Electrokinetic Characteristics of Magnetite Produced at Ambient Temperature*

by Oscar PERALES PEREZ, Yoshiaki UMETSU and Hiroshi SASAKI

The electrokinetic characteristics were investigated in the solutions containing a supporting electrolyte for magnetite particles produced at ambient temperature and those of magnetite of commercial chemical reagent. For this purpose, the variation in the zeta (ξ)-potential with pH and the corresponding isoelectric point (i.e.p.) were determined for magnetite particles suspended in diluted solution of a supporting electrolyte, KNO₃, K₂SO₄, Ca(NO₃)₂ or Al(NO₃)₃. The ξ-potential in KNO₃ solution for the fine particles of magnetite produced at ambient temperature showed values similar to those of magnetite of chemical grade and for the both magnetite the isoelectric point was 6.5. In the presence of K₂SO₄, a shift of the i.e.p. toward pH 4 was attributed to the specific adsorption of SO₄²⁻. In an Al(NO₃)₃ solution, the i.e.p. of 9.35 is considered to be brought by presence of Al(OH)₃⁺. Furthermore, in a solution containing calcium ion, the i.e.p. appeared in acidic environment probably due to non-equivalent exchange of proton on the particle surface with calcium ion in the solution. In all the cases under the conditions of this work the fine particles of magnetite prepared by ambient-temperature synthesis yields the almost same electrokinetic behavior as the chemical-grade magnetite which was treated at an elevated temperature.

KEY WORDS: Magnetite, Ambient-Temperature Synthesis, Interfacial Behavior, ξ-Potential, Specific Adsorption

1. Introduction

The possibility to produce magnetite by aerial oxidation of ferrous solutions at ambient temperature has been demonstrated in earlier publications. The less hydrated nature of the produced spinel-type precipitates explained their suitable settling and thickening behavior. These facts will permit a high efficiency in the recovery of solids during the solid-liquid separation step of wastewater treatment. Moreover, the application of an external low-intensity magnetic field is expected to make sure the total recovery of solids in the underflow of the thickening device. However, although the magnetite sludge could be rapidly settled down and the corresponding cake exhibited a compact appearance in comparison with iron hydroxide precipitates, the supernatants would eventually be determined for magnetite particles suspended in diluted solution of a supporting electrolyte, KNO₃, K₂SO₄, Ca(NO₃)₂ or Al(NO₃)₃. The ξ-potential in KNO₃ solution for the fine particles of magnetite produced at ambient temperature showed values similar to those of magnetite of chemical grade and for the both magnetite the isoelectric point was 6.5. In the presence of K₂SO₄, a shift of the i.e.p. toward pH 4 was attributed to the specific adsorption of SO₄²⁻. In an Al(NO₃)₃ solution, the i.e.p. of 9.35 is considered to be brought by presence of Al(OH)₃⁺. Furthermore, in a solution containing calcium ion, the i.e.p. appeared in acidic environment probably due to non-equivalent exchange of proton on the particle surface with calcium ion in the solution. In all the cases under the conditions of this work the fine particles of magnetite prepared by ambient-temperature synthesis yields the almost same electrokinetic behavior as the chemical-grade magnetite which was treated at an elevated temperature.

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interfacial characteristics of ultrafine particles and their interaction with solid collectors that facilitates their rapid and efficient removal from diluted aqueous suspensions. In this respect, the electric charge on a solid surface will play a key role in the stability of colloidal suspensions in a liquid. In the case of a sparingly soluble metal oxide, the electrification of its surface in an aqueous media is controlled by the interfacial interaction with potential determining ions (p.d.i.), H⁺ and OH⁻. Thus, the interfacial interaction between colloidal particles will be determined by the characteristic of their electrified surface. The surfaces with opposite charge may coagulate (attractive interaction) and those with the same charge may disperse (repulsive interaction). The related technical literature reports the behavior of different colloid particle-collector systems such as carbon black-stainless steel, polymer latexes-glass, chromium hydroxide-glass, chromium hydroxide-steel, hematite-steel, b-FeOOH-steel, silica-hematite-glass, and SiO₂-CdS-slag wool, among others.

On the other hand, the interfacial characteristics of magnetite in an aqueous electrolyte have been the research matter of different groups. Most of these works were mainly focused on the study of the behavior of magnetite, natural sample or synthesized by the co-precipitation method at temperatures above 90 °C, in the presence of KNO₃, KCl, NaCl, NaNO₃, or NaClO₄ solutions. The cited references contributed to the verification of the isoelectric point (i.e.p.), or point of zero charge (pzc) of magnetite. Iwasaki et al. investigated the relationship between the surface properties and flotation characteristics of magnetite by using anionic and cationic collectors. Blesa and Tamura et al. investigated the adsorption of Co²⁺ ions onto magnetite particles by using electrophoretic
techniques. Their results indicated that the surface of magnetite behaved as Co(OH)2 formed by earlier adsorption of Co2+ species. Furthermore, the adsorption of boric acid on magnetite in aqueous suspensions has been characterized through electrokinetic measurements and potentiometric titrations20). However, to the best of our knowledge, there is a lack of experimental evidence on how the interfacial characteristics of colloidal magnetite particles may change in different ionic environments which, in turn, would affect the interaction between particles and collector. The interactions based on surface charge effects may drastically be modified when the surface charge of interacting particles is affected by the presence of other ionic entities in the so-called specific adsorption phenomenon.

Under the above premises, the present work was undertaken to investigate the influence of both the synthesis method of magnetite and the nature of the supporting electrolyte on the electrokinetic behavior of colloidal magnetite suspended in selected electrolytes. Accordingly, this paper deals first with the z-potential measurements in KNO3 solution for magnetite particles produced from aqueous solutions by a novel method at room temperature. Next, the variation in z-potential with pH and the corresponding isoelectric point (i. e. p.) of magnetite suspended in diluted solution of supporting electrolyte, K2SO4, Ca(NO3)2 or Al(NO3)3, will be discussed. These electrolytes were selected based on their contents of ionic species commonly found in polluted effluents (minewaters, industrial wastewaters, etc) and that could be conducive to specific adsorption phenomenon. The obtained information promoted the understanding of the probable interfacial interactions in the system colloidal magnetite particles-macroscopic collector (glass wool), to be presented in a forthcoming paper. Furthermore, the electrokinetic characterization (z-potential measurement) of ultrafine magnetite synthesized by aerial oxidation of ferrous ions at ambient temperature is reported for the first time.

2. Experimental

2.1 Materials

Chemical grade reagents of KNO3, K2SO4, Ca(NO3)2 · 4H2O and Al(NO3)3 · 9H2O from WAKO Chemicals Industries were used without further purification to prepare supporting electrolytes at different ionic strengths. The “chemical-grade” magnetite was also from the same supplier. The “room-temperature” magnetite was produced by the moderate aerial oxidation of a 0.012 M ferrous sulfate solution (635.3 mg / l of Fe) and complemented by a simultaneous control of the pH at 12.0 and 22 °C following a similar procedure as detailed in references 13, 14). Under these conditions, the formation of crystalline magnetite required only 20 minutes of contact at constant pH. The precipitates were filtered off by a membrane filter of 0.65 μm pore size and washed several times with doubly distilled water (DDW). In order to eliminate any trace of amorphous iron co-precipitates that could affect the surface characteristics of the precipitates, the “room temperature” magnetite was contacted with a 1 M HNO3 solution and ultrasonically redispersed. After this acid treatment the solid was rinsed with enough amount of DDW. The described procedure was repeated three times. The pH of the magnetite-supporting electrolyte suspension was adjusted by KOH and HNO3 solutions.

The scanning electron micrographs (SEM) presented in Fig.1 revealed a notorious morphological difference between the two types of magnetite used in this study. As shown in Fig.1, spherical aggregates of less than 150 nm in diameter were generated when magnetite was precipitated at room temperature (Fig.1-a, b). In contrast, the chemical-grade magnetite (Fig.1-c, d) consisted of particles with angular shapes averaging 500 nm in length according to the information given by the supplier.

2.2 z-potential measurements

The z-potential for different pH values of selected electrolytes was determined by the electrophoresis method using a Laser Electrophoresis z-potential Analyzer, LEZA-400 of Otsuka Electronics. Typical ionic strengths of supporting electrolytes were 3×10−3, 1×10−3 and 1×10−4 M. The suspension of magnetite was ultrasonically redispersed for 10 minutes prior to its pH adjustment. After the suspension reached a set pH value, it was placed into the rectangular electrophoresis cell for the z-potential measurement.

To determine the electrokinetic behavior of the room-temperature magnetite in comparison with the chemical-grade one, z-potential measurements were performed for both types of samples using a 1×10−3 M KNO3 solution as supporting electrolyte. The non-occurrence of the specific adsorption effect in presence of the KNO3 electrolyte enables that condition to be considered as the reference surface state of the magnetite particles.

3. Results

3.1 z-potential of magnetite in KNO3 solution

Fig.1 Scanning electron micrographs of magnetite particles used in the z-potential measurements. (a), (b): ”room-temperature” magnetite; (c), (d): ”chemical-grade” magnetite.
Fig. 2 shows the variation in the z-potential with pH for magnetite particles immersed in 1 M KNO₃. As seen, the z-potential values corresponding to "chemical-grade" and "room-temperature" magnetite particles were almost the same despite the marked differences in their shape, size and preparation procedure. These results evidenced a similar interfacial behavior of the two types of magnetite and the negligible effect of the mentioned differences on the i.e.p. of magnetite (6.52), under our experimental conditions. Since no specific adsorption effect takes place in presence of an indifferent electrolyte such as KNO₃, this i.e.p. can be considered as the reference state for the surface of magnetite particles. Moreover, this determined value is in excellent agreement with the values presented in the scientific literature. For instance, Iwasaki[14] reported an i.e.p. of 6.5 for natural and artificial magnetite, produced by reduction of natural hematite. Tewari et al.[15] gave an i.e.p. of 6.55 for a magnetite produced by oxidation of ferrous precipitates with KNO₃ in an alkaline medium. Neither the temperature of precipitation nor the duration of the aging of the precipitates was reported. In turn, Tamura et al. reported a pzc value of 6.5 for magnetite in a 0.1 M NaNO₃ solution[19]. In Tamura’s work, magnetite was prepared by adding a solution of FeSO₄ to one of KOH containing KNO₃ and then aging the solid product for 4 hours at 90 °C.

3.2 z-potential of magnetite in different supporting electrolytes

The variation in z-potential with pH in different supporting electrolytes is shown in Fig. 3 through 5. Fig. 6 summarizes the variation in z-potential as a function of pH for magnetite in contact with different supporting electrolytes at a common ionic strength of 1 M KNO₃. In this figure, the adsorption effect due to co-existing ionic species is evidenced by the changes in both the z-potential values and i.e.p. with respect to the values observed for magnetite in KNO₃ solution. Table 1 shows the i.e.p. of magnetite in supporting electrolytes at different ionic strength. The effect of individual ionic species on the interfacial characteristics of magnetite is commented in the following paragraphs.

3.2.1 Effect of sulfate ions

The z-potential-pH curves for the magnetite particles suspended in K₂SO₄ solutions (Fig. 3) reveal a shift of the i.e.p. to lower pH values (around 4) with respect to the i.e.p. observed in KNO₃ (6.52). This effect was first studied by Overbeek[23] who pointed out that specific adsorption of anions will produce a negative surface charge on an oxide surface that makes necessary a larger amount of protons to achieve the isoelectric state. Accordingly, the more acidic i.e.p. values for magnetite in contact with the SO₄²⁻.
bearing electrolyte can be attributed to the strong specific adsorption of sulfate ions onto the solid surface. Moreover, the adsorption of sulfate ions would become more important at higher ionic strengths of the K$_2$SO$_4$ electrolyte as suggested by the drop in the i.e.p. from 4.4 to 3.7 when the ionic strength was increased from $1 \times 10^{-5}$ M up to $3 \times 10^{-3}$ M. These observations are also supported by the observed trend in the z-potential that was shifted toward more negative values with respect to the variation observed in presence of KNO$_3$.

The interaction of anions with oxide surfaces can be explained by different surface species including the formation of mono- and bi-dentate-, inner- and outer-sphere complexes. In this regard, Hayes et al.\textsuperscript{26} have shown that selenium adsorption data on goethite and amorphous iron oxyhydroxide are consistent with the formation of outer-sphere complexes for selenates, SeO$_4^{2-}$. Therefore, based on the well-established chemical similitude between sulfur and selenium species in solution, a preliminary approach to understand the reaction between sulfate ions and the magnetite surface (\$s$SO$_4$) could be presented as follows:

$$sOH + SO_4^{2-} + H^+ \rightarrow sOH_2^{-} + SO_4^{2-}$$  
$$sOH + SO_4^{2-} + 2H^+ \rightarrow sOH_2^{-} + HSO_4^{-}$$  
$$2sOH + SO_4^{2-} + 2H^+ \rightarrow (sOH_2)^2 + SO_4^{2-}$$

As the above reactions suggest, sulfate ions would be specifically adsorbed onto the magnetite surface as mono-dentate (equations 1 and 2) or bi-dentate-type (equation 3) outer-sphere complexes. The co-existence of a bi-dentate complex, at which two surface sites are covered by the adsorbate, can be expected at higher surface coverage\textsuperscript{29}.

3.2.2 Effect of calcium ions

In presence of calcium ions the i.e. p. was shifted towards more acidic values (with respect to the i.e. p. value of 6.52 in KNO$_3$) rather than to the opposite side expected if positive Ca$^{2+}$ species had been adsorbed onto the particles. As Fig.4 and Table 1 show, the i.e. p. was 5.7 at an ionic strength of $3 \times 10^{-3}$ M whereas ionic strengths of $1 \times 10^{-3}$ and $1 \times 10^{-4}$ M gave an almost same z-potential at pH variation and a common i.e. p. of 4.2. This trend was confirmed to be reproducible after repeated measurements of the z-potential.

Regarding to the adsorption behavior of cationic species, Dugger et al.\textsuperscript{26} reported that extensive evidence is given for cation adsorption on silica gel by ion exchange with H$^+$ from surface $s$SiOH sites. This mechanism was also proposed for the Co$^{2+}$ adsorption onto magnetite surfaces\textsuperscript{14,19}. Furthermore, Parks\textsuperscript{23} established that a slight non-equivalence in the exchange of a metal ion in solution with the protons located on the surface of the solid could also be expected. Then, the equivalents of protons released from the surface of the particles of magnetite should exceed the equivalents of adsorbed cations from the electrolyte that could create a net negative surface charge. This negative surface charge may have caused the i.e. p. to be shifted to more acidic values than in presence of KNO$_3$ electrolyte.

The above mentioned state can be explained by the following reactions between protons placed on the surface of magnetite as $\vartheta$FeOH and calcium ions in our system:

$$m(\vartheta FeOH) + \rightarrow m(\vartheta FeO)m^+ + mH^+ \quad (4)$$
$$Ca^{2+} + m(\vartheta FeO)m^+ \rightarrow Ca(\vartheta Fe)m^{2+}m^+ \quad (5)$$

For "m" greater than two, the magnetite surface would be negatively charged due to the predominance of negative Ca(\vartheta Fe)m$^{2+}m^+$ pairs leading to the necessity of an additional amount of protons to achieve the iso-electrical condition. On the other hand, the less acidic i.e. p. of 5.7 at an ionic strength of $3 \times 10^{-3}$ M (in comparison with the i.e. p. of 4.2 observed at higher ionic strengths) may indicate a lower excess of released protons. The compaction of the electrical double layer at higher ionic strengths and the consequent increase of the ionic density in the vicinity of the solid surface, i.e., a larger amount of NO$_3^-$ counter-ions, could have contributed to the neutralization of surface protons.

3.2.3 Effect of aluminium ions

The variation in the z-potential of magnetite with pH in presence of Al(NO$_3$)$_3$ at ionic strength $1 \times 10^{-3}$ M is given in Fig.5. The shift in the i.e. p. towards more alkaline values (9.35) than in KNO$_3$ solution (6.52), suggests the specific adsorption of positively charged species onto the surface of magnetite particles and can be explained in terms of a "charge reversal" model\textsuperscript{27}. In this model, the adsorption and eventual precipitation of hydrolyzable metal ions account for the charge reversal of the colloidal substrates. In our case, the adsorption of cationic aluminium species would have charged positively the magnetite surface requiring more OH$^-$ ions to establish the charge equilibrium. Furthermore, since the adsorption of the cationic specie had shifted the i.e.p. towards pH values higher than 6.5, the precipitation of aluminium hydroxide onto the surface of magnetite suspended in the Al(NO$_3$)$_3$ solution could also be expected. As stated in references\textsuperscript{23,28}, the i.e. p. of stable $\vartheta$-Al(OH)$_3$ is around 9.3. Accordingly, at pH below 9.3 the magnetite surface would be positively charged by Al(OH)$_2^+$ generated by the ionization of Al(OH)$_3$ attached to the magnetite surface. The cationic specie Al(OH)$_2^+$ is known as the most stable mononuclear hydrolysis product of Al$^3+$ in neutral and slightly alkaline solutions\textsuperscript{29}.

The thermodynamically predicted precipitation of Al(OH)$_3$ ($log K_{sp}= 33.50\textsuperscript{27}$), can also explain its co-existence with magnetite and the surface behavior commented in the previous paragraph. In the case of calcium ions, the lower value of log $K_{sp}$ for Ca(OH)$_2$ ($\approx 5.19\textsuperscript{29}$) indicates the higher stability of ionic calcium species in comparison with the corresponding hydroxide. This higher stability of cationic calcium species may be related to their particular effect on the surface characteristics of magnetite; as suggested, the magnetite surface would become negatively charged due to a non-equivalent exchange.

<table>
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<tr>
<th>Supporting electrolyte</th>
<th>Ionic strength, M</th>
<th>$3 \times 10^{-3}$</th>
<th>$6 \times 10^{-3}$</th>
<th>$9 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO$_3$</td>
<td>No determined</td>
<td>6.5</td>
<td>No determined</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
<td>3.7</td>
<td>4.0</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$</td>
<td>5.7</td>
<td>4.2</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>Al(NO$_3$)$_3$</td>
<td>No determined</td>
<td>9.3</td>
<td>No determined</td>
<td></td>
</tr>
</tbody>
</table>
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between protons on the solid surface and calcium ions.

In turn, $\text{Al(OH)}_2^+$ ions in equilibrium with $\text{Al(OH)}_3^+$ will be produced under highly alkaline conditions according to\(^{28}\):

$$2\text{Al(OH)}_3(s) + 2\text{OH}^- \rightarrow 2\text{Al(OH)}_2^+ + \text{H}_2\text{O}$$

As equation 6 suggests, the potential determining ions at pH above 9.3 would be the anionic $\text{Al(OH)}_2^+$ species.

The above discussion made evident how the interfacial characteristics of colloidal magnetite particles can vary depending on the aqueous environment. Therefore, if a process to collect such ultrafine particles is based on the surface interactions between them and a suitable collector, the specific adsorption effect of co-existing ions must necessarily be taken into account. This phenomenon would cause a severe change in the expected behavior of interacting components in the system ultrafine particles-collector that may also affect the corresponding collection efficiency.

4. Conclusions

The influence of the preparation method and the co-existence of ionic species in aqueous solution on the interfacial behavior of colloidal particles of magnetite have been investigated. The z-potential values corresponding to "chemical-grade" and "room-temperature" magnetite particles did not exhibit marked discrepancies. This fact indicates a similar "grade" and "room-temperature" magnetite particles did not exhibit marked discrepancies. This fact indicates a similar interfacial behavior and the negligible effect of the preparation method on the i. e. p. of magnetite, under our experimental conditions.

The adsorption effect due to co-existing ionic species was evidenced by the changes in both the z-potential and i. e. p. with respect to those values observed for magnetite in KNO\(_3\) solution (6.52). In the presence of $\text{K}_2\text{SO}_4$, the shift of the i. e. p. towards more acidic values (with respect to the i. e. p. value of 6.52 in KNO\(_3\)) rather than to the opposite side expected if positive Ca\(^{2+}\) ions had been adsorbed onto the particles. A non-equivalence in the exchange of calcium ion in solution with the protons located on the surface of the solid could explain this trend in the i. e. p. values. Accordingly, the specific-adsorption effect of co-existing ions must be taken into account during the evaluation of the interfacial interactions between particles in the solid-liquid separation of ultrafine particles of magnetite from very dilute and stable suspensions.

References

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室温で調製したマグネタイトの界面電動特性

Oscar Perales Perez

梅津良昭
佐々木弘

室温で調製した微粒子および市販化学試薬の2つ目のマグネタイトについて動電特性を種々の支持電解質を含む溶液中で測定し、比較した。支持電解質としてKNO\(_3\), \(\text{K}_2\text{SO}_4\), \(\text{Ca(NO}_3\)_2\)あるいは\(\text{Al(NO}_3\)_3\)のいずれかを含む溶液に懸濁したマグネタイト粒子に対し、ゼータ電位のpHに伴う変化およびそれぞれの等電点（i.e.p.）を決定した。

支持電解質KNO\(_3\)を含む溶液中では、室温において調製したマグネタイト超微粒子の電位が試薬液マグネタイトに対する値とほとんど等しく、これらの等電点はいずれも6.5であり、製法による特徴も見られなかった。

\(\text{K}_2\text{SO}_4\)溶液中では、マグネタイトの等電点がpH4の方へ変移するが、これは、\(\text{SO}_4^{2-}\)の特異吸着によるともである。\(\text{Al(NO}_3\)_3\)溶液中では、マグネタイト粒子の等電点が9.4となり、\(\text{Al(OH)}_3\)に起因すると考えられる。さらに、カルシウムイオンを含む溶液では、等電点が酸性側に現れるが、これは粒子表面のプロトンと溶液中のカルシウムイオンの交換が非等量であることにによる。いずれも、本実験の条件下では、室温で調製したマグネタイト超微粒子は試薬のマグネタイト（乾燥品）と同様な界面電動特性を示すことが観察された。

1) 工藤, 北方, 東北大学, 東北大学科学研究センター
2) 宮村, 智, 北方, 東北大学教養・総合工学科
3) 工藤, 北方, 東北大学教養・総合工学科
4) キーワード: マグネタイト, 界面電動, ゼータ電位, 特異吸着