The Feasibility of Activation of Manganese Minerals Flotation

By A. M. Abeidu*

The feasibility and the mechanism of activation of pyrolusite, manganite, and rhodochrosite with Fe (III), Cu (II) and Mn (II) in an anionic collector system using oleic acid as the collector have been investigated. The results obtained showed a certain regularity as basically determined by the acidity of the heavy metal cation and the pH of its precipitation, the pK_a of the oleic acid, the chemical composition of the manganese mineral tested, and the pH of its isoelectric point. Thus, Cu (II) and Mn (II) which are basic and hydrolyze at pHs above those of the isoelectric points of the manganese minerals investigated could, within certain specific limits of medium pH, act as activators for pyrolusite and manganite. On the other hand, Fe $(H_2O)_6^{+++}$ which is acidic, ionizes at pH 2.2 and is precipitated at pH 3.7, which is below than both the isoelectric point of the manganese minerals studied and the pK_a of oleic acid, is of no particular advantage in the activation and flotation. The response of rhodochrosite, without pre-activation, to soap flotation seems to be due to the basic property of the bivalent manganese sites in its crystalline lattice, which produces a tendency for the attachment of oleic acid. Owing to the negative surface charge of the manganese minerals at pH above 5 and the positive surface charge of the gangue minerals (barite, gypsum, calcite), the anion, $Al_2SiO_3(OH)_6^-$, resulting from the conjunction of Na_2SiO_3 with $Al_2(SO_4)_3$ is adsorbed preferentially to the surface of the latter leading to a successful differential flotation.

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I. Introduction

Each type of a manganese deposit is a problem by itself in the matter of selection of a proper method of concentration, depending on the manganese minerals and their gangue constituents. In the Elba region of the Eastern Desert of Egypt occurs a manganese deposit in which the manganese minerals are represented by pyrolusite (MnO_2) and manganite ($MnO(OH)$). Rhodochrosite ($MnCO_3$) is rather rare. Of the gangue minerals, the removal of barite ($BaSO_4$), gypsum ($CaSO_4$) and calcite ($CaCO_3$) presents the greatest difficulty. In this paper the possibility and the mechanism of activation and selective flotation of the manganese minerals were investigated.

II. Experimental Techniques

The reagents were of the analytical grade. In view of the availability of reasonably pure natural crystals of pyrolusite, manganite, rhodochrosite, calcite, barite and gypsum from the Elba region in the Eastern Desert of Egypt, natural crystals of these minerals were used. The crystals were crushed in a porcelain mortar and screened to give -100, +150 mesh fraction for flotation tests and -150, +200 mesh fraction for streaming potential studies. The description of the Hallimond tube used is given in a previous paper⁽¹⁾. The equipment used for the electrokinetic measurements was the same as that used earlier⁽²⁾. The procedure used for adsorption studies with oleic acid is with a high degree of accuracy ($\pm 10\%$) and also sensitivity (0.02%)⁽³⁾⁽⁴⁾. It is based on the measurements of the optical density of OIH in the infrared region of the

spectrum with the frequency at 1720 cm^{-1} . The procedure is described elsewhere⁽³⁾⁽⁴⁾.

III. Results and Discussion

The influence of pH on the surface electrokinetic properties of manganese and gangue minerals has been studied. The isoelectric point of pyrolusite, manganite and rhodochrosite was noticed at pH 3.8, 3.9 and 4.8, respectively. It seems likely that $>MnOH$ site predominates around the pH of the isoelectric point, whereas $>MnOH_2^+$ and $>MnO^-$ predominates below and above it, respectively. There was no change in the sign of the electrical charge of barite, calcite and gypsum in the pH range from 1.5 to 11 which means that the isoelectric points were not reached, although the value of the zeta potential decreased at high and low pH values, due presumably to the compression of the electrical double layer.

It is to be noted that the effect of metal cations on the zeta potential of a manganese mineral differs from one cation to another. Thus Fe(III) has no effect on the zeta potential of pyrolusite and manganite at pH above 2.5 and a mild effect on their zeta potential at pH below 2.5. By contrast, Cu(II) and Mn(II) affect markedly the zeta potential of manganese minerals over a wide pH range (3 ~ 9). The form of the curves for the zeta potential of manganese minerals in the presence of Cu(II) profoundly differs from those in the presence of Mn(II). Study of these curves reveals a certain regularity for the influence of each cation on the zeta potential. As seen from Figs. 1 ~ 3 Cu(II) has a maximum effect at pH of about 7 on the zeta potential, whereas Mn(II) has two maxima of effects, which were noticed at pH of about 5 and 8.5. Before

* Laboratory of Metallurgy, National Research Centre, Egypt.

(1) A. M. Abeidu: J. Less-Common Metals, 22 (1970), 355.

(2) A. M. Abeidu: J. of Mines, Metals & Fuels, 17 (1969), 80.

(3) A. M. Abeidu: Indian J. of technology, 9 (1971), 344.

(4) A. Ya. Zhavoronkova, E. I. Moiseeva, S. A. Shelkova and N. F. Mishin: The Soviet J. of non-ferr. Metals, 8 (4) (1967), 28.

Fig. 1 Zeta potential of pyrolusite as a function of pH: (1) without any additions; (2) in the presence of 50 mg/L of FeCl_3 ; (3) in the presence of 50 mg/L CuSO_4 ; (4) in the presence of 50 mg/L MnSO_4 .

Fig. 2 Zeta potential of manganite as a function of pH: (1) without any additions; (2) in the presence of 50 mg/L FeCl_3 ; (3) in the presence of 50 mg/L of CuSO_4 ; (4) in the presence of 50 mg/L of MnSO_4 .

any interpretation of the data of Figs. 1 ~ 4, it is necessary to consider the state of both the cations tested and the surface sites in the crystalline lattice of the manganese minerals over a range of pH. $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ is a fairly strong acid⁽⁵⁾ and undergoes acid ionization⁽⁶⁾ such as:

The first ionization constant for $\text{Fe}(\text{H}_2\text{O})_6^{+++}$ is comparable to the second ionization constant for sulfuric acid⁽⁵⁾, being about 10^{-2} . On the other hand, $\text{Cu}(\text{II})$ is a weak base⁽⁵⁾ and ionizes as follows⁽⁷⁾:

Fig. 3 Zeta potential of a rhodochrosite as a function of pH: (1) without any additions; (2) in the presence of 50 mg/L of CuSO_4 ; (3) in the presence of 50 mg/L of MnSO_4 . N.B.: FeCl_3 is almost without effect on the zeta potential.

Fig. 4 Zeta potential of minerals as a function of pH without any additions: (1) barite; (2) gypsum; (3) calcite. Zeta potential of minerals as a function of pH in the presence of the reagent mixture (50 mg/L Na_2SiO_3 + 50 mg/L $\text{Al}_2(\text{SO}_4)_3$): (4) barite; (5) gypsum; (6) calcite.

Similarly for $\text{Mn}(\text{II})$:

Of the ionic species, Mn^{++} , $\text{Mn}(\text{OH})^+$, $\text{Cu}(\text{OH})^+$ and to some extent Cu^{++} show a concentration of pH relationship similar to the zeta potential. Iron ionic species, Fe^{+++} , and especially its hydroxide complex, $\text{Fe}(\text{OH})^{++}$ and $\text{Fe}(\text{OH})_2^+$, do not show such a relationship. Consequently, the mechanism of activation of the manganese minerals by metal cations tested seems to be as follows:

(5) R. B. Fischer and D. G. Petters: *Basic theory and practice of quantitative chemical analysis*, 3rd ed., W. B. Saunders Company, Philadelphia, London, Toronto, (1968), p. 380, 588.

(6) L. Pauling: *General chemistry*, 2nd ed., W. H. Freeman and Co., San Francisco, (1956), p. 446.

(7) T. Moeller: *Inorganic chemistry*, John Wiley and Sons, New York, (1952), p. 502.

Similarly for Cu(II)

The symbol $>$ represents schematically the lattice surface.

In the case of Fe(III)

The hydroxide complex, $\text{Fe}(\text{OH})^{++}$ and $\text{Fe}(\text{OH})_2^+$ predominate in the pH range 2.2 ~ 3.7 but the suitable manganese surface sites $>\text{MnO}^-$ for their attachment are not available in this pH range owing to the fall of the isoelectric point of the manganese minerals at pHs above 3.5. This may explain the small change in the value of the zeta potential caused by the addition of Fe(III).

The abrupt change in the zeta potential of barite and gypsum (Fig. 4) in the pH range 2 ~ 3 coupled with the high degree of dissociation of SO_4H^- , which is about 10^{-2} are indications to the following configuration of sulphate sites:

On the other hand, the merely reduction of the zeta potential without change in its sign in the pH range 3 ~ 5 and the approaching of the zeta potential to the vanishing point in the pH range 6 ~ 10 suggest that the surface sites $>\text{BaOH}_2^+$ and $>\text{CaOH}_2^+$ predominate at pH below 5, whereas $>\text{BaOH}$ and $>\text{CaOH}$ predominate from pH 6 to pH 10. It is to be noted that the zeta potential of the gangue minerals is insensitive to the metal cations tested. It seems likely that the interfacial electrical conditions (Fig. 4) makes the attachment of the positively charged metal cation species (eqs. (1) ~ (7)) to the positively charged surfaces of the gangue minerals rather improbable. On the other hand, these surfaces could bond the anionic collector species as follows:

In the case of gypsum and calcite

In the case of barite a similar mechanism takes place but instead of the calcium sites there are barium sites. Thus, the surface sites of the calcite, the barite, and the gypsum are suitable for the attachment of the anionic collector (oleic acid) species (Fig. 5). Subsequently, they respond well to soap flotation (Fig. 6). In order to impede the co-flotation of these gangue minerals with the manganese minerals, the use of a selective and an effective depressant is indispensable.

Experimentation with the reagent mixture of water glass (Na_2SiO_3) + aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3$)

Fig. 5 The uptake of oleic acid from solution (100 mg/L) by: (1) barite; (2) gypsum; (3) calcite; Uptake in the presence of the reagent mixture (50 mg/L Na_2SiO_3 + 50 mg/L $\text{Al}_2(\text{SO}_4)_3$) by: (4) barite; (5) gypsum; (6) calcite.

Fig. 6 Recovery of gangue minerals using oleic acid (100 mg/L) as collector: (1) barite; (2) gypsum; (3) calcite; Recovery in the presence of the reagent mixture (50 mg/L Na_2SiO_3 + 50 mg/L $\text{Al}_2(\text{SO}_4)_3$) of (4) barite; (5) gypsum; (6) calcite.

showed that it strongly depresses the gangue minerals (Fig. 6) leaving the flotation of the manganese minerals unaffected. The zeta potential data of the barite, the gypsum, and the calcite in the solution of the reagent mixture (50 mg/l Na_2SiO_3 + 50 mg/l $\text{Al}_2(\text{SO}_4)_3$) are indications to the electrostatic nature of an interaction phenomena. The curves have a similar appearance and show a marked reduction of the zeta potential in the pH range 5 ~ 9. The zeta potentials ultimately change their sign indicating the adsorption of an anion.

The available data in the literature⁽⁸⁾⁽⁹⁾ suggest that the conjunction of water glass (Na_2SiO_3) with aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$ gives the complex compound $\text{Na}_2\text{Al}_2\text{SiO}_3(\text{OH})_6$, which on dissociation gives the anion $\text{Al}_2\text{SiO}_3(\text{OH})_6^{--}$. It seems likely that this hydrophilic anion possesses a tremendous affinity for the positively charged surfaces of the gangue minerals over the negatively charged surfaces of the manganese minerals. The following mechanism seems, therefore,

(8) M. A. Eigels: *Bases of flotation of Non-Sulphide minerals*, Publ. House "NEDRA", Moscow, (1964), p. 217 ~ 220 (in Russian).

(9) V. A. Glembski, V. I. Klassen and I. N. Plaksin: *Flotation*, Publ. "GOSGORTekHIZDAT", Moscow, (1961), p. 168 (in Russian).

probable:

Barium sites behave like calcium. This may explain the reverse of the sign of the zeta potentials.

Adsorption and flotation studies (Figs. 7 ~ 9) show that rhodochrosite adsorbs more oleic acid than pyrolusite or manganite, whence it responds much better to soap flotation without preactivation. However, there is a great increase in OIH adsorption with 50 mg/L of CuSO_4 , or MnSO_4 addition, at certain and specific for each cation pH range, by both pyrolusite and manganite. This may be thought to be due to the reduction of columbic repulsion forces by adsorption Cu^{++} , CuOH^+ , Mn^{++} , and MnOH^+ species onto the negatively charged surface of pyrolusite and

Fig. 7 (The continuous lines represent recovery and the dashed lines represent the adsorption). Recovery of, and the uptake of oleic acid (100 mg/L) from solution by, pyrolusite: (1 & 4) without preactivation; (2 & 5) in the case of preactivation with 50 mg/L CuSO_4 ; (3 & 6) in the case of preactivation with 50 mg/L MnSO_4 . N.B: Fe (III) shows almost no activation.

Fig. 8 (The continuous lines represent recovery and the dashed lines represent the adsorption). Recovery of, and the uptake of oleic acid (100 mg/L) from solution by, manganite: (1 & 4) without preactivation; (2 & 5) in the case of preactivation with 50 mg/L CuSO_4 ; (3 & 6) in the case of preactivation with 50 mg/L MnSO_4 . N.B: Fe (III) shows almost no activation.

Fig. 9 (The continuous lines represent recovery and the dashed lines represent the adsorption). Recovery of, and the uptake of oleic acid (100 mg/L) from solution by, rhodochrosite: (1 & 4) without preactivation; (2 & 5) in the case of preactivation with 50 mg/L CuSO_4 ; (3 & 6) in the case of preactivation with 50 mg/L MnSO_4 . N.B: Fe (III) shows almost no activation.

manganite rendering their surfaces less negative. In addition, Cu(II) and Mn(II) create active sites, suitable for the attachment of collector species. As seen from Figs. 7 and 8 Cu(II) and Mn(II) are effective activators in the pH range 6.5 ~ 8 and 8 ~ 9, respectively. On the other hand, Cu(II) and Mn(II) decrease the adsorptive capacity and floatability of manganese minerals at pHs below 6.5 and 8, respectively.

An interpretation of these results may be given if we take into consideration the state of Cu(II) and Mn(II) (eqs. (1) ~ (7)) and the state of oleic acid in solution. An infrared spectroscopy study⁽¹¹⁾ of oleic acid and sodium oleate solutions showed that the pK_a of OIH is about 8. At pH below 5.2 OIH (undissociated oleic acid molecules) is the only species present in solution. The relative concentrations of OIH at pHs 7 and 8.5 are 90 and 17%, respectively, while the corresponding values for OI^- species are 10 and 68.2%. On the bases of these data and zeta potential data (eqs. (8) ~ (11)) the following mechanism may be postulated:

The deactivating action of Cu(II) and Mn(II) on the adsorptive capacity and floatability of manganese minerals may be due to the attachment of these cations to $>\text{MnOH}$ sites (eqs. (9) and (11)), whence the attachment of oleic acid to these suitable sites (eq. (19)) become rather improbable.

(10) I. N. Kraos, V. A. Derebianskin and S. I. Kyznutsova: The Soviet J. of Non-Ferr. Metals, (7) (1968), 43 (in Russian).

(11) S. I. Polkin, G. S. Berger and I. B. Ribazachvili: Trans. of the higher Educational Establishments, Non-Ferr. Metallurgy, (3) (1968), 6 (in Russian).

Figure 9 shows that a rhodochrosite adsorbs without pre-activation with metal cations or sulfur dioxide (SO_2), oleic acid being in sufficient quantities for flotation to take place. Since the main difference between the manganese surface sites of a rhodochrosite and a pyrolusite is in that in the former the manganese is bivalent and in the latter is quadrivalent, it seems likely that the bivalent manganese site is more suitable, than the quadrivalent manganese site, for the attachment of oleic acid. Indeed, the available data in the literature⁽¹²⁾ confirm that Mn(II) compounds are stable, whereas those of Mn(IV) are unstable. In addition, the low dissociation constant of both H_2CO_3 (10^{-7}) and HCO_3^- (10^{-11}) promotes the attachment of oleic acid to the carbonate sites. Thus, the mechanism by which oleic acid is attached to the surface of a rhodochrosite is:

IV. Conclusions

The suggestion of some investigators⁽¹³⁾⁽¹⁴⁾ that sulfur dioxide (SO_2) introduces manganese ions in the

(12) H. Remy (Translated by J. S. Anderson; Ed. by J. Kleinberg), *Treatise on inorganic chemistry*, Vol. 2—Subgroups of the periodic table and general topics. Elsevier Publishing Company, Amsterdam, London, New York Punceton, (1956), p. 218 ~ 225.

(13) S. J. McCarroll: *Trans. AIME*, **199** (1954), 289.

(14) Ellis H. Gates: *Trans. AIME*, **208** (1957), 1368.

pulp solutions which are directly responsible for the activation of the manganese minerals soap flotation is partly incorrect, since a rhodochrosite responds fairly well to soap flotation without pre-activation with metal cations or with sulfur dioxide. It seems likely that the activating action of sulfur dioxide on the manganese minerals is due to the reduction of the quadrivalent manganese, Mn(IV) , atoms in the surface of the crystalline lattice of pyrolusite and manganite to the divalent state. Also, the suggestion that heavy metal such as Cu(II) and Fe(III) could act as activators is inconsistent with the experimental evidence of this paper. It is to be noted that the feasibility of activation of a manganese mineral with a heavy metal ion is basically determined by the chemical composition of the mineral and the pH of its isoelectric point as well as the pH at which the metal ion begins to hydrolyze and precipitates. If the heavy metal ion begins to hydrolyze and precipitate at pHs equal or below that of the isoelectric point of the manganese mineral, as in the case of Fe(III) , it can not act as activator and on the contrary may act as depressant due to the adsorption of oleic acid by its positively charged colloidal precipitate.

The complex hydrophilic anion $\text{Al}_2\text{SiO}_3(\text{OH})_6^{--}$, which is formed from the conjunction of water glass (Na_2SiO_3) with $\text{Al}_2(\text{SO}_4)_3$ is an effective and selective depressant for the gangue minerals (barite, gypsum, calcite). This anion possesses tremendous affinity for the positively charged surfaces of these gangue minerals over the negatively charged surfaces of the manganese minerals leading to a successful differential flotation.