Surface Properties of Indian Hematite and Bauxite and Their Coating Mechanism with Colloidal Magnetite

S Prakash* and B Das
Regional Research Laboratory, Bhubaneswar 751 013
and
R Venugopal
Indian School of Mines, Dhanbad 826 004

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The selective coating of colloidal magnetite on hematite and bauxite for enhancing the magnetic separation techniques which depends on surface and chemical phenomena is studied. The mechanism of colloidal magnetite interaction with hematite and bauxite is investigated through electrokinetic and IR studies. The point of zero charge and electrophoretic mobilities of pure hematite, bauxite and colloidal magnetite are determined. The effect of various ions such as PO₄³⁻, SiO₂, and the surfactant such as sodium oleate on surface properties of hematite and bauxite are examined. IR spectroscopy studies indicate that oleate ions are chemically bonded with hematite while it is only physically adsorbed on the surface of bauxite at certain pH. The zeta-potential also correlates the chemical interaction of oleate on hematite. The separation of quartz from hematite and hematite from bauxite is carried out by applying selective colloidal magnetite coating followed by magnetic separation techniques. Hematite is separated in magnetic fraction for both the cases.

Introduction

Hematite is an important raw material widely used for the production of iron and steel. This can be separated from its ore by various methods. In Indian iron ore washing plants, generally washing is being practiced to separate the associated gangues. However, during the process of washing around 8 million tonnes of superfines from different washing plants of India with 48-60 per cent Fe are being generated and thrown into the iron ore tailing ponds without any further utility. Attempts have been made by different workers to recover the iron values lost by various techniques with limited success. Similarly, bauxite is also an economic non-metallic mineral used as a raw material for producing alumina and in refractory making. The low grade bauxite contains variety of gangue minerals, viz. Fe-oxides, silicates, and carbonates. Amongst them, the separation of iron is problematic one, causing difficulty in downstream processes. Roasting followed by leaching is the most general method used for dissolution of bauxite in commercial operations.

Coating and carrier methods for enhancing the magnetic and flotation separation methods have however received little attention. We have been working in our laboratory to enhance the magnetic response of weakly magnetic minerals through selective magnetic coating techniques. In this paper an attempt has been made to understand the surface chemistry and coating mechanism of oleate colloidal magnetite on hematite and bauxite through electrokinetic, IR study and the effect of other ions such as silicate and phosphates for separation in a large scale.

Experimental

The experimental study broadly consist of careful preparation of pure minerals, electrokinetic potential measurements, IR spectrophotometry and wet high intensity magnetic separation studies.

Sample

The hematite and bauxite sample, as clean as possible were used for the experimental studies. The chemical analysis of the samples is given in Table 1. The samples used were obtained from Orissa Mining Corporation. Selected pieces were crushed and hand ground in a mortar. A portion of the sample was reduced to -500 μm. After
desliming in laboratory tap water a closed sized fraction of -75+30μm was separated out by hand sieving. The bauxite sample was washed with 0.5N hydrochloric acid to eliminate any trace of iron present in the surface. This was followed by washing and rewashing with distilled water till no trace of chloride ions was detected in rinsing water. On the other hand the hematite sample was passed in a low intensity magnetic separator to remove any contaminated magnetite in it. Quartz sample was also of mineral origin and supplied by Saroj Mining Corporation, Karnataka. The chemical analysis shows that the sample contains 99.6 per cent SiO₂. The size and preparation of the material used in the magnetic separation experiment was similar to bauxite and hematite.

Reagents

Reagents used such as perchloric acid, sodium hydroxide, sodium silicate, sodium hexa metaphosphate, and potassium nitrate were all AR grade reagents. Fresh solutions of sodium oleate (analar grade) having known concentrations were prepared in situ.

Magnetic separation studies were carried out on the closed sized fractions. A portion of the sample (-75μm) was further ground and microsieved to obtain -5μm material. Electromagnetic measurement and IR spectroscopy were conducted with the help of -5μm material.

Methods

Preparation of Oleate Magnetite

The colloidal magnetite was prepared by the combination of 1:1 ferrous and ferric salts. The salts were dissolved in distilled water and heated slowly to 70°C. 5 g of sodium hydroxide dissolved in 50 cc of water was added slowly with constant stirring into the warm solution. The precipitated magnetite thus obtained was washed several times, centrifuged to remove salts and sodium hydroxide. The total volume after washing was made up to 100 cc. The oleate colloidal magnetite was prepared by the addition of 2 x 10⁻⁵ M sodium oleate at pH 11 and boiling until the magnetite is fully dispersed.

Electrokinetic Measurements

The electrophoretic mobility of the minerals and oleate magnetite were measured by using the zetameter, Rank Brother model, mark-II, UK and the mobility’s were converted into zeta-potentials using the Helmholtz-Smoluchowsky equation. Samples for the zetapotential tests were prepared by making a solution of the desired pH by adding the pH regulators, i.e., HClO₄, or NaOH. 0.01 g of the sample was added into the 100 ml required solution and it was conditioned for 1h at the room temperature. In all the experiment KNO₃ (2 x 10⁻³ M) was used as the supporting electrolyte. The mobility of the suspension was determined by adding portion of the solution into the given cell connected with two Pt electrodes.

IR Spectroscopy

The IR spectra was recorded by a JASCO Fourier transform IR model 5300 spectrophotometer in 400-4000cm⁻¹. The sample used in the spectrophotometer studies was prepared by grinding in an agate motor to a very fine power. One to 2 g of the mineral sample was conditioned at a given pH for 1h with the surfactant and the oleate magnetite. After conditioning, the solids were separately dried at 50°C and the FTIR measurements were taken.

Magnetic Separation Studies

The magnetic separation studies were carried out by a wet magnetic separator supplied by Rapid Box Mag separator, England. The magnetic intensity could be varied with current and grid gaps. The slurry was prepared by adding different proportions of minerals and required quantities of distilled water. The pH of the slurry was adjusted by adding NaOH or HClO₄ which was monitored throughout the experiment. Oleate magnetite or magnetite fines were added in desired quantity into the suspension. A small quantity of sodium hexa metaphosphate (0.01 per cent) was added as dispersant whenever necessary. The mineral mixture was then conditioned for 10 min. The slurry was then passed through the magnetic separator slowly. The magnetic fraction was retained on the grid whereas the non-magnetic fraction was collected at the bottom. The magnetic fraction was taken out of the grid by flushing and washing with water in the absence of the magnetic field. The magnetic and non-magnetic fraction thus collected were dried separately and analysed for Fe, SiO₂, Al₂O₃, etc. to determine the quality and recovery.
are given in Figure 1. The point of zero charge of hematite is found to be around 7.2 and that of bauxite is around 8.6. The zero point of charge of hematite reported in the literature is at 7.6 to 8.0 (ref.10) and that of bauxite is at pH 8.5 to 9.4 (ref.11). For oxide minerals, H+ and OH- ions have since been considered to be potential determining ions. The various concentrations of these ions change the magnitude and sign of electrokinetic potentials. So these ions are also the potential determining ions for hematite and bauxite, as reported earlier. The pzc of magnetite obtained in the present investigation is around pH 6.8. Above this pH, magnetite has got negative charge. The pzc of synthetic oleate magnetite is about 5.5. The synthetic compound resulted a shift in iso-electric point.

**Effect of Phosphate and Silicate Ions**

Figure 2 and 3 show the electrokinetic potential of bauxite in the presence of sodium hexametaphosphate (SHMP) and silicate ions. Both these ions play a vital role in the dispersion and thereby the separation of minerals. It is seen that the adsorption of silicate ions or hexametaphosphate ions makes the surface more negatively charged bauxite and thereby the particles remain in dispersed phase due to mutual repulsion of the strongly negative charged particles and even at lower pH, the particles remain in suspension. Therefore, either of these ions can be used as a dispersant in the separation of hematite from bauxite by selective magnetic coating.

Similar observations are made with hematite-sodium silicate (Figure 4) or hematite hexametaphosphate (Figure 5). The electropotential suddenly decreases to negative sides after the addition of the 10^-5M concentration of sodium silicate. Further addition of the reagent dose...
not change the potential in a significant way. However the mineral possess a constant negative potential of 31-35 mv in the pH range 5 to 9. Only at pH 3.5 the potential drops from +18 mv to around -10 to 15 mv. Sodium silicate is therefore one of the most widely used modifying reagent in flotation.

The zeta-potential-pH curve for hematite in the presence of different concentration of sodium hexa metaphosphate is shown in Figure 5. It suggests that the point of zero zeta potential has shifted from pH 6.8 to more on acidic side. From the examination of these curves, it is noted that the addition of hexa metaphosphate to the hematite suspension has produced a change in zeta-potential at all the pH values studied. The hexa metaphosphate has acted as a good dispersing agent of hematite. The interaction between hematite and reagent may also be due to complex formation as phosphates and polyphosphates are good complexing agents for a wide variety of metal cations.

**Effect of Sodium Oleate on the Zeta-potential of Hematite**

Figure 6 shows the values of zeta-potential of hematite at different initial concentration of sodium oleate with respect to pH at constant ionic strength. In a selective magnetic coating, surfactants are used along with magnetite or separately as oleate magnetite in order to control surface charge or better magnetite coating of the surface. The adsorption of oleate and magnetite takes place either through the electrostatic interaction or by the chemical interaction between the surfactant and mineral. In the present case, an increase in negative potential starts around 10^{-4} M concentration of oleate and continues to increase with further addition of oleate. The increase in negative potential clearly demonstrates the successive oleate adsorption on the surface of the mineral. In the present case the negative oleate ion can only be adsorbed on the mineral surface chemically resulting in the net increase of negative surface charge of the mineral indicating specific adsorption.

The zeta potential obtained in the presence of sodium oleate (5x10^{-3}M) as a function of silicate and meta phosphate concentration have also been studied. It shows the surface potential is the same -31 mv until the 10^{-4}M meta phosphate concentration and further level of these two ions increases in negative zeta potential. As the increase of this potential is marginal, it can be concluded that low effect of these ions might have masked in the presence of oleate similar to apatite and calcite. It has been stated that adsorption of sodium oleate on hematite greatly reduces after treatment with modulus 3.3 sodium silicate.

On the other hand, it has been stated that the presence of oleate could possibly cause desorption of silicates due to high chemical interaction between the cations and the oleate ions.

**Results of Infra-red Spectroscopy**

The spectra of hematite, hematite conditioned with oleate magnetite at pH 7.2 and the spectra of oleate magnetite are shown in the Figure 7. Hematite is characterised by the presence of peaks around 410-415 cm^{-1}, 450-470 cm^{-1} and 670-680 cm^{-1}. The absorption bands were detected at 1559 cm^{-1} and 1525 cm^{-1} due to the -C-C and -CH_{2}-CH-C- indicates the formation of ferric oleate (Figure 7 III). Similar peaks detected at 1590 cm^{-1} and additional peak at 1034 cm^{-1} recorded in the case of hematite interacted with oleate magnetite prove the chemical interaction of oleate on mineral surface. The peak observed at 1034 cm^{-1} has been attributed due to -C-O-C cross-linking between the hydrocarbon chains. IR study carried out earlier proved that ferrous oleate and aluminum oleate had the characteristic peak at 1595 cm^{-1} and 1615 cm^{-1}, respectively. Figure 8 shows the IR spectra of bauxite and bauxite coated with oleate magnetite. Gibbsite the main mineral for bauxite is characterised by the stretching vibration due to OH group at 3615 cm^{-1}, 3460 cm^{-1} and OH bending vibration at 1005-1035 cm^{-1} and 970-990 cm^{-1} (ref.16). The IR spectra of bauxite did not alter when bauxite sample was conditioned with oleate magnetite. There is no chemical interaction between bauxite and oleate species. So the adsorption, if any, may be due to physical adsorption. The mineral conditioned with oleate magnetite was washed several times with distilled water and its IR spectra was recorded again. The IR spectra was unchanged and no new spectra appeared.

**Result of Magnetic Separation Studies**

The separation of hematite from quartz was performed by wet magnetic separation methods by applying the coating techniques. Both oleate magnetite prepared synthetically and finely divided natural magnetite (-5µm) were used as the coating agents. The best results obtained under the optimum conditions are summarized in Table 1 and 2. A synthetic mixture of hematite to quartz (1:1) was used. The experiments were conducted at natural pH at which zeta-potential of hematite is also found to be zero and the maximum adsorption of oleate coating takes
Table 1 — Chemical analysis of hematite and bauxite

<table>
<thead>
<tr>
<th>Material</th>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>LOI</th>
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</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>97.02</td>
<td>0.92</td>
<td>1.20</td>
<td>0.06</td>
<td>0.03</td>
<td>0.35</td>
</tr>
<tr>
<td>Bauxite</td>
<td>1.14</td>
<td>1.85</td>
<td>64.85</td>
<td>0.05</td>
<td>0.03</td>
<td>32.0</td>
</tr>
</tbody>
</table>

Table 2 — Results of magnetic separation of hematite and quartz mixture using colloidal magnetite (H:Q 1: 1, pH:7.2, SHMP 0.01 per cent)

<table>
<thead>
<tr>
<th>Details</th>
<th>Mag intensity, k gauss</th>
<th>Weight, per cent</th>
<th>Grade, per cent</th>
<th>Recovery, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic I</td>
<td>3.0</td>
<td>35.1</td>
<td>95.3</td>
<td>66.8</td>
</tr>
<tr>
<td>Magnetic II</td>
<td>5.0</td>
<td>47.5</td>
<td>94.2</td>
<td>89.3</td>
</tr>
<tr>
<td>Magnetic III</td>
<td>6.5</td>
<td>51.6</td>
<td>93.5</td>
<td>96.3</td>
</tr>
<tr>
<td>Magnetic IV</td>
<td>7.8</td>
<td>53.3</td>
<td>92.6</td>
<td>98.6</td>
</tr>
<tr>
<td>Non-magnetic</td>
<td>-</td>
<td>46.7</td>
<td>1.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figure 6 - Zeta potential of hematite as a function of pH and sodium oleate concentration

The magnetic separation with natural magnetite also suggested that a Fe₂O₃ recovery of 90.3 per cent was place at this pH than at the other pH values. The results indicate that a Fe₂O₃ grade of 91 per cent with more than 97 per cent recovery was obtained by using a magnetic intensity of around 7.8 k gauss. Generally hematite is feebly magnetic in nature and a magnetic intensity of 13-14 k gauss is required for its effective separation. Since the intensity required is much less than the hematite separation by a magnetic separation it can be concluded that magnetite response of hematite has been increased by the addition of a small proportion of colloidal magnetite. The addition of sodium oleate as a surfactant with colloidal magnetite further helped for selective attachment with hematite surface.

The magnetic separation with natural magnetite also suggested that a Fe₂O₃ recovery of 90.3 per cent was
Table 3 — Results of magnetic separation of hematite-bauxite mixture
(H:B 1:1, pH 7.2, SHMP 0.01 per cent)

<table>
<thead>
<tr>
<th>Details</th>
<th>Magnetic Intensity, k gauss</th>
<th>Weight, per cent</th>
<th>Product per cent</th>
<th>Recovery, per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic I</td>
<td>3.0</td>
<td>12.2</td>
<td>87.2</td>
<td>12.8</td>
</tr>
<tr>
<td>Magnetic II</td>
<td>5.0</td>
<td>44.4</td>
<td>92.8</td>
<td>7.2</td>
</tr>
<tr>
<td>Magnetic III</td>
<td>6.5</td>
<td>54.1</td>
<td>92.8</td>
<td>7.8</td>
</tr>
<tr>
<td>Magnetic IV</td>
<td>7.8</td>
<td>55.4</td>
<td>90.7</td>
<td>9.3</td>
</tr>
<tr>
<td>Non-magnetic</td>
<td>-</td>
<td>44.6</td>
<td>1.0</td>
<td>99.0</td>
</tr>
</tbody>
</table>

Figure 8 - FTIR spectra of: (I) Bauxite and (II) Bauxite coated with oleate magnetite

achieved assaying around 98 per cent Fe₂O₃ by using around 6 kg/tonne of magnetite⁸. The quantity required is very high compared to the oleate magnetite. However, it has been established that ground magnetite can be used as the coating agents in the system like other minerals⁹, ¹⁰.

For the separation of bauxite from hematite which is a very potential impurity in the ore body, a mixture of hematite and bauxite was fed into the magnetic separator using the colloidal oleate magnetite. In this case, sodium hexa metaphosphate and sodium silicate were used in order to change the surface properties of bauxite. The sign of zeta-potential becomes negative. Therefore the probability of interaction between oleate magnetite with bauxite decreases. As a result, hematite is separated easily from bauxite which has got a chemical interaction with oleate. However, SHMP gave far better results than sodium silicate. The results of the study using 0.012 g/kg of oleate magnetite and 0.01 per cent SHMP are presented in Table 3. A 99 per cent Al₂O₃ with 90 per cent recovery has been reported in the non-magnetic fraction. In the absence of SHMP, it has been found that some bauxite was reported in magnetic fraction.

Conclusions

Separation of quartz from hematite or hematite from bauxite can be obtained by using a small fraction of colloidal magnetite in a low to medium intensity of magnetic separator. The selective coating and the corresponding separation mostly depends on the surface properties of the minerals. Both phosphate and silicate ions play a role in the zeta potential of the minerals. It has also been concluded that colloidal magnetite is chemically bonded with hematite, whereas it is physically adsorbed with the bauxite.

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References