SINTERING OF MAGNETITE PELLETS UNDER CARBON MONOXIDE

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ABSTRACT

Iron ore concentrates pellets are currently induration heat hardened (sintered) under oxidizing conditions. Pellets produced from magnetite ore concentrate are completely oxidized during induration and finish as hematite pellets. These pellets then require a blast furnace to reduce the hematite to metallic pig iron. Partially reduced pellets would save energy and fuel during transportation and further reduction. It has been stated in the literature "the most important single factor responsible for the development of strength in fired magnetite pellets containing no additive is the oxidation of the magnetite to hematite and the subsequent recrystallization and grain growth of this constituent." However experiments shown in this paper reveal that oxidation is not necessary to produce high-strength pellets. Magnetite concentrate pellets developed similar strength when indurated at 1350°C under either oxidizing (air) or inert (argon) atmosphere; the pellets sintered under argon remained magnetite. In addition, magnetite concentrate pellets indurated under reducing (CO) atmosphere also remained as magnetite, but required induration temperature of approximately 150°C less than the other pellets.

INTRODUCTION

In the United States during 2000, virtually all of the 61 million metric tons of iron ore produced for the U. S. iron and steel industry was pelletized (Kirk, 2001). These iron ore pellets are induration heat hardened to provide them with sufficient strength for handling, transportation, and smelting in a blast furnace. Currently, iron ore pellets are heat hardened to obtain the final strength necessary to survive handling, transportation, and the compressive forces from loading in the blast furnace. The hardening process is done within an air atmosphere and the pellets are oxidized. Oxidation is counterproductive because the pellets must be reduced to metal to make the iron.

It is difficult to predict how ironmaking and steelmaking will evolve. The probability that new blast furnaces will be built in the U.S. is very remote. One likely direction is the use of a high performance partially-reduced "superpellet" feed produced from iron ore concentrates. Such a feed may improve blast furnace efficiency or lend itself to alternative uses such as mini-mill processing or as a cupola feed. The first step for evaluating such a pellet is to make the pellets and measure their compressive strengths. An acceptable compressive strength is needed to allow the pellets to remain intact during handling, shipping, and further processing into iron.

Indurated strength

Iron ore pellets are oxidation heat hardened to obtain the final strength necessary to survive transportation and the forces within the blast furnace. Currently, there are understood to be three potential binding mechanisms that occur during the heat hardening or sintering of iron ore pellets.

Slag bonding

The remaining silicate gangue in the iron ore concentrate and the binder that is added can melt during heat hardening. When the pellets are cooled, this slag can solidify and bond. Bonding by slag formation occurs when a glassy melt of gangue and/or binder forms a matrix in which the crystalline constituents are partially or completely embedded. Some slag bonding can be beneficial, while too much can weaken the pellet because the slag bond is weaker than the sinter or recrystallization bond.

Sintering

Sintering occurs at the particle:particle contact points between combinations of the bentonite, magnetite, and silica gangue particles (e.g. bentonite:bentonite, bentonite:magnetite, and magnetite:magnetite particle contact points). There is a thermodynamic driving force to reduce the total particle surface area because surface area energies are greater in magnitude than grain boundary energies. The mass transport occurs by atomic diffusion. This is related to the process of recrystallization in the solid state.

Recrystallization

The following is an interesting quotation from literature that summarizes previous publications and states the current understanding of indurated strengthening mechanisms:

It has been concluded that the most important single factor responsible for the development in strength in fired magnetite pellets containing no additive is the oxidation of the magnetite to hematite and the subsequent recrystallization and grain growth of this constituent. (Callender, 1962)

The purpose of this paper was to answer the following question. Is it necessary to oxidize the pellets to achieve acceptable strengths, as it is stated in the previous quotation? In this paper, experiments were designed and conducted to answer this question.
EXPERIMENTAL

Materials

Magnetite concentrate for these experiments 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.

The bentonite binder was a Na-montmorillonite based clay that was mined from the Western United States. It was obtained from the American Colloid Company and designated SPV 200; it had a plate water absorbance (PWA) of 706 (ASTM E946, 1996), and a particle size of 85% passing 74 microns (200 mesh). Particle size analyses were performed by laser diffraction. The chemical analysis for the bentonite is shown in Table I.

Equipment

A kneader-mixer was used to mix the concentrate with binder. A laboratory-scale balling drum, was used to form the pellets. Pellets were dried in a forced-air drying oven and sintered in a high temperature laboratory tube furnace shown schematically in Figure 2. 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. Twenty pellets were used for each test. Iron assays were done by hot hydrochloric acid digestion and titration. Phases were determined by x-ray diffraction. The chemical analysis for the bentonite is shown in Table I.

Pelletization Procedure

The procedure used for forming pellets was developed by industry to closely reproduce the conditions that exist in the full-scale plant. This procedure was selected so that scale-up could be streamlined. 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 minutes. Binder dosages are reported as percentages that are by weight of moist magnetite concentrate. The mixed material was delumped through an 2.4 mm (8 mesh) screen before pelletizing. A small amount of the material was then added to the pelleting 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 mm and 11.2 mm (1/2 x 7/16 inch) in diameter were produced for testing. The time required for pelletization was approximately 20 minutes. The finished pellets were then immediately dried at 105°C (220°F), and held at this temperature for 20 to 24 hours to ensure that they were completely dried. The pellets were induration heat hardened in a high temperature laboratory tube furnace at temperatures up to 1350°C. The pellets were tested using the procedures given in Table I. This procedure used by industry is essentially equal to the ASTM standard (ASTM E382, 1996).

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).

Induration Procedure

Dry Iron ore pellets were put in an alumina crucible which was suspended by a molybdenum wire in a Thermolyne 54500 high temperature molybdenum disilicide resistance tube furnace. The tube furnace can reach temperatures up to 1700°C. Compressed breathing air, Argon (99.999%), and carbon monoxide gas were used as the process gas to indurate the iron ore pellets under oxidizing, inert, and reducing atmospheres, respectively. Before entering the furnace, the gas traveled through heated copper filings to remove any contained oxygen (except for the compressed breathing air) and then through a column of drierite (97% CaSO4, 3% CoCl2) to eliminate moisture.

RESULTS

Experiments were designed to determine whether pellets could be induration heat-hardened under a non-oxidizing or reducing atmosphere and achieve acceptable compressive strengths.
Table II: Descriptions of the tests used for evaluating pellet quality.

<table>
<thead>
<tr>
<th>Test</th>
<th>Procedure and use of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet- knock</td>
<td>A single freshly-made (undried) pellet was dropped repeatedly from a height of 18 inches onto a steel plate. The number of drops required for fracture was recorded. This was repeated for 20 pellets, and the results averaged. Measures the ability of the wet pellet to remain intact during handling.</td>
</tr>
<tr>
<td>Wet- crush</td>
<td>A single (undried) pellet was compressed using an Instron compression test machine with a cross-head speed of 40 mm/min. The load required to fracture the pellet was recorded. This was repeated for 20 pellets, and the results averaged. Measures the ability of the wet pellets to retain their shape during handling.</td>
</tr>
<tr>
<td>Dry- crush</td>
<td>Pellets were dried at 105°C (221°F) for at least 1 hour; single pellets were then compressed using an Instron compression test machine. The load required to fracture the pellet was recorded. This was repeated for 20 pellets, and the results averaged. Measures the ability of dried pellets to survive handling during the firing process. Should be at least 22 newtons (5 pounds force) per pellet. This is the most critical measurement.</td>
</tr>
<tr>
<td>Fired- crush</td>
<td>Pellets were sintered in a crucible by pre-heating at 120°C/min to 1200°C, held for another 10 minutes, and then air cooled. Individual pellets were then compression tested with an Instron compression testing machine. The peak load required to fracture the pellet was recorded. This was repeated for 20 pellets, and the results averaged. Measures the ability of dried pellets to survive handling during shipment and reduction. Should be at least 1779 newtons (400 lbf) per pellet.</td>
</tr>
</tbody>
</table>

Figure 2. X-ray diffraction of the pellets sintered under carbon monoxide at A) 1000°C and B) 1100°C. These pellets remained magnetite and were not oxidized to hematite. Copper Kα radiation was used. Peaks are shown at the 2-theta angle and identified as: M = magnetite (Fe₃O₄) and F = Fayalite (Fe₂SiO₄).

Figure 3. X-ray diffraction of the pellets sintered under carbon monoxide at A) 1200°C. These pellets remained magnetite and were not oxidized to hematite. At B) 1350°C the pellets were oxidized to hematite. Since the magnetite pellets could not have oxidized to hematite under the carbon monoxide (reducing) atmosphere, the pellets must have been reduced from magnetite to wustite which then oxidized to hematite when the pellets were removed from the furnace. Copper Kα radiation was used. Peaks are shown at the 2-theta angle and identified as: M = magnetite (Fe₃O₄), H = Hematite (Fe₂O₃), and F = Fayalite (Fe₂SiO₄).
Figure 4. Strength of iron ore concentrate pellets indurated under oxidizing (air), inert (Argon), and reducing (carbon monoxide) gaseous atmospheres. $T_{\text{final}}$ ($T_f$) is the maximum temperature at which the pellets were indurated. The dashed line represents the minimum industrially acceptable strength of 1779 newtons (400 lbf).

Table III: Pellet sintering experiments within a tube furnace.

<table>
<thead>
<tr>
<th>Step</th>
<th>Bentonite,%</th>
<th>Atm.</th>
<th>$T_{\text{final}}$ $^\circ$C</th>
<th>Strength, newtons $+/\cdot P_{95}$</th>
<th>Strength, lbf $+/\cdot P_{95}$</th>
<th>Iron assay</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>Ar</td>
<td>1350</td>
<td>2941$+/\cdot 360$</td>
<td>661$+/\cdot 81$</td>
<td>not measured</td>
<td>acceptable strengths</td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>Ar</td>
<td>1350</td>
<td>2740$+/\cdot 338$</td>
<td>616$+/\cdot 76$</td>
<td>not measured</td>
<td>acceptable strengths</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>Ar</td>
<td>1350</td>
<td>3020$+/\cdot 334$</td>
<td>679$+/\cdot 75$</td>
<td>not measured</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>Air</td>
<td>1350</td>
<td>2780$+/\cdot 369$</td>
<td>625$+/\cdot 83$</td>
<td>62.9%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>Air</td>
<td>1350</td>
<td>3193$+/\cdot 538$</td>
<td>718$+/\cdot 121$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.66</td>
<td>CO</td>
<td>1350</td>
<td>not measured</td>
<td>not measured</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.66</td>
<td>CO</td>
<td>1000</td>
<td>445$+/\cdot 44$</td>
<td>100$+/\cdot 10$</td>
<td></td>
<td>too weak, $T_f$ too low</td>
</tr>
<tr>
<td>4</td>
<td>0.66</td>
<td>CO</td>
<td>1100</td>
<td>1148$+/\cdot 222$</td>
<td>258$+/\cdot 50$</td>
<td></td>
<td>too weak, $T_f$ too low</td>
</tr>
<tr>
<td>5</td>
<td>0.66</td>
<td>CO</td>
<td>1200</td>
<td>2500$+/\cdot 160$</td>
<td>562$+/\cdot 36$</td>
<td></td>
<td>acceptable strengths</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>CO</td>
<td>1200</td>
<td>2309$+/\cdot 351$</td>
<td>519$+/\cdot 79$</td>
<td>68.4%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>CO</td>
<td>1200</td>
<td>2438$+/\cdot 262$</td>
<td>548$+/\cdot 59$</td>
<td>not measured</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.66</td>
<td>Air</td>
<td>1200</td>
<td>1165$+/\cdot 231$</td>
<td>262$+/\cdot 52$</td>
<td></td>
<td>too weak, $T_f$ too low for air</td>
</tr>
</tbody>
</table>
First, dry iron ore concentrate pellets were made at three different dosages: 0%, 0.33% (7 lb/t concentrate), and 0.66% (14 lb/t concentrate). Then, the pellets were indurated under different atmospheres of argon (inert), air (oxidizing), and CO (reducing) atmosphere. The following temperature profile was used:

\[ \text{T(room)} \rightarrow \text{800°C @ 15°C/min.; \hspace{1cm} 800°C \rightarrow T(\text{final}) \ (1350°C) @ 5°C/min.} \]

\[ \hspace{1cm} \text{Cooling: 1350°C \rightarrow 500°C @ 20°C/min.} \]

After heat hardening in the furnace, the pellets were tested for compressive strength with an Instron.

The results shown in Figure 4 and Table III are explained as follows:

Step 1: Compare the strength of iron ore concentrate pellets indurated under air with pellets indurated under Argon at 1350°C maximum temperature. From the literature, recrystallization from magnetite to hematite was considered important to achieve high strength. Magnetite pellets indurated under Argon can not oxidize into hematite. Therefore, it was expected that the pellets indurated under Argon would not be as strong as the pellets indurated under air. However, Figure shows that they were just as strong. X-ray diffraction was conducted on pulverized powder samples of the pellets, without binder, confirming that the pellets indurated under air were oxidized into hematite, while the pellets indurated under Argon were not oxidized and remained magnetite. The percent iron in the pellets without binder is shown in Table .

Step 2: Compare the strength of iron ore concentrate pellets indurated under carbon monoxide reducing atmosphere with the pellets that were indurated under air and Argon. These pellets had a typical 0.66% bentonite dosage.

The pellets indurated at 1350°C under carbon monoxide fused to each other and to the crucible. The pellets were very porous and looked like sponge iron. The pellets that were able to be removed were strength tested and they were weak, well below the minimum industrially acceptable strength of 400 lbf/force. Since there were not enough of these pellets to properly measure, their strengths are not reported. It was hypothesized that the final temperature was too high and the experiments were redesigned to use a lower final heating temperature.

Step 3: Since the pellets indurated under carbon monoxide at 1350°C had fused together, it was determined that the induration temperature was too high. Therefore, the maximum temperature was reduced to 1000°C for this experiment. The pellets remained intact and did not fuse or melt. However, the pellets had insufficient strength so the maximum induration temperature was increased by 100°C to 1100°C for the next experiment.

Step 4: Pellets with 0.66% bentonite indurated under carbon monoxide were stronger at 1100°C than at 1000°C, but they still had insufficient strength. Therefore, the maximum induration temperature was increased by another 100°C to 1200°C.

Step 5: Pellets with 0.66% bentonite were indurated under carbon monoxide at 1200°C and achieved acceptable strengths. Pellets at 0% and 0.33% bentonite were also indurated at 1200°C for comparison. The results from steps 3, 4, and 5 show that the strength of magnetite concentrate pellets indurated under carbon monoxide is related to the maximum induration temperature. Acceptable strength pellets were produced under carbon monoxide at a maximum sintering temperature that was 150°C less than when they were sintered under an air or Argon atmosphere. This is important, but in order to compare the absolute effect, pellets must be indurated with the same temperature profile to the same maximum temperature of 1200°C, but under air atmosphere. Figure 2 and Figure 3 show x-ray diffraction patterns from pulverized powder samples of the pellets with no binder, confirming that the pellets indurated under carbon monoxide remained magnetite.

Step 6: Compare the strength of iron ore concentrate pellets indurated at 1200°C under air to pellets indurated at 1200°C under carbon monoxide.

Reducing the maximum induration temperature of pellets indurated under air by 150°C from 1350°C to 1200°C significantly reduced the pellet strength by 1855 newtons (417 lbf) to an unacceptable strength of 1165 newtons (262 lbf). These result shows that it is necessary to indurate pellets under air at a higher maximum temperature than pellets indurated under carbon monoxide to achieve acceptable pellet strengths above 1779 newtons (400 lbf).

Acceptable pellet strength was obtained regardless of which of these three atmospheres was selected. These results show that it is possible to produce a non-oxidized or partially-reduced pellet that exceeds the industrial strength requirements for use in a blast furnace.

CONCLUSIONS

• Iron ore concentrate pellets indurated (sintered) under an oxidizing (air), inert (argon), or reducing (carbon monoxide) atmosphere had acceptable strengths exceeding 1779 newtons (400 lbf). Oxidation was not necessary to produce high-strength pellets.

• Pellets indurated under air oxidized to hematite.

• Pellets indurated under argon remained magnetite.

• Pellets indurated under reducing (CO) atmosphere also remained magnetite and only required an induration temperature of 1200°C, approximately 150°C less than the other pellets.

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REFERENCES


