EFFECT OF CATIONS ON IRON ORE CONCENTRATE PELLET STRENGTH

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ABSTRACT
Bentonite clay is used as a binder for iron ore concentrate pelletization. Bentonites are sensitive to cations such as calcium, magnesium, sodium, and potassium that are known to be dissolved in the moisture remaining in the iron ore concentrate. These cations affect the ability of bentonite to absorb water, as measured by the plate water absorbance (PWA) test. This paper addresses the relationships between plant water chemistry and pellet strength for a wide PWA range of bentonites. Experiments were conducted to determine the effect of concentrate moisture solute chemistry and bentonite PWA value on the wet knock and wet and dry compressive strengths of iron ore pellets. Experiments used seven different types of bentonite that had PWA values ranging from 564 to 1033. Flushing plant concentrate with distilled water to remove the dissolved cations resulted in increased pellet strengths, to a widely varying degree, for each bentonite tested; wet knock values increased an average of 92% and dry compressive strength increased an average of 46%. In addition, pellet strengths were not found to be directly related to the ability of bentonite to absorb distilled water, measured by the PWA test.

INTRODUCTION
The moisture remaining in the iron ore concentrate after vacuum disc filtration is composed of plant water. This moisture contains exchangeable cations, particularly calcium, that may affect the bentonite PWA and/or the pellet strength. This raises the following two questions: 1) How does bentonite PWA affect pellet strength? And more importantly, 2) How does the concentration of cations dissolved in the moisture remaining in the concentrate affect pellet strength? These relationships are important to understand, yet there are no systematic studies available in the published literature. Therefore, these relationships should be studied in a scientific manner.

Bentonite bonding quality is widely believed to be related to its ability to absorb water, as measured by PWA (plate water absorbance). Bentonites are composed of discrete platelets that are separated by an exchangeable cation layer. Water molecules can hydrate the cations and the surfaces of the platelets allowing the bentonite to absorb water and expand. Sodium-bentonites have sodium exchangeable cations and calcium bentonites have calcium exchangeable cations. These two bentonites behave quite differently. Sodium bentonites are more highly absorbent than calcium bentonites because the divalent calcium ions hold the clay platelets more strongly together, allowing less water between the platelets, than the monovalent sodium cations. When calcium (e.g. from the concentrate moisture) exchanges for sodium between bentonite clay platelets, the platelets are bonded more strongly together. This restricts the bentonites from expanding and dispersing into a gel which improves the pellet’s plasticity, thereby increasing wet knock value of the pellet. Different bentonites can absorb water at different rates. For example, Figure 1 shows that while calcium bentonites initially absorb water faster, sodium bentonites absorb much more total water. Sodium bentonites are important binders for iron ore pelletization, while calcium bentonites are much less effective and are not often used in this application.

Current iron ore concentrate pelletization practice was developed in the 1950s when bentonite clay became established as the most acceptable binder. Over the past 50 years, iron ore pelletization has generally expanded while the high-quality western-type bentonite reserves (located within the United States) have been depleted, allowing lower quality bentonites to be marketed. Bentonite is used primarily for improving an iron ore concentrate pellet’s dry compressive strength so that the pellets can survive handling, drying, and firing. The minimum industrially acceptable dry pellet compressive strength is typically 22 Newton (5 lbf). A typical dosage of bentonite is 0.66% or 14 pounds per ton of moist iron ore concentrate filter cake (typically 10% moisture). Adding more bentonite is a disadvantage because pellets containing more bentonite cost more to produce and contain a higher silica content. This gives the industry an incentive to use bentonites that produce adequate strength at lower dosages. The amount of water that a bentonite can absorb is related to the types of exchangeable cations it contains.

Bentonite Binding Mechanisms
Bentonite is a mixture of layered hydrated alumino-silicate clay primarily composed of the smectite class mineral montmorillonite. The ideal chemical formula for montmorillonite is: 

$$(\text{Na}_2\text{Ca}_{1/2}\text{Al}_{1.5}\text{Mg}_{1.5}\text{Si}_8\text{O}_{20})(\text{OH})_2\cdot n\text{H}_2\text{O}$$

The montmorillonite crystal structure is shown in Figure 2. Isomorphous substitution of $\text{Al}^{3+}$ by $\text{Mg}^{2+}$ alters the crystal charge balance, giving the lattice a net negative charge. This results in adsorption of cations (commonly $\text{Na}^+$ and $\text{Ca}^{2+}$) to balance the charge. The hydration of these exchangeable interlayer cations causes the bentonites to expand upon wetting (Reisch, 2000).

Bentonite increases dry strength of iron ore pellets in two ways. First, it provides a source of colloidal material that decreases inter-particle distances, and thus increases van der Waals’s forces. Second, it forms a solid bridge of hardened gel that strengthens particle contact points. Explanations of bentonite bonding are available in the literature (Elzea and Murray 1994, Smiernow et al. 1980, and Wilson, 1980). The mechanisms of bentonite bonding has been further explained in previous works by the authors (Ripke and Kawatra 2000a,b). An additional novel bentonite bonding mechanism has been identified (Ripke and Kawatra 2000c) and is summarized as follows: when bentonite clay is moistened, it begins expanding and the bonds between the individual platelets becomes relaxed allowing the platelets to slip across each other and spread like a deck of cards pushed across a table. A specific mixing type efficiently distributed the clay particles into fibers and sheets over the surface of the material being bonded. Utilization of this mechanism allowed the dry pellet compressive strengths to be doubled or allowed the bentonite...
dosages to be reduced by about half while maintaining the same strength.

In either case, the bonding mechanism relies on the ability of bentonite platelets to expand and then either disperse or slip. This expansion is directly related to the amount and type of interlayer cations present between the clay platelets. Bentonites with sodium exchangeable cations tend to expand much more than bentonites with calcium exchangeable cations. This is a concern because PWA may be related to the ability of a bentonite to expand which may be related to its bonding ability. Also, cations (e.g. calcium) present in the plant process water could exchange with the bentonite exchangeable cations (e.g. sodium) and reduce the ability of the bentonite to expand resulting in a decreased binding ability.

**Bentonite Evaluation**

The Plate Water absorbance (PWA) value of a bentonite is measured by a laboratory test to determine water absorbency of bentonite. The test determines how much water is absorbed by 2.00 grams of bentonite, expressed as a percentage of the bentonite weight.

There has been disagreement about how PWA is related to pellet strength. Most plant operators believe that bentonites having higher PWA values produce pre-fired pellets with higher dry compressive strength because over the years they have been forced to use lower PWA bentonites and have observed a drop in binding effectiveness. But meanwhile, as the PWA value of available bentonites has been decreasing, plant water has also been changing. In particular, increased reuse of plant water, addition of flux, and the use of scrubbers have changed the concentrate moisture solute chemistry. Higher calcium ion concentrations in the concentrate moisture solute may alter the effectiveness of pelletizing bentonites.

Aside from PWA, additional tests for bentonite include chemical analysis, exchangeable cations, methylene blue uptake, colloid percentage, grit, X-ray diffraction, and Marsh funnel. A survey conducted through the Iron Ore Cooperative Research Committee found that none of these specifications, singly or collectively, guaranteed that a bentonite would perform well in a plant. Thus, a particular bentonite can meet quality specifications and still perform poorly (Bleilfuss 1999, Engesser 2000b).

**Plant Water Chemistry**

When the PWA test was developed over 25 years ago, there was a concentration of less than 20 mg of total divalent cations (containing calcium and magnesium) per liter of process water in iron ore processing plants in the United States. Some plants are now using process water containing over 100 mg per liter of both calcium and magnesium. One particular study has recently been conducted to determine the effect of water chemistry on the effectiveness of this particular bentonite. Laboratory tests shown in Figure 3 indicate that softening the water with soda ash (sodium carbonate) was twice as effective for improving pellet wet knock as increasing the dosage of a particular bentonite by 1.4 kg/t (an increase from 12 to 15 pounds/ton) (Engesser 2000a).

The results available in the literature are conflicting. Research has been conducted to determine the effect of water hardness on the strengths of pellets made from a fluxed iron ore concentrate by making pellets with the concentrate before and after re-slurrying (washing) up to three times with water deionized by reverse osmosis. It was reported that in general the “washing had no effect to a slight negative influence on the bentonite effectiveness (CCI-CMSC 1994).” However, the report also showed a particular instance where there was a very large negative effect. Bentonite effectiveness was measured by wet knock and wet and dry compressive strengths of the pellets. These tests are described in Table I. Pellets made from the rinsed iron ore concentrate gave wet knock values reduced by as much as from 24.8 to 8.5 drops. Dry compression strengths were also typically slightly lower for the rinsed concentrate.

**EXPERIMENTAL**

**Equipment**

A laboratory-scale balling drum, was used to form the pellets. A Readeo Type A kneader-mixer was used to mix the concentrate with the binder. Pellets were dried in a forced-air drying oven at 105°C. An Instron 4206 was used with an 8896 newton (2000 lbf) load cell at a constant cross-head speed of 40 mm/min. (1.57 in/min.) to crush the pellets and determine their ultimate compressive strength. Particle size analyses were performed with a Microtrac SRA (formerly of Leeds and Northrup Division, Allied Signal, USA). Materials Magnetite concentrate in these experiments was unfluxed filter cake used for pelletization feed. It was obtained from an iron ore concentrator located in the Lake Superior district of the United States. The sample weighed 411 kg (907 lb); 112 samples weighing an average of 3.2 kg (7.1 lb) were divided by coning, quartering, and incremental sampling (according to ASTM E877 1996) and sealed in individual plastic bags. The concentrate had 10% moisture, a particle size of 80% passing 25 microns (500 mesh), and contained 4.9% silicate gangue.

Bentonite clay binder samples were obtained from Cleveland-Cliffs industrial research laboratory and categorized according to their reported PWA value (ASTM E946 1996). The bentonites were Na- montmorillonite based clays that were mined from the Western United States. Particle size distributions for the bentonite are shown in Figure 4 and Table II.
The previously described pelletization procedure. Pellets were then made according to the controlled with oven drying and distilled water addition to the was replaced with distilled water. The final moisture was carefully made with a concentrate that had the plant water replaced with pellets made with standard concentrate were compared to pellets made with a concentrate that had the plant water replaced with distilled water. The plant water was replaced with distilled water following the procedure explained previously in the Experimental section. Table III shows the ion concentrations analyzed for the following water samples: 1. Magnetite concentrate moisture solute - water was extracted from the concentrate by flushing fifty grams of the magnetite concentrate containing 10.2% moisture with 100% distilled water of grams of distilled water. The resulting solution was diluted by a factor of 20.6. 2. Plant filtrate water - The water removed from the concentrate by vacuum filtration through disc filters. 3. A sample of U.S. Lake Superior district tap water - shown for comparison. 4. Distilled water - The concentrations of the ions were not detectable. The analysis for distilled water is not shown in the table.

### Table III. Ionic concentrations of water samples. Values are reported as mg/L (ppm).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Magnetite conc. moisture (undiluted)</th>
<th>Plant filtrate water</th>
<th>Tap water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>5088</td>
<td>9.3</td>
<td>39.6</td>
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<tr>
<td>Magnesium</td>
<td>5993</td>
<td>14.7</td>
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<tr>
<td>Potassium</td>
<td>1680</td>
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<tr>
<td>Sodium</td>
<td>725</td>
<td>151</td>
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</tr>
<tr>
<td>Sulfate</td>
<td>803</td>
<td>54</td>
<td>21</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

#### How is bentonite PWA affected by particle size?

Figure 4 shows the particle size distributions of seven bentonites with different plate water absorbance (PWA) values. The size distributions were measured with laser diffraction of each bentonite in a distilled water slurry. The bentonites with the finer particle size distributions tended to have the higher PWA values. This was expected for two reasons. First, finer size bentonites have a higher specific surface area and can adsorb more water. Therefore, the finer the bentonite, the higher its PWA value. Second, since bentonites with a higher PWA absorb more water, the individual platelets disperse more easily than a bentonite with a lower PWA. It is more likely that platelets in a bentonite with a lower PWA will remain together and be measured as one larger particle, resulting in the appearance of a coarser particle size distribution.

#### Water absorption rates of bentonites

The plate water absorbance (PWA) value is used as the primary parameter to select bentonites for iron ore concentrate pelletization. The PWA value measures the weight percent of distilled water absorbed by the bentonite after it has been allowed to absorb the water for 18 hours (ASTM E946-92 1996). However, in the pellet plants, the bentonite does not have 18 hours to absorb water. Pelletizing bentonites only have a few minutes to absorb moisture from the concentrate before the pellets are formed, dried and fired.

The standard 18 hour measurement is relevant as long as these bentonites absorb water at a consistent rate. However, as can be seen in Figure 5, the rate of water absorption is quite variable. These lines represent the water absorption rates of the bentonites with PWA values of 850 and 757. Bentonites that initially absorbed water at a relatively high rate actually had a much lower 18 hour PWA value. Since it was not known whether the 18 hour value or the absorption rate was the most important parameter, both were measured.

#### How do the cations effect pellet strength?

Laboratory pelletization tests were conducted to determine if plant process water affects the strength of the iron ore pellets. Pellets made with standard concentrate were compared to pellets made with a concentrate that had the plant water replaced with distilled water. The plant water was replaced with distilled water following the procedure explained previously in the Experimental section.

Table III shows the ion concentrations analyzed for the following water samples: 1. Magnetite concentrate moisture solute - water was extracted from the concentrate by flushing fifty grams of the magnetite concentrate containing 10.2% moisture with 100% distilled water of grams of distilled water. The resulting solution was diluted by a factor of 20.6. 2. Plant filtrate water - The water removed from the concentrate by vacuum filtration through disc filters. 3. A sample of U.S. Lake Superior district tap water - shown for comparison. 4. Distilled water - The concentrations of the ions were not detectable. The analysis for distilled water is not shown in the table.
The magnetite concentrate moisture solute is the water that remains in the concentrate after the plant filtrate water is removed by vacuum filtration. Therefore, it was expected that the magnetite concentrate moisture solute would have similar ionic concentrations as the plant filtrate water. However, the results in Table III show that the moisture remaining in the magnetite concentrate had a much higher concentration of the ions than the plant filtrate water. Even more surprising, the plant filtrate water had a lower concentration of these cations than the tap water.

These results can be explained because the positive cations are attracted to the negatively charged surface of the magnetite concentrate. The phenomena is caused by the electric double layer in water adjacent to the solid. The charge on the mineral surface causes a sharp concentration gradient of ions in the water immediately adjacent to the solid. The negative surface charge in this situation results in a large excess of positive ions over negative ions adjacent to the surface. Higher ionic charges increase the concentration gradient of dissolved ions in the electric double layer. The resulting concentration factors are significantly higher for Ca$^{2+}$ and Mg$^{2+}$ than for K$^+$ and Na$^+$ (Railey, 2001).

These concentration difference are important because these cations are known to strongly affect the performance of bentonite as a binder. The concentration of these cations in the filtered concentrate can be much higher than expected from filtrate water analysis.

**Wet Knock Strength**

The wet 18 inch drop (wet knock) value of an iron ore concentrate pellet was described in Table 1. This test measures the ability of wet pellets to remain intact during handling. Moisture content is one variable that has a strong influence on the wet knock value. Generally the wet knock increases with increased moisture content (for typical moisture values from 8% to 10%). Figure 6 shows that the wet knock value of the pellets improved significantly by an average of 92% (5.1 additional drops) after the concentrate was rinsed with distilled water. These data show that wet knock is affected by the ions in the concentrate moisture solute. The calcium in the concentrate moisture solute can exchange with other ions in the exchangeable cation layer of the bentonites and render them a less effective binder. It was observed that the magnitude of this effect varied among the different bentonite samples.

**Wet Compressive Strength**

Figure 7 shows that the wet compressive strength was not affected by the plant water chemistry. The bentonite gel binder in the wet pellets does not impart a significant amount of compressive strength and wet strength is therefore not affected by the cation concentration in the concentrate moisture solute.

**Dry Compressive Strength**

Figure 8 shows that when plant water was replaced with distilled water, dry compressive strength increased an average of 46% (3.5 additional lbf). The calcium and other divalent cations in the plant water interacted with the bentonites and reduced the ability of it to expand and disperse. When the plant water was replaced with distilled water, the bentonites were more effective because they could expand and form a more evenly dispersed gel. Then when the pellets were dried, they were bonded by a more evenly distributed dry clay matrix that more effectively bonded the magnetite concentrate resulting in higher compressive strength pellets.

Now the disagreement in the literature of whether iron ore concentrate pellet strength is affected by the plant water can be explained. It was important to have studied multiple bentonite samples. As shown in Figure 8, pellets made with some of the bentonites were significantly stronger while other bentonites were not. Previously studies presented in the literature were conducted with a single bentonite specimen.

CONCLUSIONS

Bentonites that initially absorbed water at a relatively high rate actually had a much lower 18 hour PWA value than other bentonites that absorbed water more slowly. The ionic concentration of the plant filtrate water varied significantly from the moisture remaining in the filtered concentrate. Calcium is known to decrease the effectiveness of sodium bentonites, and calcium was 500 times more concentrated in the concentrate moisture solute than in the filtrate water.

Plant process water reduced the effectiveness of bentonite binder. Flushing cations from the concentrate moisture with distilled water resulted in increased pellet strengths for each bentonite tested; wet knock strength increased an average of 92% (5.1 additional drops) and dry compressive strength increased an average of 46% (3.5 additional lbf).

Iron ore pellet strength was not directly related to bentonite PWA measured with distilled water.

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REFERENCES


Figure 1. Water adsorption by sodium and calcium montmorillonite (after White and Pichler 1959, verified later by Fuerstenau and Clark 1981). Calcium bentonites absorb more water initially, but sodium bentonites eventually absorb a much greater percentage of water.
Figure 2. Three dimensional structure of bentonite showing two platelets each having an octahedral layer of oxygen atoms and hydroxyl groups sandwiched between two tetrahedral layers of silica arranged in hexagonal rings (after Grim, 1968).
Figure 3. Effect of softening iron ore concentrate moisture with soda ash. For iron ore pellets made with moisture ranging from 9.2 to 9.8%, softening the water had a greater effect on wet knock than increasing the bentonite dosage (after Engesser 2001). 0.55% = 12 lb./Lt.; 0.68% = 15 lb./Lt.
Figure 4. Volume percent size distributions of the bentonites tested, as determined by laser diffraction of the particles in aqueous suspension. The graph is truncated at 100.
Figure 5. Distilled water absorption kinetics of bentonites used in industrial iron ore pellet plants. The solid lines cross, showing that these bentonites did not absorb distilled water at a consistent rate, thus the initial rate does not correspond with the final PWA value.
Figure 6. Number of 18 inch drops onto a steel plate required to fracture wet iron ore pellets. Pellets made with the plant water replaced by distilled water in the concentrate were significantly stronger. The dashed line shows the minimum industrially acceptable
Figure 7. Plant water did not effect the wet compressive strength of the pellets. The dashed line shows the minimum industrially acceptable specification of 10 newtons (2 lbf).
Figure 8. Ultimate compressive strength of dried iron ore pellets. Pellets made with plant water replaced by distilled water in the concentrate were significantly stronger. The dashed line shows the minimum industrially acceptable specification of 22 newtons (5lbf).