SURFACE CHEMISTRY OF IRON ORE THROUGHOUT A PROCESSING PLANT

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ABSTRACT
An extensive study was carried out to completely characterize the Zeta potential of an iron ore as it proceeded through a full-scale iron ore processing plant. This was done for two reasons: (1) to produce a ‘snapshot’ of the conditions during a period where the plant was performing correctly to provide a basis for comparison if the plant performance later changed; and (2) to determine how the actual surface chemistry of the ore particles in an operating plant differed from those reported in the literature for pure minerals under controlled conditions. From these results, it was seen that the actual Zeta potentials were much different than what had been assumed when the process was designed. Re-design of the processes to take into account the actual Zeta potentials of the ores being processed could potentially lead to significant process improvements, because zeta potential has a strong effect on particle-particle and particle-chemical interactions.

Keywords: surface chemistry, zeta potential, iron ore, hematite, magnetite

INTRODUCTION
The concept of Zeta potential is important for understanding every aspect of the processing of iron ore slurries. The Zeta potential is related to the excess charge that develops on the surface of the particles as a result of ion exchange with the solution. For oxide minerals such as iron oxides and silicates, it is typically a function of pH, and minerals generally have a specific pH (the isoelectric point, or IEP), where the Zeta potential changes sign from positive to negative. It influences interactions of particles with each other and with chemical reagents, due to electrostatic attraction/repulsion effects. In particular, the effects of Zeta potential on flocculation, reagent adsorption, and slime coating of particles changes the performance of separation and dewatering operations. In spite of the importance of Zeta potential throughout iron ore processing plants, a full-scale plant study to determine how the Zeta potential varies as processing proceeds has never been carried out. Also, the majority of the Zeta potential studies that are published in the literature use high-purity and synthetic minerals, which have been shown to have Zeta potentials different from those of natural ores (Parks, 1965; Kosmulski, 2002, 2004).

The majority of literature states that natural hematites have lower IEPs than synthetic hematites. The difference between natural and synthetic minerals is most likely caused by the coating of fine silica on hematite surfaces (Quast, 2006) by a process known as dispersion-flocculation-redispersion (Esumi et al, 1988). There is not much literature relating zeta potential measurements of natural ores to processing plant performance. Hunter (2001) published a paper on the theory of measuring zeta potential in concentrated industrial slurries, but this review only touched the theory of applying an online zeta potential measuring system. Also, previous studies have shown that the filtration rate was increased by 23 per cent at one iron ore processing plant by adding CO₂ (Eisele et al, 2005). Some lab scale tests were done, but no samples were collected from the plant to determine the exact effects of CO₂ on the zeta potential of hematite concentrate. A full scale plant study has never been implemented and published in literature.

The study described here is the first characterization of zeta potential variations throughout a processing plant. The hematite plant chosen for this study utilizes selective flocculation and reverse
flotation, both of which rely heavily on the ability to control zeta potential. Chemicals added during processing include sodium hexametaphosphate (SHMP) dispersants, cationic amine collectors, starch depressants, CO₂, and calcite/dolomite flux, all of which can affect zeta potential (Ramos-Tejada et al, 2003; Chibowski and Wisniewska, 2002; Shibata and Fuerstenau, 2003; Quast, 2006; Tombacz et al, 2006).

It is important to note that the measurements contained in this paper are bulk zeta potentials of the samples, so there is no distinction between the different minerals within the samples. For this reason, some of the change in zeta potential throughout the plant were ultimately due to the changing concentration of hematite throughout the process.

EXPERIMENTAL

Method

Because of the broad size distributions, Zeta potential measurements were carried out using both an Electro Kinetic Analyzer (EKA) for particles too coarse to remain in suspension, and a microelectrophoresis unit for particles that were fine enough to remain suspended for extended periods.

Streaming potential

The EKA was an Anton Paar streaming potential unit, with a remote controlled titration device for automatically varying the pH. It applied a fluid flow across a stationary bed of particles and measures the voltage drop. The limitation to this unit was that the sample must contain particles coarser than 25 micrometres. The following operating procedure was used:

- 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 15 mm in diameter and 5 mm deep.
- The loaded test cell was inserted into the EKA.
- The proper background electrolytes were pumped into the EKA until all the air was removed from the system. Depending on the sample analyzed, the background electrolyte was ether a one millimolar solution of KCl in distilled water, or water decanted from the plant samples.
- Each analysis began at an alkaline pH, either by adjusted to approximately ten by adding NaOH, or by starting at the natural pH of the plant slurry.
- After the streaming potential was measured, the pH was automatically lowered by adding nitric acid in small, precisely measured increments using the remote titration unit. The streaming potential was measured after each addition of nitric acid from a range of pH 10 to 2.
- The streaming (zeta) potential was then plotted as a function of pH.

Microelectrophoresis

The microelectrophoresis unit was a Pen Kem Laser Zee Meter, Model 501. Micro-electrophoresis applies a high voltage current across a suspension of particles in a liquid, which causes the particles to migrate through the liquid media. The velocity of the migrating particles was measured by a rotating prism. This velocity was directly related to the particle Zeta potential. The technique depends on particles remaining in suspension, and so it was most suitable for very fine particles less than approximately 5 micrometres in diameter. Microelectrophoresis was used both because it would allow the measurements of Zeta potential of the very fine particles, and because it could be performed relatively quickly on samples as soon as they arrived in the laboratory. The following operating procedure was used:

- The pH was measured immediately upon arrival of the sample at the laboratory and all measurements were made within 24 hours of arrival.
- The samples were then injected into the test cell with plant water as the background electrolyte.
- The zeta potentials were measured at the plant pH.
Materials and handling

Hematite concentrate (from iron ore processing plant Fe₂O₃)

Samples of hematite concentrate were taken from a hematite processing plant (Plant A) in Michigan. The simplified process flow diagram, along with all of the sampling points can be found in Figure 1. Five-gallon (19 litre) buckets of slurry were taken from points before and after each processing step and reagent addition. The plant water was decanted into separate containers and was used as the background electrolyte for their respective EKA measurements. It has been reported in the literature that aging of iron oxide results in a reduction of the IEP (Plaza et al., 2002; Cromieres et al., 2002), so a separate one litre bottle of slurry was also taken and put on ice to slow any aging effects before being run on the Zeta Meter (Microelectrophoresis). These 1-litre samples were then analyzed within 24 hours.

Hematite (test chips) Fe₂O₃

Experiments were done in the laboratory to determine the effects of sodium hexametaphosphate (“Glass H”), since this reagent is used as a dispersant in the plant and has strong effects on the hematite surface chemistry. For these experiments, hematite test chips from Hoyt Lakes, MN were purchased from Ward’s Natural Science. The hematite test chips were sent through a series of crushers to reduce them to a fine enough particle size for Zeta potential measurements.

Reagents for testing of plant samples

Plant water corresponding to each sample was used as the background electrolyte. A 50 per cent NaOH solution and a 0.1 M nitric acid solution were used as pH modifiers during zeta potential measurements.

Reagents for testing of commercially purchased hematite

A 1 millimolar KCl solution was used as a background electrolyte. “Glass H” for lab tests was provided by the hematite processing plant. A 50 per cent NaOH solution and a 0.1M nitric acid solution were used as pH modifiers during zeta potential measurements.

FIG 1 - This schematic represents the Simplified Process Flow Diagram (PFD) of Plant A. During the sampling campaign, 5 gallons (18.9L) of slurry was collected at each of the 13 sampling points, represented by the numbered circles.
RESULTS AND DISCUSSION

Effects of reagent additions on zeta potential of iron bearing hematite

Effects of sodium hexametaphosphate (SHMP) dispersant

Samples of hematite bearing slurry were taken before and after the addition of Glass H and analyzed in plant water using the EKA. The results are shown in Figure 2. It was observed that the IEP of the primary grinding product was much less than three, which was much different than previously reported in literature. The results were actually closer to the IEP reported in literature for silica. This was most likely due to the large amount of silica in the sample.

Figure 1 shows that the addition of Glass H did not appear to affect the zeta potential in the majority of the pH range studied. However, there was a notable change at pH values less than 4. The sample before adding Glass H appeared to approach an IEP of approximately 2, while the sample after adding Glass H showed no sign of approaching an IEP, with the Zeta potential becoming even more negative.

Microelectrophoresis was used to determine the zeta potential of the particles which did not settle out of the slurries at the plant operating pH. Using microelectrophoresis the zeta potentials were -55.1 (at pH 11.5) before adding Glass H, and -53.8 (at pH 11.5) after adding Glass H, which showed that at the plant pH the Glass H addition did not have a strong effect on Zeta potential.

A second set of experiments were run using a commercially purchased sample of hematite with the addition of Glass H at the same dosage as used in the plant to validate the observations made from Figure 2. The results can be found in Figure 3. The IEP of the commercially purchased hematite without Glass H was about 2.5, which is consistent with studies done on natural hematite in literature (Quast, 2006). However, this was different from the behavior shown in Figure 2 of the hematite before adding Glass H, which showed very little pH dependence. The effects of Glass H on the commercially purchased hematite were to lower the IEP and flatten the response of Zeta potential to pH variations. Adding Glass H appeared to make the hematite behave much more like the ore in the plant. It is possible that there was enough Glass H in the plant recirculation water that all of the samples collected from the plant contained it, and so it would even affect the behavior of the ore before the nominal Glass H addition point.

![Figure 2](image-url) - Effects of Glass H on Streaming Potential of Hematite Bearing Slurry. Sample: Primary grinding circuit product before and after Glass H addition. Method: Electro Kinetic Analyzer. Background Electrolyte: Plant water.
Effects of starch

As shown in Figure 1, starch was used in two different places in the circuit. First, starch was used to selectively flocculate the hematite before the desliming process. Secondly, the starch was used as an iron depressant in the flotation process.

Samples of hematite bearing slurry were taken before and after the first addition of starch and analyzed in plant water using the EKA. The results are shown in Figure 4.

From Figure 4, it was observed that the addition of starch before selective flocculation caused a reduction in the zeta potential of the hematite bearing slurry. Similarly, the microelectrophoresis unit gave Zeta potentials of -54.1 mV (at pH 11.2) before adding starch, and -43.1 mV (at pH 11.1) after starch addition.

Starch was also added to the process before froth flotation to act as an iron ore depressant. In this case the goal was to get the cationic amine collector to selectively adhere to the surfaces of the silica particles. Since both hematite and silica have negative zeta potentials at the plant pH, starch was used to selectively coat the hematite surfaces and act as a shield against collector absorption so that only the silica would absorb the collector and float. The results for the addition of starch before flotation can be found in Figure 5.

At the alkaline pH where the plant operates, there appeared to be no effect on the zeta potential of the coarse particles. However, as the pH was lowered in the laboratory, an increase in zeta potential after the starch addition was observed. For the fine suspended particles, microelectrophoresis measurements yielded zeta potentials of -46.3 mV (at pH 11.0) before starch addition, and -52.1 mV (at pH 11.0) after starch addition. This increase in zeta potential may have been caused by the increased flocculation of ultra fine silica onto the hematite, producing results even more related to silica.

Effects of CO₂

CO₂ has been reported as an iron ore filtration aid (Eisele et al., 2005). In previous experiments, it was determined that filtration rate increased at a magnetite processing plant by 23 per cent by using CO₂ to lower the pH, which reduced the Zeta potential of the magnetite and increased the degree of flocculation, leading to faster filtration.

CO₂ is injected in the hematite processing plant before the hematite concentrate filtration step, and its effect on Zeta potential is shown in Figure 6. Addition of CO₂ changed both the pH and zeta potential. Addition of CO₂ caused the entire zeta potential/pH curve to shift closer to zero. This result proves that CO₂ did more than just lower pH; it actually altered the particle surfaces. For the fine suspended particles, microelectrophoresis measurements yielded zeta potentials of −47.3 mV (at pH 10.9) before adding CO₂, and −32.3 mV (at pH 7.9) after CO₂ addition. This phenomenon was recreated in the lab with the commercially provided hematite. The results for this test are found in Figure 7, which again showed that adding CO₂ shifted the entire curve closer to zero.


**FIG 7** - Effects of CO₂ on Streaming Potential of Purchased Hematite. Sample: Commercially purchased Hematite from Ward's Natural Science before and after CO₂ addition. Method: Electro Kinetic Analyzer. Background Electrolyte: 1mM KCl.
Effect of calcite/dolomite flux
Calcite/dolomite flux is commonly added to iron ore before firing pellets to enhance slag removal in the blast furnace. To determine the effects of flux in a hematite processing plant, samples of hematite bearing slurry were taken before and after the addition of calcite/dolomite flux and analyzed in plant water using the EKA. The results are shown in Figure 8.

For the fine suspended particles, microelectrophoresis measurements yielded zeta potentials of -32.3 mV (at pH 7.9) before flux addition and -31.5 mV (at pH 8.5) after flux addition.

Effects of separation processes on zeta potential of iron bearing hematite
Selective flocculation and desliming
Samples of hematite bearing slurry were taken around the desliming process and analyzed in plant water using the EKA. The results are shown in Figure 9.

When analyzing the results in Figure 9, one must keep in mind that compositions were varying greatly. The overflow had a large of amount of fine silica slimes, which theoretically have higher zeta potentials. In contrast, the underflow had larger amounts of iron bearing minerals (mostly hematite), which theoretically have lower zeta potentials at the plant pH of 10 to 11. This is consistent with the observations shown in Figure 9, which shows that the high-Fe deslimed underflow had a lower Zeta potential than the high-silica deslimed overflow. This difference in Zeta potential was less predominant for the fine suspended particles, most likely due the fact that entrained silica particles are still present in the underflow sample. Microelectrophoresis measurements yielded zeta potentials of -46.3 mV (at pH 11.0) in the iron-rich deslimed underflow, and -51.9 mV (at pH 11.2) in the silica-rich deslimed overflow.

The most important difference appears to be the shape of the zeta potential curves. As observed from Figure 9, it appears the sample with higher percent iron (ie deslimed underflow) has a much flatter curve, whereas the samples containing higher amounts of silica and gangue (deslime overflow) were much more responsive to pH changes.
**Cationic amine reverse flotation**

Samples of hematite bearing slurry were taken around the flotation process and analyzed in plant water using the EKA. The results are shown in Figure 10.

Froth flotation samples with higher concentrations of silica gangue (Tailings) had slightly larger zeta potentials at the plant pH than samples with higher percent iron bearing minerals (Rougher Concentrate). Microelectrophoresis measurements yielded zeta potentials of -47.3 mV (at pH 10.9) for the rougher concentrate and -41 mV (at pH 11) for the tailings.

More importantly, the samples with higher percent iron (ie feed and rougher concentrate) have much flatter curves, whereas the sample containing higher amounts of silica and gangue (tailings) was much more responsive to pH. This observation is consistent with the findings in the desliming results. Figure 11 shows that another high percent Fe sample (scavenger returns) also possessed the same flat curve. This also confirms that the addition of earlier reagents (Glass H, Starch, or both) affect the silica and iron bearing minerals quite differently.

**CONCLUSIONS**

The purpose of this study was to create a snapshot of the zeta potentials which actually occur throughout an operating hematite processing plant. The surface chemistry of hematite and other iron ores have been studied extensively throughout literature, but a full scale plant study had never been performed. The results obtained in this study have shown that zeta potentials which exist in a processing plant are much different from those reported throughout literature. From this study, the following observations were made.

The zeta potential curves for hematite bearing samples under plant conditions are much less responsive to pH changes than those reported in literature for hematite in inert/indifferent background electrolytes. Glass H appeared to have some effect on the flattening of the zeta potential curves.

Starch initially causes a reduction in the entire zeta potential curve as it is used to coat the hematite particles, but adding additional starch at a later point in the process had a much smaller effect on the Zeta potential.
**Figure 10** - Streaming Potential of Hematite Bearing Slurry Around Flotation. Sample: Feed, Iron (Rougher) Concentrate, and Tailings samples around the Reverse Flotation Circuit. Method: Electro Kinetic Analyzer. Background Electrolyte: Plant water.

**Figure 11** - Comparison of Rougher Concentrate and High % Fe Scavenger Returns Sample: Rougher Concentrate and High % Fe Recycle (Scavenger) Returns. Method: Electro Kinetic Analyzer. Background Electrolyte: Plant water.
More importantly, the samples with higher percent iron have much flatter Zeta potential vs. pH curves, whereas the samples containing higher amounts of silica and gangue were much more responsive to pH. This observation was consistent with the findings in the results around both the desliming and flotation circuits. This confirms that the addition of earlier reagents (Glass H, Starch, or both) effect the silica and iron bearing minerals quite differently. More studies are needed to determine the exact effect each reagent has on the minerals. It is clear at this point that zeta potentials which exist in plant conditions are much different from those studied in literature.

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REFERENCES


