Laboratory studies for improving green ball strength in bentonite-bonded magnetite concentrate pellets

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Abstract

The performance of bentonite binders in magnetite concentrate balling has been difficult to predict due to a lack of understanding of the binding mechanisms and of the effects of water chemistry. Results are presented that indicate that the most effective binding occurs when the bentonite platelets slide past one another to form sheet-like or fiber-like structures, which is produced by compressive shear mixing. It has also been determined that the effects of water chemistry on bentonite performance are much greater than had previously been believed. This is because the water retained in magnetite filter cake has been shown to have a considerably higher concentration of ions (particularly calcium and magnesium) than was present in the bulk solution, and these ions strongly impact the swelling behavior of the bentonite. Results showing the benefits of fiber development and showing the effects of the water chemistry are presented. By taking advantage of bentonite fiber development and dealing with the effects of water chemistry, the strength of bentonite-bonded magnetite concentrate pellets can be increased. These studies have brought to light a number of previously unsuspected effects, which are critically important for further improving the theories of bentonite-binding behavior. © 2003 Elsevier B.V. All rights reserved.

Keywords: strength; bentonite; magnetite

1. Introduction

The binding of iron oxide grains by bentonite clay to form pellets is a complex process, with a large number of variables, many of which have never been adequately examined in past investigations. This has introduced many problems in attempts to understand the pelletization process, because much of the theory of bentonite binding suffers from a lack of data, and this lack of data is often not realized either by investigators or by plant engineers. This has lead to much confusion and apparently contradictory results in the published literature. This paper therefore presents investigations of the effects of a number of these factors: (1) the manner of applying mixing energy; (2) the chemistry of the water retained in iron ore concentrate filter cakes, and (3) variations in chemical sensitivity of bentonites.

Current practice for pelletizing iron ore concentrates was developed in the 1950s. At that time, bentonite clay became established, and remains today as the most acceptable binder due to its combination...
of effectiveness and relatively low cost. Dry bentonite is added to iron ore concentrate filter cake, which contains approximately 10% moisture. The bentonite absorbs this moisture and binds the filter cake into a plastic mass that can be easily pelletized, and continues to bind the pellets together after drying.

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 N (5 lbf). A typical dosage of bentonite is 0.66% of the moist (typically 10% moisture) iron ore concentrate filter cake, or 6.25 kg/metric ton (14 lbs/long ton). The dosage of bentonite needs to be kept as low as possible, because pellets containing more bentonite cost more to produce and contain a higher silica content. This gives the industry an incentive to use bentonites in ways that produce adequate strengths at lower dosages.

In previous papers (Kawatra and Ripke, 2001, 2002; Ripke and Kawatra, 2000c), the authors proposed a novel mechanism of bentonite binding that could result in more effective bonding of the grains making up iron ore pellets. This mechanism was expected to be promoted by the application of a combination of compression and shear to the iron oxide/bentonite/water mixture, and it was confirmed that the use of a roll press to apply such forces approximately doubled the pellet strength that could be achieved. In order to confirm the mechanism that improves the binding properties under these conditions, it is necessary to examine microscopically how bentonite distribution is affected by the application of compressive shear forces.

It is also well-known that bentonite bonding is affected by water chemistry. Bentonite grains absorb water and expand because they are composed of discrete platelets that are separated by an exchangeable cation layer. The water absorption behavior of bentonite varies depending on whether the exchangeable cations are mostly sodium or mostly calcium. Sodium bentonites are more highly absorbent than calcium bentonites (as measured by the plate water absorbance [PWA] test, ASTM E946-92, 1996) because the divalent calcium ions hold the clay platelets more strongly together than monovalent sodium ions, allowing less water between the platelets. The level of Ca\(^{2+}\) in plant process water is particularly important, because it can convert high-absorbance sodium bentonites into low-absorbance calcium bentonites, as shown in Fig. 1. In order to make bentonite more effective, it is necessary to understand the effects of pellet water chemistry and the actual binding mechanisms involved.

2. Background

2.1. Bentonite-binding mechanisms

Bentonite is a mixture of layered hydrated aluminosilicate clay primarily composed of the smectite

![Fig. 1. Effect of Ca\(^{2+}\) ions in water on the expansion of sodium bentonite. (A) Water contains no ions, bentonite expands freely. (B) Calcium in the water can displace sodium and increase the bonding between bentonite platelets so that the expansion is reduced.](imageURL)
class mineral montmorillonite. The ideal chemical formula for montmorillonite is generally given as:

\[(\text{Na}, \text{Ca})_{0.33}(\text{Al}_{1.67}, \text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}\]

The crystalline structure of bentonite is extensively discussed in the literature (Grim, 1968) and consists of highly stable three-layer aluminosilicate platelets that are loosely held together by electrostatic forces. Isomorphic substitution of \(\text{Al}^{3+}\) by \(\text{Mg}^{2+}\) within the platelets 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 allows water to be absorbed between the layers of the crystal, causing it to expand upon wetting (Ripke and Kawatra, 2000c).

Bentonite increases dry strength of iron ore pellets in two ways. First, it provides a source of colloidal material that decreases interparticle distances, and thus increases van der Waals 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; Wilson, 1980). The mechanisms of bentonite bonding have been examined elsewhere (Ripke and Kawatra, 2000a,b; Kawatra and Ripke, 2001, 2002), and a novel bentonite-bonding mechanism has been identified (Ripke and Kawatra, 2000c), which can be summarized as follows: when bentonite clay is moistened, it begins expanding and the electrostatic attraction 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. When a combination of compression and shear forces are applied, the platelets that make up the clay particles slide to form fibers and sheets over the surface of the material being bonded. It should be noted that the platelets themselves do not deform or alter, it is simply their association with each other that is altered. Utilization of this mechanism allowed the dry pellet compressive strengths to be doubled at a constant bentonite dosage, or alternatively allowed the bentonite dosages to be reduced by about half while maintaining the same strength.

In either mechanism, the bonding 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. Methods for evaluating bentonite quality focus on either directly or indirectly measuring the expandability of the bentonite.

2.2. 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 g of bentonite, expressed as a percentage of the bentonite weight.

There has been disagreement about how bentonite PWA is related to iron ore pellet strength. While visiting operating plants to determine the “state of the art”, the authors were told the following by different plant engineers:

High PWA bentonite is increasingly used for cat litter and other high-demand consumer products, and will become difficult to get. We do not yet know the quality of pellets made with low PWA bentonites

Bentonite PWA has no effect on pellet quality over the ranges of PWA that are sold for iron ore pellet binders

We have always known that there is an optimum value of PWA around 900 where pellet strength is highest. When PWA is above 900, the pellet strength falls.

The reasons for this obvious disagreement about the importance of PWA for pellet strength are not yet known, but it is likely that it is due to differences in water chemistry, concentrate properties, and sources of bentonite between plants.

It is important to note that as the PWA value of available bentonites has been decreasing, plant water has also been changing in most, but not all, plants. In particular, increased reuse of plant water, addition of flux, and the use of scrubbers has changed the quantities of dissolved ions in the moisture contained in the concentrate, particularly calcium and magnesium. Higher calcium ion concentrations in the concentrate moisture may alter the effectiveness of pel-
letizing bentonites independently of changes in the PWA, but these changes could be mistakenly attributed to variations in bentonite PWA.

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

It is interesting to note that the rate at which bentonite absorbs water is not necessarily related to the total amount of water that it can absorb over a long period of time. For example, Fig. 2 compares a sodium bentonite to a calcium bentonite. While the sodium bentonite absorbed more total water at very long times, the calcium bentonite initially absorbed water faster. This is important for iron ore pelletization, because the bentonite is added to the ore concentrate only a few minutes before the pellets are made, and the ability to absorb water quickly can be as important as the total amount of water that could ultimately be absorbed.

2.3. 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 Fig. 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 the bentonite binder from 5.3 kg/metric ton (12 lb/long ton) to 6.7 kg/metric ton (15 lb/long ton), a 26% increase in dosage (Engesser, 2000a).

However, not all investigators agree on the importance of water chemistry for bentonite performance in pelleting. 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 for the ore and bentonite examined, “washing had no effect to a slight negative influence on the bentonite effectiveness (CCI-CMSC, 1994)”. The report also showed a particular instance where there was a very large negative effect from washing the concentrate. Bentonite effectiveness was measured by wet-knock and wet and dry compressive strengths of the pellets. In the CCI-CMSC (1994) study, 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. In contrast, a similar study discussed in the same report stated that “recent correlation work at LTVSMC (LTV Steel Mining Company) has shown that bentonite consumption is affected by water hardness” and that soda ash addition (which softens water by precipitating dissolved calcium ions as calcium carbonate) was able to reduce bentonite consumption.

The limitation in each of these previous studies was that they each used only a single bentonite. The bentonites used by each investigator obviously differed in their responses to dissolved calcium and magnesium in the water, leading to conflicting results. In order to resolve the conflict, it was necessary to examine multiple bentonites in a single study. In the study reported here, eight different bentonites were obtained to determine the range of responses to water hardness that could be expected from bentonite.

This study was therefore conducted to answer the following fundamental questions:

1. What effects lead to increased bonding strength when bentonite is mixed with a substrate by compressive shear mixing?
2. Does the water chemistry in iron ore pelletization plants significantly affect the pellet strength?
3. How much do the effects of water chemistry vary between bentonites?

3. Experimental

3.1. Materials

Glass shot was used as a substrate to make strength specimens to examine the effects of roll pressing on the mixing and distribution of bentonite. This was selected because it was a uniform, smooth material composed of spherical particles with standardized sizes that would minimize uncontrolled effects of particle shape and size, and would lend itself to examination by electron microscopy. The particle size was 80% passing 121 μm with a narrow size distribution of 95% between 62 and 176 μm.

Magnetite concentrate used in the studies of the effects of water chemistry was unfluxed filter cake (pelletization feed). It was obtained from an iron ore concentrator located in the Lake Superior district of the United States. The concentrate had 10% moisture, a particle size of 80% passing 25 μm (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 E946-92, 1996). The bentonites were Na-montmorillonite-based clays that were mined from the Western United States, and which were selected to have a wide range of water absorbencies. Particle size distributions of the bentonites are shown in Table 1. The dry screen analysis gave a coarser distribution than the wet laser diffraction analysis because bentonite particles remained agglomerated when dry.

3.2. Equipment

A JEOL 35C scanning electron microscope (SEM) was used to image bentonite distributed over glass shot surfaces. The principles and capabilities of scanning electron microscopy are extensively discussed in the literature (Goldstein et al., 1992). Particle size analyses were performed with a Microtrac SRA laser diffraction unit (Leeds and Northrup Division, Allied Signal, USA). Conventional mixing was conducted with a kneader-mixer. A laboratory-scale balling drum was used to form the pellets. Drying was done in a forced air oven. Standard American Foundry Society

<table>
<thead>
<tr>
<th>ID#</th>
<th>Bentonite PWA (%)</th>
<th>Size distributions in distilled water suspension by Microtrac (μm)</th>
<th>Dry screened wt.% passing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>1</td>
<td>871</td>
<td>1.7</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td>841</td>
<td>1.7</td>
<td>4.1</td>
</tr>
<tr>
<td>3</td>
<td>758</td>
<td>1.8</td>
<td>4.8</td>
</tr>
<tr>
<td>4</td>
<td>751</td>
<td>1.5</td>
<td>4.0</td>
</tr>
<tr>
<td>5</td>
<td>717</td>
<td>1.7</td>
<td>4.7</td>
</tr>
<tr>
<td>6</td>
<td>733</td>
<td>1.6</td>
<td>4.5</td>
</tr>
<tr>
<td>7</td>
<td>556</td>
<td>1.8</td>
<td>5.3</td>
</tr>
<tr>
<td>8</td>
<td>505</td>
<td>1.6</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Dry screen analysis showing the percent passing 75 μm (200 mesh) and 45 μm (325 mesh).
(AFS) equipment was used to make and test 50.8 × 50.8-mm (2 × 2-in.) cylindrical specimens of glass shot, bentonite, and water mixtures. An Instron 4206 was used with an 8896 N (2000 lb) 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. Denver type-D laboratory rolls were used to apply the combination of compressive and shear forces that were expected to develop the bentonite into a fibrous structure.

3.3. Strength-test specimen procedure for bentonite distribution studies

Glass shot was mixed with 6% moisture and 6% bentonite with a kneader-mixer and either a mixer-muller or a roll press. Then approximately 150 g of the mixture was rammed three times in a test cylinder to produce 50.8 × 50.8 mm (2 × 2-in.) cylindrical specimens. The specimens were completely dried and then tested for compressive strength.

3.4. Pelletization procedure

The basic procedure used for forming pellets was developed by industry to closely reproduce the conditions that exist in the full-scale plant, and detailed descriptions of the procedure are given elsewhere (Kawatra and Ripke, 2001, 2002; Ripke and Kawatra, 2000a,b,c). Bentonite was added to the magnetite in a kneader-mixer and mixed at 350 rpm with a 150-rpm orbital motion for up to 5 min. Binder dosages are reported as percentage by weight of the magnetite concentrate. In addition to the standard procedure, a laboratory sized rolling mill/press was used to provide the type of shear forces that were expected to promote fiber formation. The mixed material was passed through the rolling mill up to 20 times at a moderate feedrate of 24 kg/min. One test each with a high (120 kg/min) and a low (4 kg/min) feedrate was also performed. The mixed material was delumped through a 2.4-mm (8 mesh) screen before pelletizing. A small amount of the material was then added to the pelletizing drum, rotating at 25 rpm, to create pellet “seeds”. The seeds were moistened with water mist to retain moisture content while adding additional material to enlarge them into pellets. The pellets were removed from the drum periodically and screened to control the pellet diameter. This procedure was continued until 1–2 kg (2–5 lb) of finished pellets, screened between 12.7 and 11.2 mm (1/2 × 7/16 in.) in diameter, were produced for testing. The time required for pelletization was approximately 20 min. The finished pellets were then immediately dried at 105 °C (220 °F), and held at this temperature for 20–24 h to ensure that they were completely dried. The pellets were tested using standard procedures (ASTM E382-97, 1998).

For each value reported, the mean and standard deviation were determined for 20 pellets. The error bars shown on the graphs represent the 95% confidence intervals (P95) calculated using the t-distribution, described in standard statistics texts (Dixon and Massey, 1983).

3.5. Procedure for removing the dissolved cations for studies of water chemistry effects

To flush plant water out of the concentrate and replace it with clean water, individual 3.2-kg samples of the magnetite concentrate were slurried with an equivalent weight of distilled water in an impeller mixer and then pressure filtered; this rinsing was done twice for each sample used in experiments where the plant water was replaced with distilled water. The final moisture was carefully controlled with oven drying and distilled water addition to match the original 10.2% moisture that was present in the as-received filter cake. Pellets were then made according to the previously described pelletization procedure.

3.6. Procedure for analyzing the dissolved cations

Water was extracted for analysis from the as-received concentrate by first mixing 50 g of the magnetite concentrate containing 10.2% moisture with 100 g of distilled water. This suspension was filtered to recover the water. The resulting water sample contained the cations originally present in the moisture contained in the concentrate, diluted by a factor of 20.6 by the added distilled water. The water was sent for analysis by a certified laboratory, and the 20.6 dilution factor was used to back-calculate the original concentrations of cations in the filter cake moisture.
4. Results and discussion

4.1. Bentonite fibers and roll mixing

First, a series of tests were conducted to quantitatively determine the effect of bentonite fiber development on strength. Compressive strength-test specimens were made using a combination of glass shot and bentonite, with the materials first mixed by kneader mixing followed by either processing in a mixer-muller or roll pressing. Glass shot was used in these experiments for two reasons: (1) to eliminate interferences due to variations in particle shape or other properties and (2) to provide particles with a smooth surface where bentonite could be easily distinguished on the particle surfaces by the SEM. Test specimens were made and completely dried and their compressive strengths were compared. Fig. 4 shows how mulling time compared to roll mixing on the effect of specimen strength. The conventional mixer-muller produced test specimens with strengths of about 1380 kPa (200 psi). Specimen strengths were approximately doubled to 2550 kPa (370 psi) when roll pressing was used.

Second, electron microscope images were taken of samples of the compressive strength-test specimens that are shown in Fig. 5 for each roll-pressed interval. These images show how the bentonite is distributed over the glass shot forming the fibrous network that improved the strength. It is particularly important to note that in these images, it is obvious that the glass shot was not being broken by the roll pressing operation even after passing through the rolls 20 times. This demonstrates that the changes in the binding performance of the bentonite are due to the bentonite itself, not to accumulation of fine particles from breakage of the glass shot. In one of the iron ore research laboratories in North America, a superficially similar study was carried out using high-pressure grinding rolls to process magnetite concentrate. They were successful in producing stronger pellets, but had considerable difficulty making pellet “seeds” and so they abandoned this approach. A closer examination of their work showed an important point: the objective of their high-pressure grinding rolls was to reduce the particle size of the iron ore concentrate, generate more fines, and increase the pellet strength by that means. In contrast, the studies carried out by the investigators at Michigan Technological University were specifically avoiding breakage of the substrate particles and were simply applying sufficient shear forces to develop the bentonite fibers without any further comminution.

4.2. Water chemistry in pelletization

Laboratory tests were conducted to determine if plant process water affected the strength of the magnetite pellets. Pellets that were made with standard concentrate were compared to pellets made with a
concentrate that had the plant water replaced with distilled water.

Table 2 shows the ionic concentrations measured for the following water samples:

1. Moisture extracted from the magnetite concentrate.
   The values in Table 2 are back-calculated using the dilution factor of 20.6 that was calculated for the extraction process.
2. Plant filtrate water. This is the water removed from the concentrate in the plant by vacuum filtration through disc filters and is the recycle water that is returned to the process.
3. A sample of Houghton, MI, tap water, shown for comparison.
4. Distilled water was also sent for analysis as a check on the laboratory analytical results. The concentrations of the ions were not detectable with the

<table>
<thead>
<tr>
<th>Ion</th>
<th>Mag. concentrate moisture (undiluted)</th>
<th>Plant filtrate water</th>
<th>Tap water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>5088</td>
<td>9</td>
<td>40</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5995</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td>Potassium</td>
<td>1680</td>
<td>11</td>
<td>2</td>
</tr>
<tr>
<td>Sodium</td>
<td>725</td>
<td>151</td>
<td>17</td>
</tr>
<tr>
<td>Sulfate</td>
<td>803</td>
<td>54</td>
<td>21</td>
</tr>
</tbody>
</table>

Values are reported as mg/l (ppm).
procedures used to analyze the other samples. The analysis of the distilled water is therefore not shown in the table.

The magnetite concentrate moisture is the water that remains in the concentrate after the plant filtrate water is removed by vacuum filtration. Therefore, it was expected that the ion concentrations in the magnetite concentrate moisture would be similar to the plant filtrate water. However, the results in Table 2 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 very low concentration of these cations, similar to the tap water.

The large difference between the concentrations in the recycle water and the concentrations in the concentrate moisture is believed to be due to the tendency of the positive cations to be attracted to the negatively charged surface of the magnetite concentrate, as shown in Fig. 6. This phenomenon is caused by the electric double layer in water adjacent to the mineral surface. A simplified explanation of this is that 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. Multivalent ions are more strongly influenced by this effect than monovalent ions, and as a result, the concentration factors are significantly higher for Ca\(^{+2}\) and Mg\(^{+2}\) than for K\(^{+}\) and Na\(^{+}\) (Railey, 2001).

4.3. Effects of the presence of cations on pellet strength

Having determined that the ion concentrations in the iron ore concentrate were several hundred times higher than had been expected, laboratory tests were conducted to determine if plant process water affects the strength of the magnetite pellets. Pellets that were made with standard concentrate were compared to pellets made with a concentrate that had the plant water replaced with distilled water by the procedure explained previously in the Experimental section.

4.3.1. Wet-knock strength

The wet 46-cm (18 in.) drop (wet-knock) value of an iron ore concentrate pellet is described in Table 3. 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%).

Fig. 7 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. In particular, the calcium in the concentrate moisture 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 sam-

![Fig. 6. Retention of ions by particle surfaces in the filter cake during filtration. The effect will be strongest when the surface charge of the iron ore concentrate is highly negative.](image-url)
sensitive to changes in the rheology of the wet bentonite, with wet-knock increasing as the viscosity of the bentonite increased. This would be due to the high viscosity increasing the resistance of the pellet to sudden deformation.

4.3.2. Wet compressive strength

Fig. 8 shows that each bentonite water chemistry, although it did vary between bentonites. However, there was not a direct correlation between bentonite water absorption capacity and wet pellet strength, which indicates that the relation between bentonite type and wet strength is more complex than simple variations in absorption/immobilization of different amounts of water. Changes in the bentonite rheology are expected to have a relatively small effect on the wet-crushing strength, because crushing of the wet pellets is done sufficiently slowly that rheology does not contribute significantly to resisting deformation, and the most important factor contributing to the strength is the surface tension.

4.3.3. Dry compressive strength

Fig. 9 shows that plant water was replaced with distilled water, dry compressive strength increased an average of 46%. 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 there was no dissolved calcium present to convert the bentonite to a less active form. The bentonites could therefore expand more fully 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 effectively bonded the magnetite concentrate, resulting in higher compressive strength pellets.

It is important to note that some bentonites were much more affected by the presence of calcium ions than others. This large variation in the response of bentonite to the presence of dissolved cations resolves the disagreement in the literature and among plant operators of whether iron ore concentrate pellet strength is affected by the plant water. It was important to have studied multiple bentonite samples. As shown in Fig. 9, pellets made with some of the bentonites were significantly stronger when the water in the filter cake was replaced with distilled water, while pellets made using other bentonites were not. Previous studies presented in the literature were conducted with single bentonite specimens, and so were not accounting for the significant variations between bentonites.

The reasons for the differences in calcium ion sensitivity between bentonites are not yet known. It is believed that the sensitivity depends on properties such as the magnitude of the charge on platelets, which varies with the degree of substitution of Mg for Al in the montmorillonite crystal lattice. The nature of the exchangeable cations originally present in the bentonite may also have an effect.

Since the experiments were conducted using bentonites with PWA values ranging from 505% to 871%, it is also possible to see whether the PWA correlates with any of the measured pellet properties. It is immediately obvious that neither the wet-knock values nor the wet-crush values correlate well with the PWA, either using the as-received concentrate or the concentrate rinsed with distilled water. In the case of the dry-crush values, there is no particular trend with the as-received concentrate, but the rinsed concentrate shows a steady increase in pellet strength as the PWA increases up to approximately 750%. After this point, the strength remains constant as the PWA continues to increase.

5. Conclusions

The binding of iron oxide grains by bentonite clay to form pellets is a complex process, with a large number of variables, many of which have never been adequately examined or even considered in past investigations. This has introduced many problems in attempts to understand the behavior of bentonite in the pelletization process, because much of the theory of bentonite binding suffers from a lack of data, and this lack of data is often not realized by the investigators developing the theories. This has lead to much confusion and apparently contradictory results in the published literature. In particular, three factors have been neglected: (1) The effects of the method of applying mixing forces to the iron ore/bentonite/water mixture. In the past, only the total quantity of energy has been considered, not the manner in which the energy is applied. (2) The influences of the water chemistry of the moisture contained in the filter cake. It is not sufficiently appreciated that due to ion-exchange effects between the iron oxide surfaces and the liquid, the quantity of ions that is retained in the filter cake moisture can be very much higher than what remains in the water removed by the filters, and as a result, the bentonite can be much more strongly affected by the water chemistry than would be expected by simple analysis of the bulk plant water. (3) The differences in behavior between different
Bentonites are not completely predictable simply from measurements of water absorption capacity. Other bentonite properties, which are as yet poorly understood, have a strong influence on the binding strength of a given bentonite and on its sensitivity to dissolved ions in the water. In their efforts to understand the influences of these neglected factors on pelletization performance, the authors have collected a great deal of data that was not previously available and have reached the following conclusions.

- It was determined that mixing glass shot with bentonite using a roll press resulted in superior strengths compared to mixing the same material with a conventional mixer-muller. The higher strengths achieved with the roll press are due to the application of shear stresses that appear to develop the bentonite particles into a “fibrous” structure that provides superior bonding. It is important to note that these fibers are composed of normal clay platelets, which have slipped relative to one another so that grains composed of these platelets are drawn out in one dimension, spreading the platelets without ever forcing them to fully lose mechanical contact with their neighbors. The highly stable silica tetrahedra and alumina octahedra that make up the three-layer platelets are in no way altered by this mechanism. Examination of the bentonite-bonded glass shot by electron microscopy confirmed the fibrous spreading of the roll-pressed bentonite platelets over the particle surfaces and also showed that the roll press was not comminuting the glass shot substrate to a finer size. The lack of comminution of the glass shot confirms that the increased strength of the test specimens was due to better utilization of the bentonite, not to accumulation of fines from broken substrate particles.

- The negative surface charge of magnetite surfaces in suspension under normal processing conditions tends to preferentially attract cations to the particle surface. This results in a much higher concentration of cations in the moisture retained in the filter cake than was present in the plant recycle water. When water was extracted from the filter cake and analyzed, it was determined to contain approximately 500 times as much Ca\(^{+2}\) as would have been expected from the concentrations in the recycle water. Calcium is known to decrease the effectiveness of sodium bentonites, and so this high concentration of cations will have a strong influence on the performance of a given bentonite. This is of crucial importance because all past studies of water chemistry on bentonite-binding performance have assumed that the relevant ion concentrations were those that were measured in the water that was filtered out of the iron ore concentrates, when the actual concentrations that must be considered are those that remain in the concentrate after it is filtered. Theories of bentonite binding that do not take this effect into account are therefore seriously flawed and must be corrected.

- Seven different bentonites were used to make magnetite concentrate pellets, using both as-received concentrate and concentrate that had been flushed with distilled water to remove the excess cations. It was determined that for all the bentonites, the wet-drop number and the dry compressive strength were higher using the flushed concentrate than using the as-received concentrate. This difference was due to the presence of calcium ions in the as-received concentrate, which degraded the bentonite performance in ways that are not yet entirely clear. Interestingly, not all of the bentonites were affected to the same degree by the presence of the cations in the as-received concentrate. Some bentonites showed only a slight difference in performance when the ions were removed from the concentrate, while others changed performance dramatically under the same conditions. This accounts for the conflicting reports in the literature concerning the effects of cations on bentonite-bonding performance. Some investigators were obviously using bentonites that were minimally affected by Ca\(^{+2}\), while others were using bentonites that were more strongly affected. These differences in calcium ion sensitivity were emphatically not directly related to the water-absorption capacity of the bentonites in question. There are obviously other factors controlling ion sensitivity that remain to be determined, and it is critically important to determine these factors.

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