EFFECTS OF CO₂ ON THE ZETA POTENTIAL OF HEMATITE

J. J. Carlson, Michigan Tech, Houghton, MI
T. C. Eisele, Michigan Tech, Houghton, MI

ABSTRACT

An important factor in filtration is the zeta potential of the particles. Since zeta potential is a function of pH, it was hypothesized that adding CO₂ would lower the pH and zeta potential. A reduction in zeta potential should enhance the flocculation and increase the filtration rate. This paper describes the effects CO₂ on the zeta potential of both pure hematite and samples of hematite concentrate from an iron ore processing plant. A significant shift in the zeta potential, as a function of pH, curve was observed. These results point to an alteration of the particles mineralogy, not just a shift in pH.

INTRODUCTION

For wet forms of iron ore processing, iron concentrate slurry must be filtered to provide a low moisture filter cake to be used in the pelletization process. If the filtration rate drops too low, filtering becomes the bottle neck of the process. Since iron ore is such a high volume business, even the smallest changes in filtration can affect the bottom line.

Permeability of a bed of particles is the measure of how well a fluid will flow through the bed. In its most basic form, the general equation for determining permeability of a bed of particles is given in eq. (1) (Bear, 1972):

\[ k = f_1(s)f_2(n)d^2 \]  

where:
- \( k \) = permeability [mm²/s]
- \( f_1(s) \) = shape factor, which influences the way that particles interlock in a packed bed [dimensionless]
- \( f_2(n) \) = porosity factor, a measure of how tightly packed the particle bed is [dimensionless]
- \( d \) = effective or mean diameter of the particles [mm]

Flocculation increases both the bed porosity and effective diameter in eq. (1), which in return increases permeability (i.e. filtration rate). In a previous study, filtration rate fluctuations of 60% at a magnetite processing plant were investigated (Carlson et al., 2008). The authors determined through circularity analysis that particle shapes were not varying from sample to sample, so therefore could not be causing the changes in filtration rate. Likewise, particle size distributions were also determined to be constant. Fluctuations in filtration rate were attributed to differences in mineralogy (composition) and surface chemistry (i.e. zeta potential).

Flocculation is governed by two main forces, electrostatic repulsion (i.e. zeta potential) and van der Waals attraction. The net effect of repulsive and attractive forces into net interaction energy is clearly stated in the DLVO theory (Derjaguin, Landau, Verwy and Overbeek). By bringing the zeta potential close to zero, the attractive forces become dominant and flocculation occurs.

Zeta potential is a function of pH. Altering the pH to decrease the zeta potential should increase filtration rate. The maximum filtration rate should be obtained at the pH where the zeta potential is zero, commonly known as the iso electric point (IEP). One study has even used a filtration rate technique to determine the zero point of charge of iron oxides (Ankomah, 1991).

Both the zeta potential and IEP of hematite has been disputed throughout literature for a long time. Many of the disputes surround the differences between synthetic and naturally occurring minerals. The argument stems from the fact that natural hematites have some silica impurities, which coat the hematite particles causing them to have an IEP similar to silica (< pH 3), while the IEP of synthetic hematite varies from pH of 6.5 to 9 (Quast, 2006; Parks, 1965; Kosmulski 2002, 2004). In any event, most iron ore processing plants in the Northern Minnesota and Michigan areas operate under neutral to basic conditions, which are well above the IEPs reported for natural hematite. It was hypothesized that by reducing the pH at the filters, the degree of flocculation and filtration rate would increase.

A previous study was able to use CO₂ to increase the filtration rate by 23% at a magnetite processing plant (Eisele et al., 2003). The authors hypothesized that CO₂ would form a weak carbonic acid, which would lower the pH and zeta potential of the particles. They also determined the IEP of the magnetite filter cake to be between 3.0 and 3.5 by using microelectrophoresis and streaming potential methods. The authors determined that a pH of 7 was easily obtainable by sparging the system with CO₂. Such a decrease in pH should have lead to a drop in zeta potential from -28 to -20 mV (a 28.5% decrease) (Eisele et al., 2005).

The work done by Eisele et al. (2005) set a new bench mark for cost effective filtration aids in iron ore processing, but more research was needed to understand how the CO₂ was effecting the filtration rate. The purpose of this study was two fold: (1) determine the effects of CO₂ on the zeta potential of commercially purchased hematite in a background electrolyte containing inert ions (1mM KCl), (2) repeat this work with samples taken from a hematite processing plant which utilizes CO₂ as a filtration aid.

EXPERIMENTAL

Materials

Hematite (Test Chips)Fe₂O₃. For the controlled CO₂ experiments done in the lab, hematite test chips were purchased from Ward’s Natural Science. These test chips were taken from Hoyt Lakes, Minnesota. The hematite test chips were sent through a series of crushers to simulate plant processing.

Siderite (Test Chips) FeCO₃. Siderite test chips were also purchased from Ward’s Natural Science. The siderite test chips were sent through a series of crushers to simulate plant processing.

Plant Samples: Hematite Concentrate. Samples of hematite concentrate were taken from an iron ore processing plant in Michigan. Five-gallon buckets of slurry were taken from points before and after the addition of CO₂ on two separate days. The plant water was decanted into separate buckets and was saved to be used as the background electrolyte in the EKA measurements.

Methods

Tests were carried out on both an Electro Kinetic Analyzer (EKA) and a microelectrophoresis unit to determine zeta potentials. The EKA was produced by Anton Paar and was coupled with a remote controlled titration unit. The micro electrophoresis unit (Zeta Meter) was produced by Pen Kem, Inc. and was a Lazer Zee Meter model number 501.
Streaming Potential. The Electro Kinetic Analyzer (EKA) is a streaming potential unit. It applies a fluid flow across a stationary bed of particles and measures the voltage drop. The EKA began by measuring the voltage drop at an initial pH of about 10. Nitric acid was titrated into the system over time to lower the pH. The zeta potential was then plotted as a function of pH. This zeta potential is also referred to as the streaming potential. The limitation to this unit is that the sample must contain particles coarser than 25 micrometers.

The following procedure was followed for the purchased (controlled) samples of hematite and siderite. Since the EKA test cell required material coarser than 25 micrometers, a desliming procedure was used to remove the fine material. The coarser particles remaining were then loaded into the test cell to form a circular bed of particles 15mm in diameter and 5mm deep. The loaded test cell was inserted into the EKA. A one millimolar solution of KCl in distilled water was used as the background electrolyte. This solution was pumped into the EKA until all the air was removed from the system. At this point, the pH of the media was adjusted to about 10 by adding NaOH. The EKA began by measuring the streaming potential (zeta potential) at this pH. After the streaming potential was measured, the EKA lowered the pH by automatically adding nitric acid over time. The streaming potential was measured after each addition of nitric acid from a range of pH 10 to 2.

Samples of hematite which were taken from the iron ore processing plant were deslimed and loaded into the cell. Streaming potential measurements were taken using plant water as the background electrolyte.

Microelectrophoresis. Micro-electrophoresis applies a high voltage current across a suspension of particles in a liquid, which causes the particles to migrate through the liquid medium. The velocity of the migrating particles is measured by a rotating prism, and directly correlates the zeta potential of the particle at that particular pH. A new solution needs to be prepared for each data point over the required pH range, since there is no automatic titration unit. The suspended particles must be much finer than 25 micrometers.

Test solutions ranging from a pH of 2 to 10 were prepared. The test solutions were prepared by adding 0.2 grams of ore sample to an Erlenmeyer flask containing 200mL of a 10 millimolar solution of NaCl in distilled water at room temperature. These test solutions were then allowed to sit for 2 hours to come to equilibrium. After 2 hours the pH was measured, the sample was injected into the test cell, and the zeta potential was measured.

RESULTS AND DISCUSSION

Lab Studies of Commercial Hematite

As stated before, the purpose of this study was to determine the effects of CO₂ on the zeta potential of commercially purchased hematite in a background electrolyte containing inert ions (1mM KCl). The streaming potential for the hematite sample is plotted found as a function of pH in Figure 1.

Figure 1 shows that the purchased sample of hematite has a similar IEP for natural hematite shown in previous studies (Eisele et al., 2005; Quast, 2006). This phenomenon is most likely due to fine silica present in the ore sample as shown in literature (Esumi et al., 1988).

Table 1 shows the minimum pH that can be obtained by adding CO₂ to hematite slurry is almost 4.5. In this case, the pH reaches its minimum after 1 minute.

At any rate, when compared with Table 1, adding CO₂ to obtain a pH of 4.5, a drastic zeta potential reduction of 50% would occur.

However, the plant which used CO₂ as a filtration aide reported a reduced pH of 7, which is close to that reported by Eisele (2005). This more moderate reduction would theoretically only account for a 16.7% reduction in zeta potential, which raises the question, “is pH the only factor altered by adding CO₂?”

The next step of the project was to introduce CO₂ into a slurry of the same hematite and determine how the zeta potential changed. Hematite/CO₂ slurry was prepared by taking 36 grams of hematite and 250mL of distilled water and sparging with CO₂ for 5 minutes to ensure complete saturation. Once saturated with CO₂, the slurry was deslimed and the coarse fraction was analyzed using the streaming potential unit in 1mM KCl background electrolyte. The results are shown in Figure 2.

Table 1. Effects of CO₂ on the pH of a Hematite Slurry.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.11</td>
</tr>
<tr>
<td>1</td>
<td>4.57</td>
</tr>
<tr>
<td>2</td>
<td>4.82</td>
</tr>
<tr>
<td>5</td>
<td>4.77</td>
</tr>
</tbody>
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The addition of CO₂ caused a shift in the entire zeta potential curve. These results proved that a factor other than pH was controlling zeta potential and filtration rate. This result is significant because 

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Figure 1. Zeta Potential of Hematite as a Function of pH. From these results, lowering the pH with CO₂ from 10.5 to 4.5, this would cause a 50% reduction in the magnitude of the zeta potential. However, studies at a hematite processing plant showed that the pH decreased to about 7 with CO₂ addition, corresponding to only a 16.7% reduction in zeta potential.

Figure 2. Zeta Potentials of Hematite Before and After CO₂ Additions. The addition of CO₂ to the hematite slurry caused the whole curve to shift downward. This was an important result because it showed that the zeta potential wasn’t just lowered by pH adjustment. This means that there must have been a surface reaction taking place to neutralize the surface charge.

The addition of CO₂ caused a shift in the entire zeta potential curve. These results proved that a factor other than pH was controlling zeta potential and filtration rate. This result is significant because it was originally believed that the pH shift was causing the reduction in...
zeta potential, but from our results, we have shown that there is an actual change in the surface of the ore particles themselves.

Because of its close structure and composition, a sample of siderite was purchased and its zeta potential was measured in 1 mM KCl for comparison purposes. Figure 3 shows the results of the siderite tests. The zeta potential of the siderite is very close to that of the hematite with CO$_2$ at an alkaline pH, but as the pH is lowered, the hematite with CO$_2$ curve shifts back toward the pure hematite curve.

Previous work done in literature has shown hematite can be used to trap CO$_2$ (Palandri et al., 2005). However, for this reaction to take place, reduced sulfur (in the form of SO$_2$) must be present to reduce iron(III) (hematite) to iron (II). The overall reaction is shown below (Palandri et al., 2005):

$$\text{Fe}_2\text{O}_3 + 2\text{CO}_2 + \text{SO}_2 + \text{H}_2\text{O} = 2\text{FeCO}_3 + \text{H}_2\text{SO}_4$$

This is an unlikely scenario because SO$_2$ should not be present. Another scenario would be the presence of magnetite in the sample as the iron(II) source, but is also unlikely.

We must also take into account that any calcium or magnesium ions in this solution would also be affected by the presence of CO$_2$, so all possible scenarios must be looked at in further detail before a concrete theory can be developed.

In any event, we have proven that when CO$_2$ is added to hematite, there is a shift in the entire zeta potential curve, but more experiments are needed to explain this phenomenon in greater detail.

**Lab Studies on Plant Samples**

It has been proven that the filtration rate of an iron ore processing plant was increased by 23% by adding CO$_2$ (Eisele et al., 2005). The results from the previous section have shown that this increase in filtration rate was caused by a shift in the entire zeta potential curve of hematite.

It was then important to collect samples at the plant which utilizes CO$_2$ as a filtration aide. Zeta potential was measured in plant water from samples taken before and after the addition of CO$_2$ on two different operating days. The results for the zeta potential testing of both samples are shown on Figure 4.

Figure 4 shows that the zeta potential curve for the sample without CO$_2$ is extremely flat. It is important to note that numerous surfactants (i.e. collectors, dispersants, etc.) are added throughout the process, so flattening of the curves is not necessarily unusual.

From Figure 4, the magnitude of the zeta potential is not dropping due to a decrease in pH. Instead, the results show that the addition of CO$_2$ caused a shift in the zeta potential curve similar to the shift observed in the early lab scale studies.

**CONCLUSIONS**

The purpose of this project was to determine the effects that CO$_2$ had on pH and zeta potential of hematite. It had been proven in a previous study that the filtration rate was increased at an iron ore processing plant by adding CO$_2$ to the slurry before filtration. The original hypothesis was that the CO$_2$ was forming carbonic acid, which lowered the pH, in return lowering the zeta potential. This study was performed to test this theory by running more in-depth CO$_2$ testing.

Lab scale tests using high purity hematite and siderite tests chips were performed. It was observed that adding CO$_2$ to the pure hematite caused a shift in the whole zeta potential curve, not just a reduction in pH. This result showed that a surface reaction must have occurred in order to reduce and stabilize the surface potential.

After testing a pure siderite sample, it appeared that at pH greater than 6 results for hematite with CO$_2$ were similar to siderite. On the other hand, for pH less than 6, the hematite with CO$_2$ results shifted back to the pure hematite curve.

Since iron(II) would be needed to form siderite, it is unlikely that actual siderite was formed on the particle surface. Instead, more testing is needed to determine the actual mineralogical changes on the hematite surface.

With samples of hematite concentrate collected from an operating plant, it was observed that just a reduction in pH would not affect the zeta potential at all because the shape the initial hematite curve was flat. When CO$_2$ was added into the hematite slurry, the zeta potential curves were shifted downward similarly to the tests done on the high purity natural hematite. Since the magnitude of the zeta potentials of hematite/CO$_2$ were considerably less than that of just hematite, particle flocculation was increased, therefore increasing filtration rate.

**REFERENCES**


