Adsorption Mechanisms in Nonmetallic Activation Systems

by M. C. Fuerstenau, D. A. Elgillani, and J. D. Miller

Adsorption of lead and ferric iron on quartz and alumina is presented as a function of pH. Only the hydrolyzed species of these metal ions, $FeOH^{++}$ and $PbOH^+$, adsorb significantly on each of these minerals. Zeta potentials of quartz were measured as a function of pH in the presence of various additions of aluminum, lead, and magnesium salts. Sign reversal occurs at the pH values where significant concentrations of hydroxy complexes are formed. Models of adsorption are presented in the absence and presence of collector.

The mechanism of adsorption of metal and collector species in the activation of nonmetallic minerals is still the center of considerable discussion in spite of the extensive study given this system. Until recently, the view was widely held that hydrated metal ions were responsible for this phenomenon. This fact is surprising, since it had been shown that the pH range in which flotation is effected corresponds to that in which metal ion hydrolysis occurs.[1] Additional support of this concept was provided by the work of Wolstenholme and Schulman in another system.[2]

Later work has shown that hydroxy complexes of metal ions are the active species. These studies have also indicated that basic aqueous complexes of metal-collector may be necessary for flotation.[3-7] Depending on the molecular weight of the collector, formation of these complexes may occur before or after precipitation of the metal-collector salt has occurred. Ion pair formation can occur when low molecular weight collectors are involved because relatively high concentrations of metal hydroxy complex and collector can be present in solution before precipitation occurs. This is not the case when high molecular weight collectors are used.

A model of aqueous complex adsorption has been presented[6,7] in which it has been assumed that adsorption occurs by the formation of water from adsorbed hydroxyl and hydrogen of the hydroxyl contained in the complex. Other authors[8] have suggested that hydroxy complexes are involved in these systems but that collector adsorption occurs by replacement of the hydroxyl of the adsorbed metal hydroxy complex with a fatty acid anion.

All of these investigations have involved mineral surfaces that were negatively charged so that it is not possible to state with certainty whether hydrated metal ions or hydroxy complexes are the active species in this system. Use of a positively charged mineral should be helpful, however, since the hydrated metal ion will be repelled from this surface. On the other hand, if the hydroxy complex adsorbs by splitting out water, surface charge should have no effect because of the free energy decrease that the system will experience when water is formed. In this regard, sapphire is well-suited for study, since its surface is positively charged until approximately pH 9.

Electrokinetic studies of quartz in the presence of various metal ions should also be useful in establishing the mechanisms of adsorption in these systems. That is, if the hydroxy complexes adsorb by water formation, drastic changes in the zeta potential should occur in the pH range in which hydrolysis occurs.

In this view, adsorption of ions of widely different hydrolysis characteristics on both sapphire and quartz was measured. In addition, zeta potentials of quartz were measured as a function of pH in the presence of various metal ions and compared with flotation responses obtained under similar conditions.

Experimental Materials and Techniques

Reagent-grade aluminum, ferric and magnesium chlorides, and lead nitrate were used in this investigation. Adjustments in pH were made with reagent-grade HCl or KOH. Conductivity water, made by passing distilled water through an ion exchange column, was used in all of the experiments.
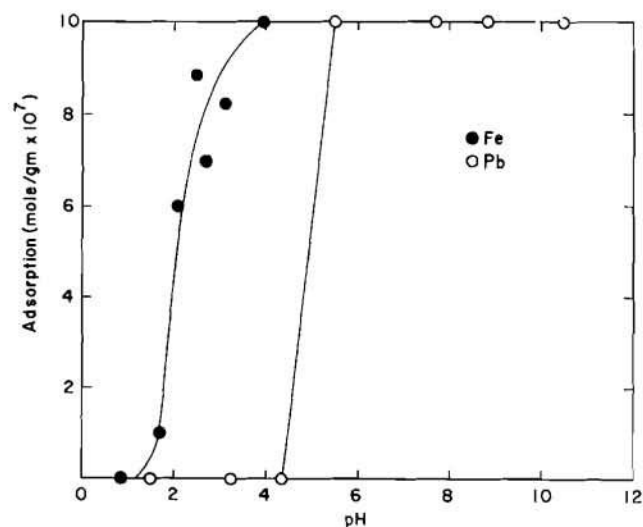
Fig. 1—Adsorption of ferric and lead species on sapphire as a function of pH.

In the adsorption studies, each experiment involved conditioning 10 g of −400-mesh sapphire or −200-mesh quartz in 100 ml of solution containing 1×10^{-4} mole per 1 $FeCl_3$ or $Pb(NO_3)_2$ for 20 min. After conditioning, the pH of the system was measured, and it is this pH value that is reported. The pulp was centrifuged for about 1 hr, and the supernatant solution was analyzed for residual iron or lead concentration with an atomic absorption unit.

Zeta potentials of quartz were measured with a Zeta Meter. Experimentally, 50 mg of −5-μ quartz particles were conditioned in 150 ml of solution containing various additions of Al^{+++}, Pb^{++}, or Mg^{++} for 15 min at various values of pH. The electrophoretic mobility of the particles was then measured and converted to zeta potential.

Experimental Results

The first series of experiments involved measuring the adsorption of ferric and lead ion species on sapphire. As shown in Fig. 1, no adsorption of ferric iron or one of its hydrolyzed species occurs at pH 0.9, whereas essentially complete adsorption occurs at pH 2.5. In the case of lead, no adsorption occurs at pH 4.4 and below, while abstraction is complete at pH 5.5 and above.

In the case of quartz, no ferric iron was adsorbed at pH 1.8 and below, while approximately 50% of the added iron was abstracted at pH 3.6. See Fig. 2. Adsorption experiments were not conducted at pH values above pH 4 because of the precipitation of ferric hydroxide under these conditions. When lead nitrate was added, essentially all of the added lead was adsorbed from about pH 7 to 11.5.

The zero-points-of-charge (zpc) of sapphire and quartz were determined with a Zeta Meter. A zpc of pH 9.0 was determined for sapphire, which agrees well with another reported value.[9] The zpc of quartz was measured to be pH 1.8 under these conditions, which is in the range of reported zpc's for quartz[10].

As shown in Fig. 3, when 1×10^{-5} mole per 1 aluminum chloride was added to the quartz system, zeta potentials of about −30 mv were measured from pH 3 to 3.8. The sign of the zeta potential was noted to change from negative to positive above pH 4.5 and from positive to negative above pH 7.4. Increasing the level of addition of Al^{+++} by an order of magnitude resulted in lowering the pH at which sign reversal occurs by about one unit in acid medium and also in raising the pH of sign reversal by one unit in basic medium.
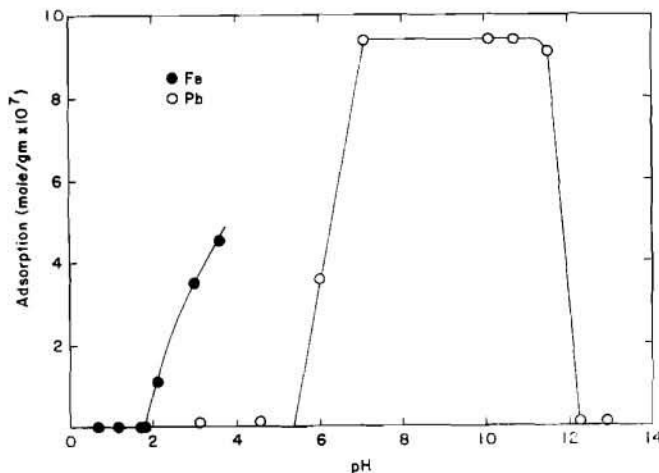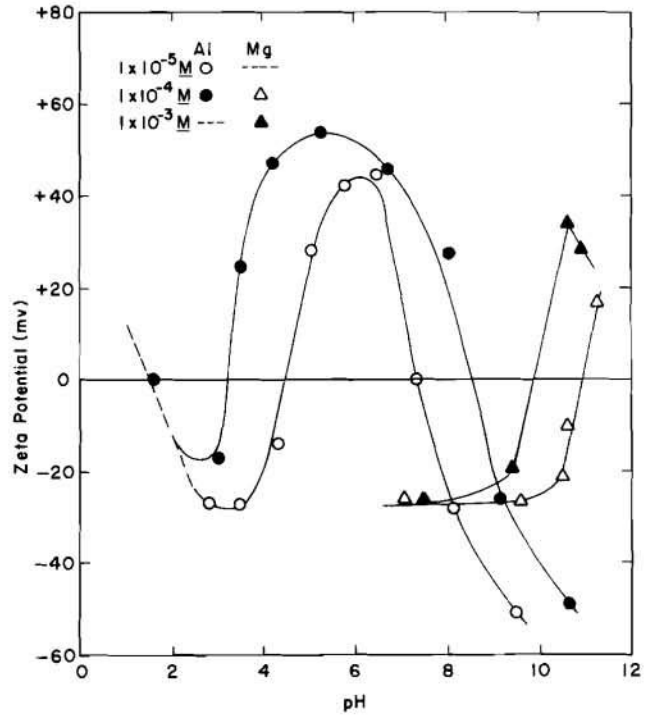

Fig. 3—Relationship between zeta potential of quartz and pH in the presence of various additions of aluminum and magnesium chlorides.

Magnesium ion or one of its species is also capable of changing the sign of the zeta potential (Fig. 3). With additions of 1×10^{-4} and 1×10^{-3} mole per 1 $MgCl_2$, sign reversal occurs at pH 10.9 and 9.9, respectively.

Similar results were also obtained with lead ion. As shown in Fig. 4, reversal of sign occurs exactly one unit in pH lower in acid medium when 1×10^{-3} mole per 1 lead nitrate is added as compared with 1×10^{-4} mole per 1.

Discussion of Results

The surface of alumina is positively charged below pH 9, and at pH 6, for example, a zeta potential of +26 mv was measured. From electrostatic considerations, moving a mole of Pb^{++} from infinity (bulk solution) to the Stern plane will require 1.3 kcal per mole, assuming that the zeta potential is measured at the Stern plane. This is readily calculated from the expression

$$W = ze\xi \qquad (1)$$

where z is valence, e is electronic charge, and ξ is zeta potential.

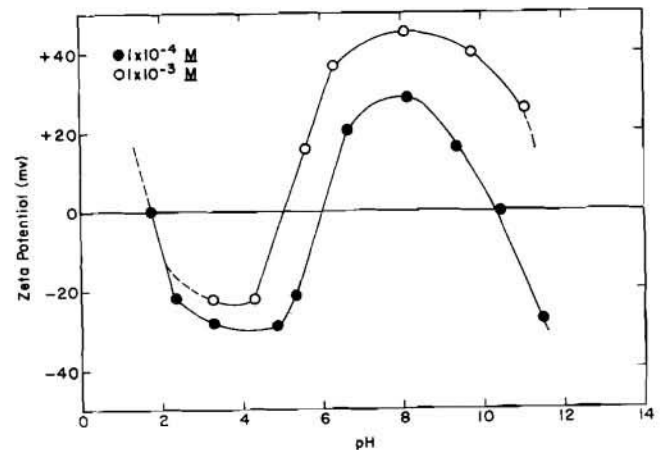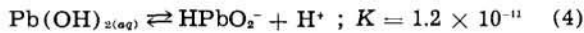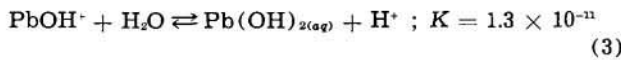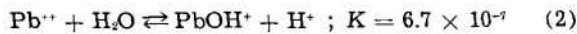Fig. 2—Adsorption of ferric and lead species on quartz as a function of pH.

Fig. 4—Relationship between zeta potential of quartz and pH in the presence of two additions of lead nitrate.

For Pb^{++} to adsorb under these conditions, the system must experience a decrease in free energy greater than 1.3 kcal per mole. In this view it is apparent that hydrated Pb^{++} ions are not adsorbing. As a matter of fact, the data in Fig. 1 show that Pb^{++} ions are repelled from the alumina surface. This phenomenon is made clear from the hydrolysis scheme of Pb^{++}.[11]

$$Pb^{++} + H_2O \rightleftarrows PbOH^+ + H^+ \; ; \; K = 6.7 \times 10^{-7} \quad (2)$$

$$PbOH^+ + H_2O \rightleftarrows Pb(OH)_{2(aq)} + H^+ \; ; \; K = 1.3 \times 10^{-11} \quad (3)$$

$$Pb(OH)_{2(aq)} \rightleftarrows HPbO_2^- + H^+ \; ; \; K = 1.2 \times 10^{-11} \quad (4)$$

At pH 4, almost all of the dissolved lead is Pb^{++}; while at pH 6, 40% of the dissolved lead is $PbOH^+$.

As contrasted to Pb^{++} adsorption, the adsorption of $PbOH^+$ will result in a considerable decrease in free energy. This is due to the formation and splitting out of water. That is, representing the fracture scheme of alumina in Fig. 5 as:
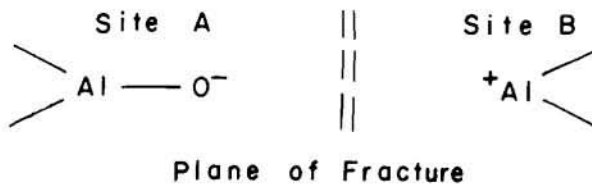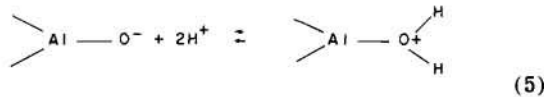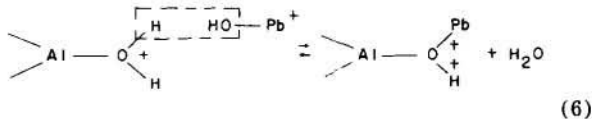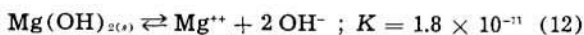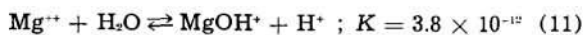
Fig. 5—Fracture scheme of alumina.
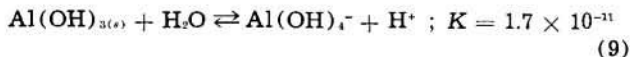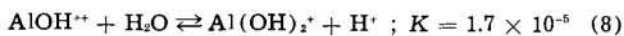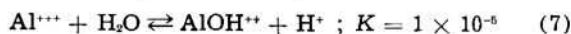
Site A functions as a weak acid and at pH 6 may look as follows:

$$(5)$$

Adsorption of $PbOH^+$ probably then occurs by splitting out water:

$$(6)$$

With reference to the following equilibria, it can be seen that the cationic hydroxy complexes of aluminum and magnesium are also responsible for changing the sign of the zeta potential of quartz.

$$Al^{+++} + H_2O \rightleftarrows AlOH^{++} + H^+ \; ; \; K = 1 \times 10^{-5} \quad (7)$$

$$AlOH^{++} + H_2O \rightleftarrows Al(OH)_2^+ + H^+ \; ; \; K = 1.7 \times 10^{-5} \quad (8)$$

$$Al(OH)_{3(s)} + H_2O \rightleftarrows Al(OH)_4^- + H^+ \; ; \; K = 1.7 \times 10^{-11} \quad (9)$$

$$Al(OH)_{3(s)} \rightleftarrows Al^{+++} + 3 OH^- \; ; \; K = 5 \times 10^{-33} \quad (10)$$

$$Mg^{++} + H_2O \rightleftarrows MgOH^+ + H^+ \; ; \; K = 3.8 \times 10^{-12} \quad (11)$$

$$Mg(OH)_{2(s)} \rightleftarrows Mg^{++} + 2 OH^- \; ; \; K = 1.8 \times 10^{-11} \quad (12)$$

These equilibria were taken from Refs. 12 and 13. $AlOH^{++}$ will be present in significant concentration at about pH 4, while $MgOH^+$ becomes significant at about pH 10.5 with relatively low additions of each salt.*

The only way that the sign of the zeta potential could change from negative to positive with the addition of inorganic salts would be to exchange a more positive

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* Aluminum is known to form polymerized hydroxy species (Refs. 14 and 15), but from the standpoint of brevity, only monomeric species have been considered.

species for one of lesser charge. As shown by the reaction in Eq. 6, this is readily accomplished by removing one hydrogen ion to form and split out water as indicated, while divalent lead remains at the surface.

The reversal in sign from positive to negative observed in basic medium in both the aluminum and lead systems can probably be attributed to the formation and stability of the anionic species; aluminate (AlO_2^- or $Al(OH)_4^-$ written as hydrated) and plumbite ($HPbO_2^-$ or $Pb(OH)_3^-$ written as hydrated.) The negative zeta potentials observed under these conditions are those of the mineral in the absence of adsorption of hydrolyzed species of lead and aluminum.

The reversal in the sign of the zeta potential of quartz when aluminum salts are added has been observed before.[16] This phenomenon has been termed specific adsorption of polyvalent metal ions and has been attributed to hydrated metal ions rather than hydroxy complexes.

Comparison of the adsorption of ferric iron and lead species on quartz with the flotation responses obtained in their presence supports the premise, suggested previously, that the first hydroxy complexes are the active species in these systems.[5,6] This concept is supported additionally by the adsorption studies of Clark and Cooke[17] and the electrokinetic studies of Mackenzie and O'Brien.[18] Adsorption of collector may occur in one of two manners. That is, the hydroxy complex may adsorb on the mineral surface first, which would result in a positively charged surface. Negatively charged collector ions could then be attracted to the surface and result in flotation. Other evidence,[6,7] however, indicates that an aqueous species of the metal hydroxy complex and collector (termed a basic aqueous complex) is probably the species adsorbing at the interface:

$$(13)$$
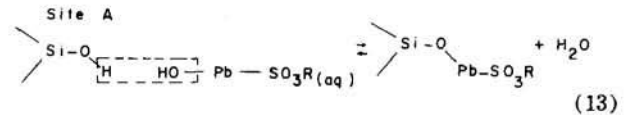
This mechanism is slightly different from that presented earlier,[5,7] but it seems likely that adsorption of the hydroxy complex by itself or when it is contained in a basic aqueous complex will be the same. Further, in view of the very weak acid properties of bulk silicic acid,[19] first and second dissociation constants being 4.2 $\times 10^{-10}$ and 5.1 $\times 10^{-17}$, it seems reasonable to assume that considerable H^+ will still be adsorbed on quartz at relatively high values of pH and available for reaction with $PbOH^+$, $MgOH^+$, or $CaOH^+$.

This model, however, raises an important question concerning these systems. That is, why are only the hydroxy complexes of metal ions capable of functioning as activators? In this regard, Gaudin and Chang[20] have shown that substantial coadsorption of Ba^{++} and laurate ions occurs on negatively charged quartz. Flotation is not effected, however, until a significant amount of Ba^{++} has hydrolyzed to $BaOH^+$. The only difference between adsorption of metal ions and their hydroxy complexes is the distance that the ion remains from the surface. In the case of metal ions, such as Pb^{++} or Ba^{++}, these ions will adsorb as hydrated entities and will be separated from the surface by water molecules. Such is not the case with hydroxy complexes which have to come sufficiently close to the surface for water to form, as suggested earlier. When an air bubble adsorbs on a solid particle, the air-solid interface should contain little or no water; the adsorption of hydroxy complexes provides one means of dehydrating the surface.

References

[1] Gutzeit, G., Trans. AIME, Vol. 153, 1943, p. 505.
[2] Wolstenholme, G. A., and Schulman, J. H., Transactions, Faraday Society, Vol. 46, 1950, p. 475.
[3] Fuerstenau. M. C., Martin, C. C., and Bhappu, R. B., Trans. AIME, Vol. 226, 1963, p. 449.
[4] Fuerstenau, M. C., and Atak, S., Trans. AIME, Vol. 232, 1965, p. 24.
[5] Fuerstenau, M. C., Miller, J. D., and Pray, R. E., Trans. AIME, Vol. 232, 1965. p. 359.
[6] Fuerstenau. M. C., and Elgillani, D. A., Trans. AIME, Vol. 235, 1966, p. 405.
[7] Fuerstenau. M. C., and Cummins, W. F., Trans. AIME, Vol. 238, 1967, p. 196.
[8] Schuhmann. R., and Prakash, B., Trans. AIME, Vol. 187, 1963, p. 449.
[9] Fuerstenau, D. W., and Modi, H. J., Journal of the Electrochemical Society, Vol. 106, 1959, p. 336.
[10] Parks, G. A., Chemical Review, Vol. 65, 1965, p. 177.
[11] Latimer, W. M., Oxidation Potentials, Prentice-Hall, Englewood Cliffs, N. J., 1952, p. 281.
[12] Raupach, M., Australian Journal of Soil Research, Vol. 1, 1963, p. 28.
[13] Butler, J. N., Ionic Equilibrium, Addison-Wesley, Reading, Mass., 1964. p. 287
[14] Brosset, C., Biedermann, G., and Sillen, L. G., Acta Chemica Scand., Vol. 8, 1954, p. 1917.
[15] Matijevic. E. Mathai, K. G., Ottewell, R. H., and Kerker, M., Journal of Physical Chemistry, Vol. 65, 1961, p. 826.
[16] Gaudin A. M., and Fuerstenau, D. W., Trans. AIME, Vol. 202, 1955. p. 66.
[17] Clark, S. W., and Cooke, S. R. B., Trans. AIME, Vol. 241. 1968, p. 334.
[18] Mackenzie. J. M. W., and O'Brien, R. T., Trans. AIME, Vol. 244, 1969. p. 168.
[19] Harmon R. W., Journal of Physical Chemistry, Vol. 32, 1932, p. 44.
[20] Gaudin. A. M., and Chang. C. S., Trans. AIME, Vol. 193, 1952, p. 193.

Value of Geophysico-Statistical Methods in Finding Soft Iron Ore in Northern Canada

by Maurice K. Seguin

It is a difficult task to find enriched soft iron ore deposits in the central part of the Labrador Trough, New Quebec, Canada, when the areas investigated are covered by glacial drift. A qualitative interpretation of either a combined gravity-magnetic-seismic-resistivity survey or gravity-magnetic-seismic or gravity-magnetic-resistivity survey permits (with a low probability level) the detection of iron formations and ore zones as well as their delineation from most of the country rocks. This is possible because most of the altered iron formation underwent a slight increase in density through enrichment and because the accompanying geochemical alteration changed their magnetic properties. In order to increase the chances of success in finding ore bodies when using geophysical methods, different types of correlation were done for many deposits. These are: 1) A quantitative correlation of the residual gravity anomaly intensities with the specific gravity, the iron content, the silica content, the porosity factor, and the dimensions of the underlying ore bodies. 2) A quantitative correlation of the ground magnetic intensity relative to a reference lithologic unit with the percentage of Fe_3O_4 recovery and with the volume ferromagnetic susceptibility. A few discoveries already have been made with this method.

The details of the location, the description of the geology, and the history of previous geophysical surveys and their qualitative interpretation have already been given.[1,2] A very brief paragraph describing the regional and local geology is necessary in order to facilitate the understanding of this paper. The sedimentary iron formations of the Labrador Trough consist of a 700-mile geosynclinal segment composed of tightly folded and faulted Proterozoic sediments, volcanics,

and intrusives that are rich in mineral deposits. The complex sequence rests unconformably on the basement of Archean granitic gneisses. The direct-shipping iron deposits are scattered along a northwest-trending strip, 5 to 10 miles wide and some 60 miles long in the facies rich in iron oxides and preferentially in localities where the original sedimentary environment favorized the deposition of a large concentration of magnetite associated with chert by physicochemical processes, e.g., oxidation-reduction potential, pH, temperature, pressure. Once leached of its silica and/or iron carbonate content and enriched with secondary α-hematite (occasionally goethite), this original magnetite associated with some primary hematite makes the blue direct-shipping ore which constitutes the important ore reserves in this mining district.

M. K. SEGUIN is with Dept. of Geology, Faculty of Science, Laval University, Quebec, Canada. TP 69L205. Manuscript, Feb. 20, 1969. Discussion of this paper, submitted prior to Mar. 15, 1970, will appear in SME Transactions, June 1970, and in AIME Transactions, 1970, Vol. 247.