation maxima, one at pH 4 and the other at pH 8.5. The flotation response in the acidic pH range is due to electrostatic interaction between the positively-charged manganese oxide and negative collector. However, the flotation peak at pH 8.5 is due to chemisorption of oleate on the mineral surface. Kharlamov and his co-workers (Kharlamov et al., 1966; Kharlamov and Kirnosov, 1966) have also observed two maxima, one at neutral pH and the other in the alkaline range. In another study, infrared analysis of the oleate adsorption reaction as a function of pH

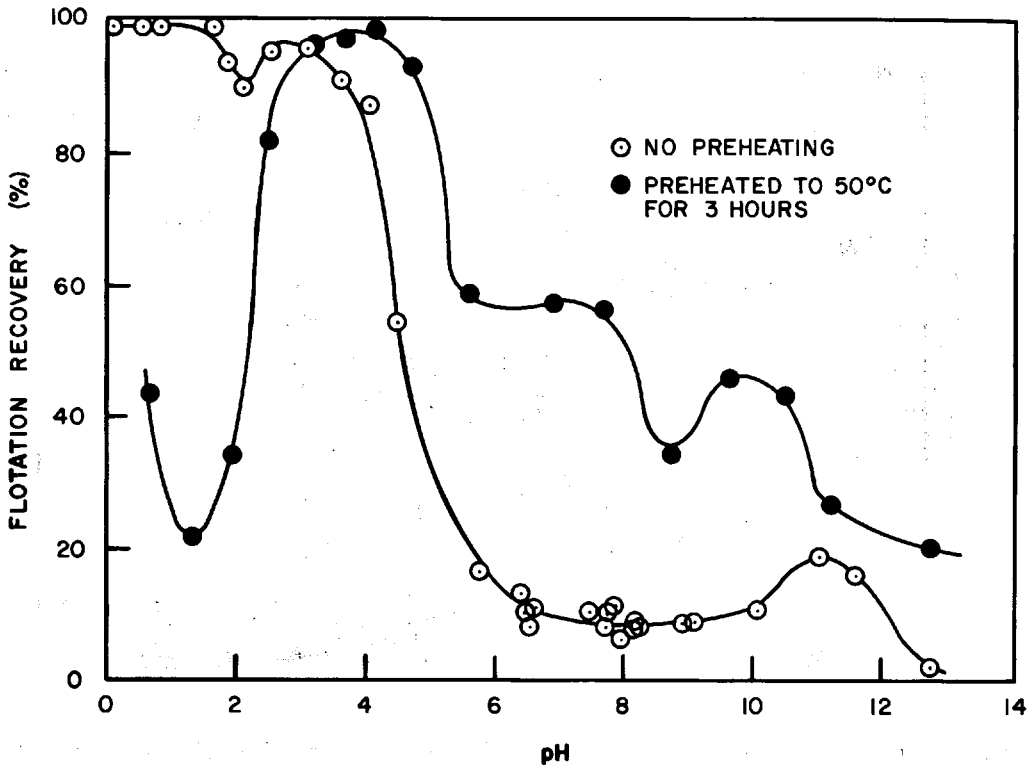


Figure 7. Flotation recovery of chromite as a function of pH in the presence of 1×10^{-4} M dodecyl sulfate (Smith and Allard, 1983).

Table IV. Flotation of Benbow, Montana ore.
(Sullivan and Wodkentine, 1964)

Major Minerals: chromite, serpentine, orthopyroxene

Ore size: -65 mesh

Reagents: Fuel oil, tall oil and petroleum sulfonate - 10-25 lb/ton
Sodium silicate - 1 lb/ton
Ultrawet 30-DS - 0.56 lb/ton
Sodium fluoride - 4 lb/ton
Sulfuric acid - 4.25-11.25 lb/ton

Flotation results: Cr_2O_3 upgraded from 8% to 16.1-28.1% with 65-72% recovery

has indicated that strong adsorption occurs between pH 5 and pH 8 (Bondarenko et al., 1969).

Rhodonite also responds to flotation at the same pH with hydroxamate as collector (Figure 10; Palmer et al., 1975a). This is the pH at which Mn^{++} hydrolyzes significantly to MnOH^+ . See Figure 11. Supporting evidence of the role that MnOH^+ assumes in this system is provided by the electrokinetic data in Figure 12. Zeta reversal occurs at pH 7.6, and a maximum positive value occurs at pH 8.7. This is

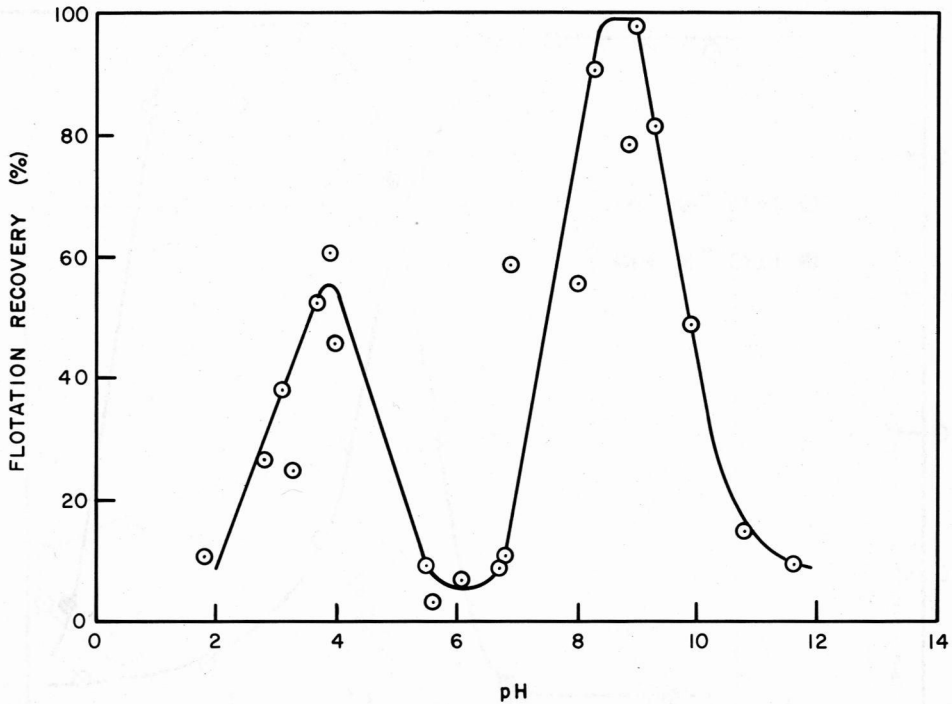


Figure 8. Flotation recovery of pyrolusite as a function of pH in the presence of 1×10^{-4} M sodium oleate (Fuerstenau and Rice, 1968).

Table V. Flotation of George Len, Oregon ore. (Sullivan and Stickney, 1960)

Major minerals: chromite, dunite, peridotite, serpentine

Ore size: -100 mesh

Reagents: Sodium fluoride - 2 lb/ton
 Fuel oil - 15.3 lb/ton
 Tall oil/petroleum sulfonate - 19 lb/ton
 Sulfuric acid - 3 lb/ton

Flotation results: Cr_2O_3 upgraded from 31.2% to 37.1% with 91% recovery

Table VI. Flotation of Benbow, Montana ore. (Smith et al., 1981)

Major minerals: chromite, serpentine, enstatite

Ore size: -100 mesh

Reagents: Armac C (primary amine) - 0.4-1 lb/ton
 Sulfuric acid - 20-50 lb/ton

Flotation results: Cr_2O_3 upgraded from 10% to 40% with 79% recovery

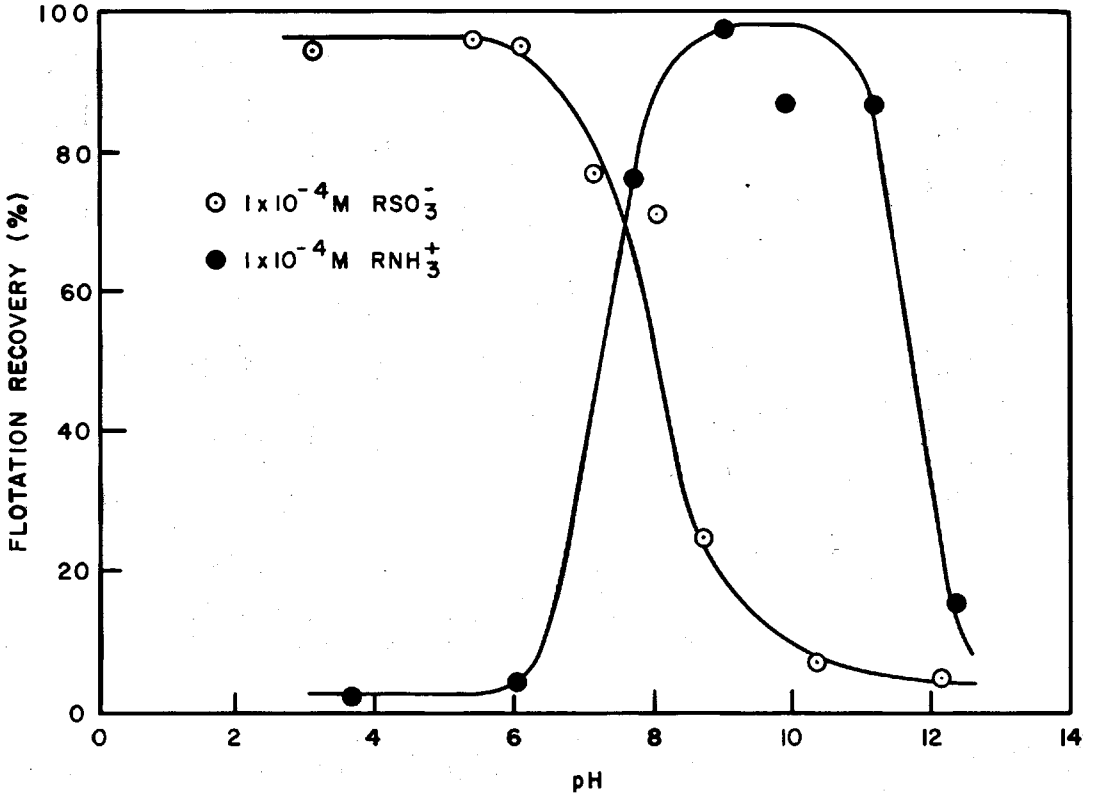


Figure 9. Flotation recovery of pyrolusite as a function of pH in the presence of dodecyl sulfonate and dodecylamine (Fuerstenau and Rice, 1968).

believed to be due to the strong adsorption of MnOH^+ on the oxide surface. The maximum recovery at pH 8.5 is also thought to be due to MnOH^+ adsorption on the mineral surface.

Pyrolusite is manganic oxide, and formation of the hydroxy complex of manganous ion could occur only after slight mineral dissolution has occurred, followed by a redox reaction between Mn^{+4} and water. In practice dissolution of pyrolusite has been enhanced by the addition of sulfur dioxide or MnSO_4 to ore systems (McCarroll, 1954; Fahrenwald, 1957). Dissolution can also be enhanced with elevated temperature. The response of a sample of pyrolusite at 23° and 60°C is given in Figure 13. Recovery is minimal at 23°C, while complete recovery is obtained at 60°C.

Considerable research has been done to establish the relative order of flotation of manganese oxide minerals (Goldberg et al., 1968a, 1968b, 1969; Kharlamov et al., 1966; Kharlamov and Kirnosov, 1966). In these studies, it has been shown that flotation with anionic collectors decreases in the order: manganite, pyrolusite, and psilomelane. This order was observed for both oleic acid and tridecyl acid and was explained by Goldberg et al. (1968b) to be established by the corresponding order of increase in surface hydration energies.

Natarajan and Fuerstenau (1983) have investigated flotation behavior of $\gamma\text{-MnO}_2$ in the presence of octyl hydroxamate and sodium dodecyl sulfonate. As shown in

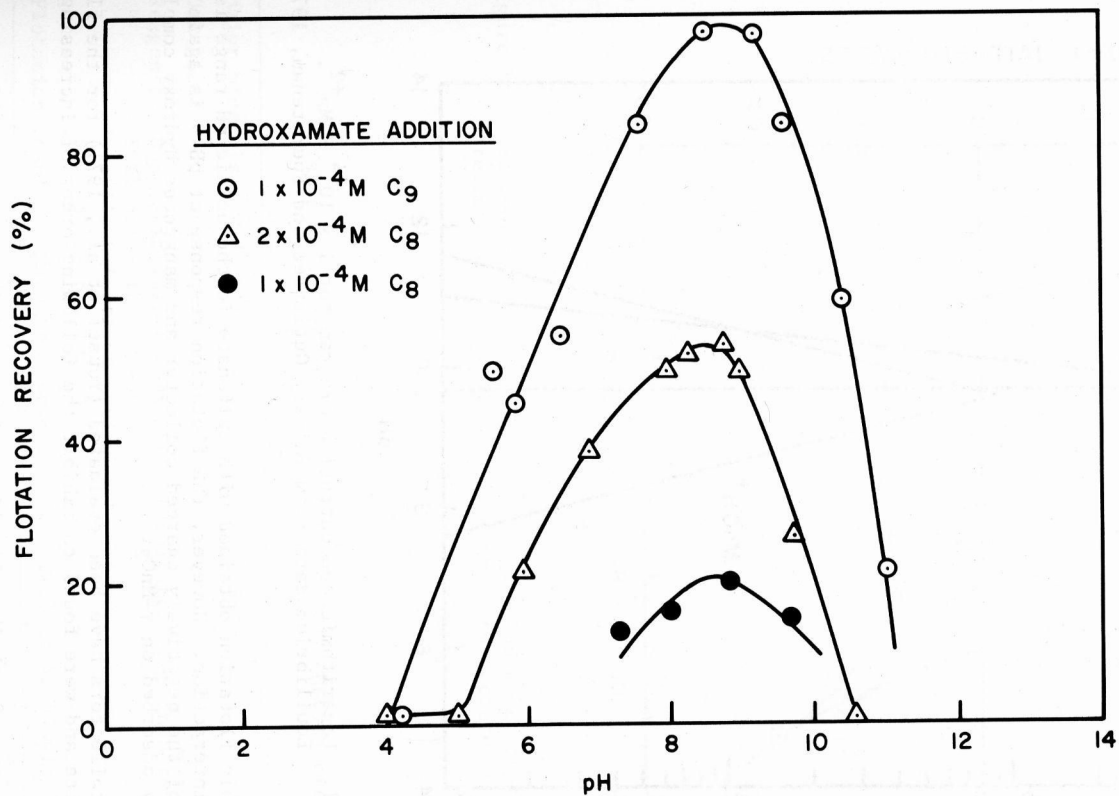


Figure 10. Flotation recovery of rhodonite as a function of pH in the presence of octyl and nonyl hydroxamate (Palmer, Gutierrez and Fuerstenau, 1975).

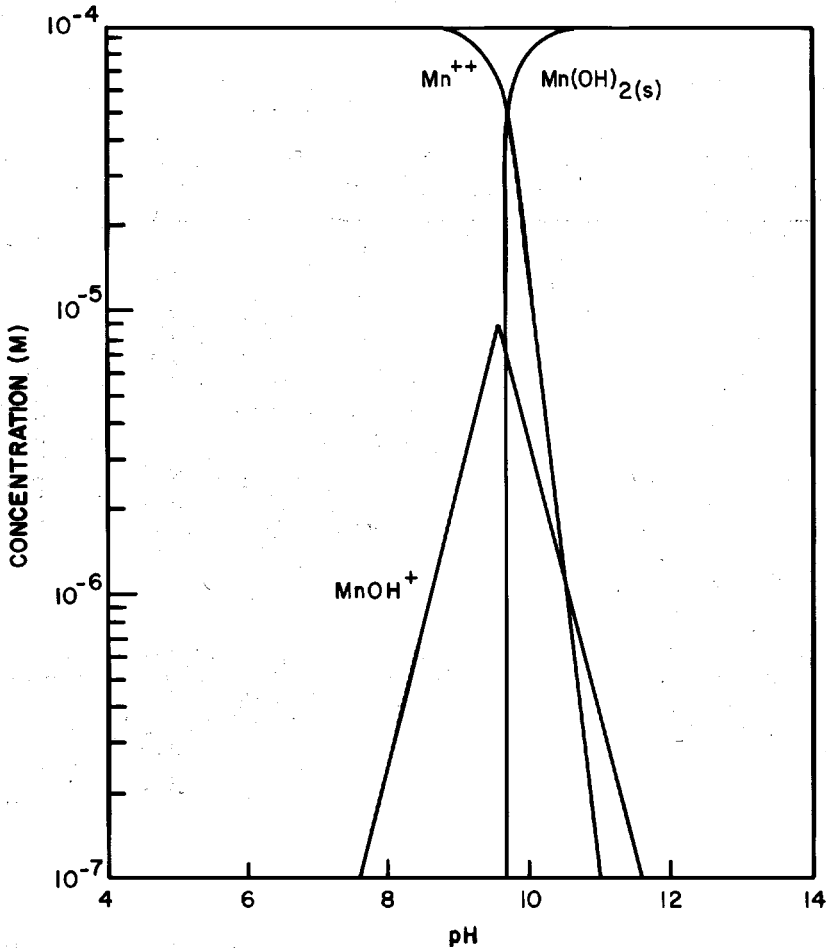


Figure 11. Logarithmic concentration diagram for 1×10^{-4} M Mn^{+2} . Equilibrium data from Palmer, Gutierrez and Fuerstenau, 1975.

Figure 14, favorable flotation obtained with sulfonate in the acidic pH range is due to electrostatic interaction. However, the flotation response at pH 9 is again due to chemisorption of the negatively charged collector and manganese hydroxy complex which are strongly adsorbed on γ - MnO_2 .

Other anionic collectors have been evaluated (Yousef et al., 1971) for the flotation of pyrolusite and were found to exhibit the following order of increasing effectiveness:

dodecyl sulfate < 2-ethylhexyl sulfosuccinate < dodecylbenzene sulfonate.

When manganese ores have been floated, fatty acids have been used as collector (McCarroll, 1954; Kurova, 1970; Goldberg et al., 1986a; Kharlamov et al., 1966; Fahrenwald, 1957). As in the case of chromite flotation, the effect of foreign ions on the floatability of manganese ores is substantial. Table VII presents flotation results of a manganese ore located in the U.S.

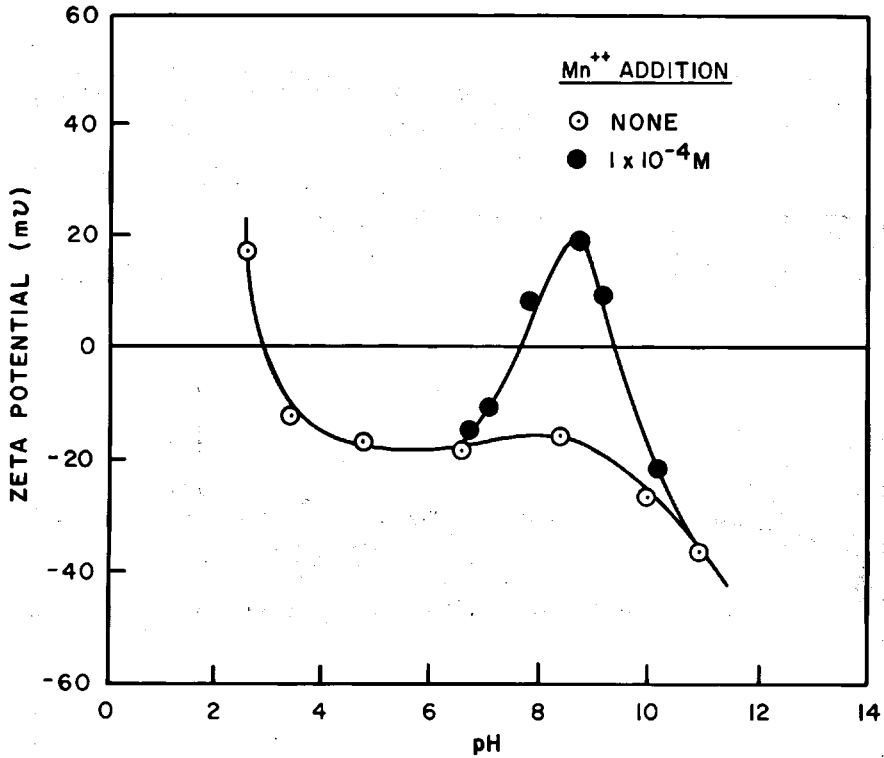


Figure 12. Zeta potential of rhodonite as a function of pH in the absence and presence of Mn²⁺ (Palmer, Gutierrez and Fuerstenau, 1975).

Table VII. Flotation of the Three Kids, Nevada ore. (McCarroll, 1954)

Major minerals: wad, psilomelane, silica, alumina

Ore size: -65 mesh

Reagents: Soap skimmings (by-product of sulfate paper industry) - 40 lb/ton

Fuel oil - 120 lb/ton

Oronile S (wetting agent) - 6 lb/ton

SO₂ (5%) - 8.5 lb/ton

Flotation results: Manganese upgraded from 21.3 to 45.5% with 84% recovery

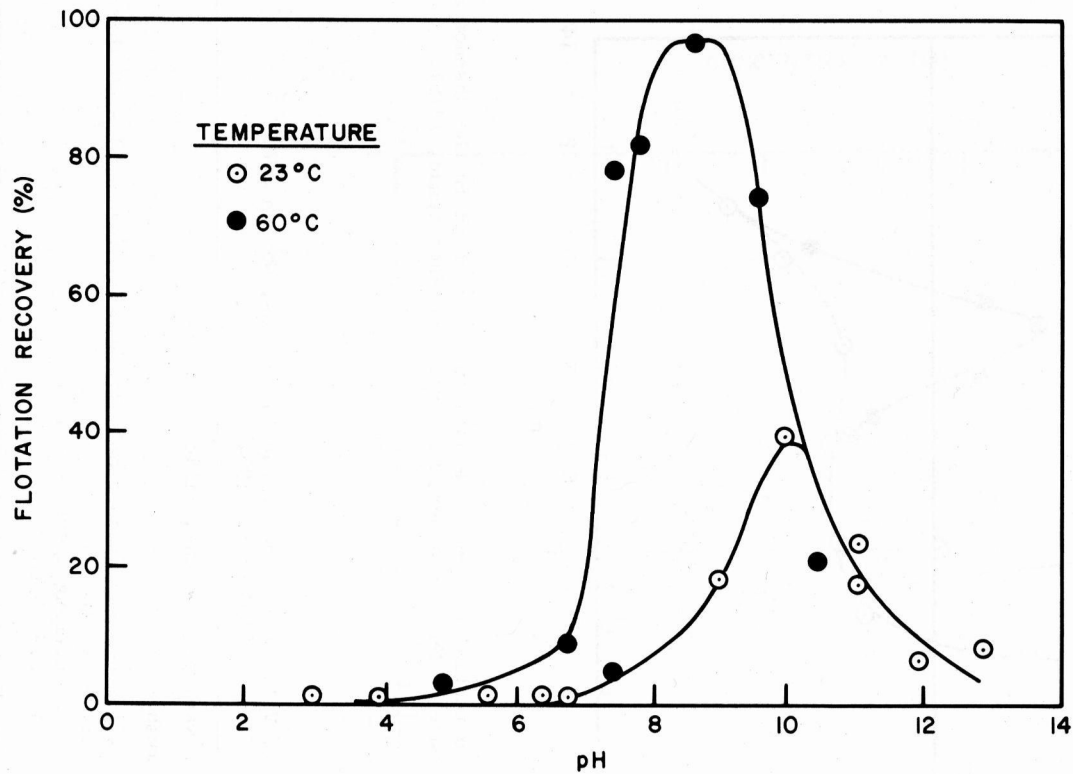


Figure 13. Flotation recovery of pyrolusite as a function of pH and temperature in the presence of 1×10^{-4} M oleate (Fuerstenau and Rice, 1968).

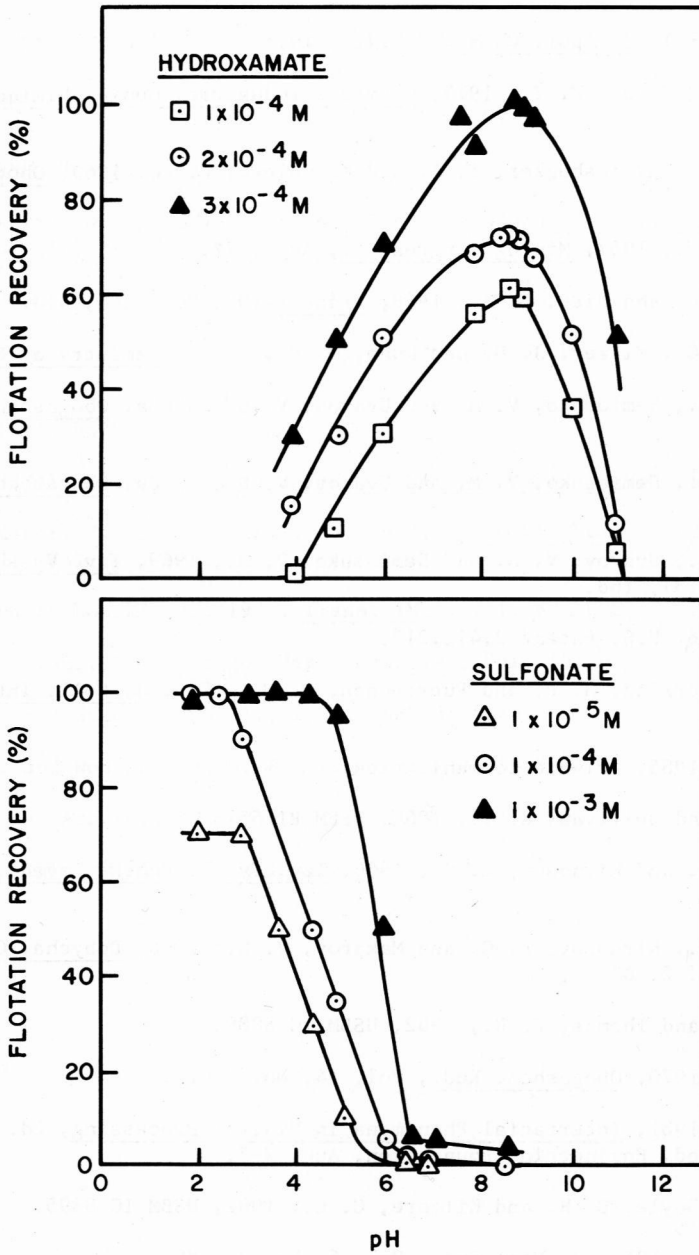


Figure 14. Flotation recovery of $\gamma\text{-MnO}_2$ as a function of pH in the presence of octyl hydroxamate and dodecyl sulfonate (Natarajan and Fuerstenau, 1983).

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