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Cold Bonding of Iron Ore Concentrate Pellets

JOSEPH A. HALT, SAMUEL C. ROACHE, and S. KOMAR KAWATRA

Department of Chemical Engineering, Michigan Technological University, Houghton, Michigan, USA

Iron ore concentrate pellets are traditionally hardened at high temperatures in horizontal grates and grate-kiln furnaces. However, heat induration requires tremendous quantities of energy to produce high-quality pellets, and is consequently expensive. Cold bonding is a low-temperature alternative to heat induration. Pellets can be cold bonded using lime, cement, sponge iron powder, and organic materials such as starch and flour. Cold bonding consumes less energy than heat induration, and has found favor for bonding self-reducing pellets and for refractory ores that are difficult to heat-treat. Herein, we review the principal cold bonding methods and their fundamentals.

Keywords: agglomeration, cold bonding, iron ore, pelletization

Introduction

Iron ore concentrate pellets are traditionally hardened (indurated) at high temperatures in horizontal grates and grate-kiln furnaces. Firing temperatures generally range from 1200–1350°C. Shaft furnaces are also used, but their pelletizing capacity is low. While heat induration produces pellets with the physical and metallurgical properties required by blast furnaces, they require tremendous quantities of energy to do so. Reported figures for energy consumption during heat induration of magnetite concentrates range from 700,000 btu/t pellets (Haley and Apuli 1961) to 300,000–450,000 btu/t pellets (U.S. DOE 2013). The latter values were achieved by installing better heat recovery systems on induration furnaces. Energy consumption for nonmagnetite ores will be higher due to the absence of exothermic, oxidation reactions.

Cold bonding is a low-temperature alternative to heat induration. Cold bonded pellets are usually hardened at temperatures lower than 300°C. Different processes can be used to harden cold bond pellets, but most involve chemical reactions that form new phases among the iron bearing grains in the pellet. Cold bonding methods consume less energy than heat induration, and can effectively bond refractory (heat resistant) concentrates, can bond self-reducing pellets that would burn during heat induration, and can bond mixed wastes from iron and steel-making operations. Herein, we review the major types of cold bonding and their fundamentals, and contrast cold bonding with traditional heat induration.

Carbonate Bonding

During carbonate bonding, iron ore concentrates are mixed with hydrated or “slaked” lime, pelletized, and reacted with carbon dioxide, as shown in Equation (1).

$$\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$  (1)

Carbonation usually occurs under flowing CO$_2$-rich streams. The CO$_2$ content in air is quite low (approximately 400 ppm) so under ambient conditions, calcium carbonate
formation is negligible. Sah and Dutta (2010) reported complete carbonation after applying a CO₂ stream of 1500 cc/min for 4–8 min, while Franklin, Guseman, and Pelczarski (1965) reportedly carbonated the pellets for 30 minutes. Schulte (1972) used exhaust gases from pellet reduction (15%–20% CO₂, 90–150°C) to carbonate pellets for 90 min. Miyashita et al. (1987) used a carbonation gas containing 5%–95% CO₂ and 5%–95% saturated steam. If the carbonation gas contained less than 5% CO₂, calcium carbonate formation was insufficient to strengthen pellets. They applied the carbonation gas for nine hours.

Various additives increase the efficacy of carbonate bonding. The additives increase lime solubility or increase CO₂ hydration rates. Molasses, dextrose, and sugar can be used to catalyze calcium carbonate formation (Imperato 1969; Srb and Ruzickova 1988; Sah and Dutta 2010). The catalyst reactions are shown in Equations (2) and (3) using sucrose as the catalyst.

\[
\text{Ca(OH)}_2 + \text{Sucrose (sugar)} \rightarrow \text{Calcium saccharate} + \text{H}_2\text{O} \\
\text{(2)}
\]

\[
\text{Calcium saccharate} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{Sucrose (sugar)} \\
\text{(3)}
\]

The lime and sucrose form a viscous colloidal complex or gel that aids calcium carbonate formation. Imperato (1969) used calcium chloride (CaCl₂), and sodium hydroxide (NaOH) to increase the solubility of lime. Franklin, Guseman, and Pelczarski (1965) used sodium tetraborate (borax/Na₂B₄O₇•10H₂O) to catalyze the hydration of CO₂ in the pellet moisture. Hassler and Kihlstedt (1977) report a variation on carbonate bonding, where lime is substituted with water glass (sodium silicate). Upon treatment with CO₂, a silica gel precipitates and strengthens the agglomerate. The sodium silicate/carbon dioxide bonding process has been used in foundries for core-making.

**Cement Bonding**

Cement is an effective cold bonding binder that is easy to use. Moist iron ore concentrate is mixed with cement, agglomerated into balls or pellets and cured. Pellets harden during the curing process as the cementitious minerals in the cement hydrate or react with water. See Table 1 for typical pellet strengths using cement binders. The curing process can be conducted under ambient conditions, requiring an extended hardening time, or in a humid environment. Variations in the cement curing environment have led to a number of industrial cold bonding processes, such as the Grangcold and Chor processes (described in Goksel 1977). The cement type or composition can also be varied to affect the curing time and eventual pellet strength. Portland cement, cement clinker, iron and steelmaking slags, or any materials which supply the hydraulic minerals necessary for the hydration reactions to occur, can be used as cement binders (Dutta et al. 1992).

Cement hardening occurs due to hydration reactions. Figure 1 shows a simplified representation of the hydration reaction.

**Table 1. General comparison of cold bonding processes**

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Additive/Dose</th>
<th>Pellet strengths</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonate</td>
<td>Slaked lime/1–10%</td>
<td>30–450 lb/pellet</td>
<td>Elevated CO₂ partial pressure in curing gas.</td>
</tr>
<tr>
<td>Cement</td>
<td>Portland cement/9–12%</td>
<td>280–400 lb/pellet</td>
<td>28 day air cure or steam cure to reduce time to 4 h to 4 day.</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>Slaked lime/5–7% Fine silica/1–3%</td>
<td>250–600 lb/pellet</td>
<td>Pressurized autoclave (10–300 psig).</td>
</tr>
<tr>
<td>Rust</td>
<td>Sponge iron powder/2–8%</td>
<td>20–110 lb/pellet</td>
<td></td>
</tr>
<tr>
<td>Organic</td>
<td>Starch/3–7%</td>
<td>&gt;300 lb/pellet</td>
<td>a: 10–20% coal</td>
</tr>
<tr>
<td></td>
<td>Starch/0.5–1.5%</td>
<td>20–45 lb/pellet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dextrin/3–4%</td>
<td>60–100 lb/pellet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lignosulfonate/1%</td>
<td>&gt;5 lb/pellet</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Funa/1.5%</td>
<td>60 lb/pellet</td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 1. Progression of cement bonding and pellet hardening by mineral hydration. (a) Moist mixture of magnetite (Fe₃O₄) and calcium silicate and aluminate cement particles; (b) cement particles dissolve and react with water to form a hydration layer of calcium silicate hydrates, designated C-S-H, that precipitate onto undissolved particles; (c) particles with slower dissolution and reaction rates begin reacting; and (d) as the hydration reactions progress to completion, particles are mortared together and pellet strength increases.](image-url)
product precipitation and growth occurring inside of the pellet. Principally, calcium aluminates and silicates dissolve and react with water to form hydrated minerals. Hydrated mineral products precipitate onto undissolved particles. As the hydration reactions progress, pellet strength increases. These are very complicated reactions that depend on the cement chemistry. For Portland cement, Takano and Mourão (2003) present the most important reactions to be

\[ 2 \text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{CH} \]  
\[ 2 \text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{CH} \]

where \( \text{C}=\text{CaO}, \text{S}=\text{SiO}_2, \) and \( \text{H}=\text{H}_2\text{O} \). Equations (4) and (5) describe how tricalcium silicate (\( \text{C}_3\text{S} \)) and dicalcium silicate (\( \text{C}_2\text{S} \)) hydrate to form a calcium-silicate-hydrate gel. \( \text{Ca(OH)}_2 \) is also generated during both reactions, and can be carbonated to produce additional bonds (Liu 2011). Tricalcium silicate and calcium aluminates react quickly and are responsible for the initial pellet hardening, while the slower dicalcium silicate hydration reaction gives the pellet its final strength after a long cure (Takano and Mourão 2003).

Although pellets develop sufficient cold strength using Portland cement binder, the cement reaction products decompose at temperatures exceeding 480–650°C (Takano and Mourão 2003; Robinson 2005). This may weaken pellets during the reduction process. Pellet weakening can be counteracted in blast furnaces, where temperatures are high enough for sintering to occur, but in some direct reduction furnaces, pellet will remain weak and friable and generate fines and dust. A potential solution may be to replace calcium silicate cements with high alumina cements (Aota and Morin 2004; Aota et al. 2006).

In a direct comparison with Portland cement, pellets bonded with calcium aluminate cement showed a 6% loss in strength from 500–800°C, while Portland cement bonded pellets lost 60% of their strength over the same temperature range (Aota et al. 2006). The authors report that alumina cements are used in the high-temperature ceramic industry, and should be investigated further for use as a cold bonding pellet binder.

Pellets can be cured under ambient conditions, which requires 5–30 days for pellet strengths to reach necessary levels, or under humid, warm environments for a more rapid set. Elevated temperatures alone can accelerate curing, but the reactions are more rapid in the presence of steam: steam-cured pellets have lower porosity and higher hydration levels than air cured pellets (Dutta et al. 1992). Contrucci and Marcheze (2003) reported a continuous rapid curing process where pellets are partially dried at 80–180°C, cured under saturated vapor at 70–110°C and completely dried at 80–180°C. Curing takes 4–12 h to complete. Liu (2011) reported a curing process using a humid, CO₂-rich (10% CO₂) gas at 100–300°C. The curing process takes 24–96 h to complete.

Longer curing cycles can also be reduced by adding excess cement binder (Takano and Mourão 2003). For cement doses ranging from 6% to 8%, increasing the curing period from 7 to 30 days significantly increased pellet strengths. At a cement dose of 10%, pellet strength was not as sensitive to cure time.

**Hydrothermal Bonding**

A number of cold bonding processes (MTU and COBO) use autoclaves to bond pellets containing lime and silica-rich materials. These are called “hydrothermal” cold bonding processes (Goksel 1977; Hassler and Kihlstedt 1977). Figure 2 shows a flow diagram describing the MTU hydrothermal cold bonding process. The MTU process is similar to the COBO process.

To complete hydrothermal bonding, moist iron oxide, burnt lime (CaO) or slaked lime (Ca(OH)₂), fine silica powder, and a reducing agent are mixed together. The mixture must be aged if burnt lime is used instead of slaked lime. The mixture is ballasted or agglomerated into pellets, partially dried, and pellets are fed into an autoclave. Pellets are cured in the autoclave at 300 psig and 220°C for 1 h.

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**Fig. 2.** MTU hydrothermal cold bonding process flow diagram (after Goksel and French 1979).
Cold Bonding of Iron Ore Concentrate Pellets

Under the hydrothermal conditions in the autoclave, minerals partially dissolve and react to form gels and hydration products with no reported crystalline structure (Goksel 1977). The reaction products precipitate out onto undissolved particle surfaces and bind the pellets together. As indicated in Figure 2, blast furnace quality pellets can be produced using the hydrothermal process (Goksel and French 1979). Typical pellet strengths obtained using hydrothermal bonds are shown in Table 1.

The partial drying process is common to both the MTU and COBO process. Partial drying is recommended in order to decrease heating time in the autoclave; minimize occurrences of thermal shock that causes pellet cracking and breakage; and increase heat transport in the pellets due to unfilled pores (Goksel, 1977; Hassler and Kihlstedt, 1977).

One drawback to the high-pressure autoclave is that it is a batch operation and is subject to mechanical problems (Eisele and Kawatra 2003). Lower pressures can be used to harden pellets, so long as pellets are cured for longer periods of time (Goksel 1977). In the large quantities used, the lime-silica binding materials may strengthen pellets even without a pressurized curing cycle due to their natural pozzolanic activity. Pozzolanic fly ashes with high calcium contents have been used to effectively bond iron ore concentrate pellets (Kawatra et al. 1998; Ripke and Kawatra 2000).

**Rust Bonding**

Sponge iron powder has been used to cold bond pellets made from magnetite concentrates (Xilun 1980, 1983). In the presence of pellet moisture and magnetite particles, the iron powder electrochemically corrodes, and the corrosion products cement particles together and harden the agglomerate. In simple terms, the pellets “rust” and the rust bonds the pellets. Pellet strengths from rust bonding are shown in Table 1, and the rusting process is shown in reactions (6) through (10) (Xilun 1980).

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{++} + 2 \ e^- \\
\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2 \ e^- & \rightarrow 2 \ \text{OH}^- \\
\text{Fe}^{++} + 2 \ \text{OH}^- & \rightarrow \text{Fe(OH)}_2 \\
2 \ \text{Fe(OH)}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} & \rightarrow 2 \ \gamma - \text{FeO(OH)} + 2 \ \text{H}_2\text{O} \\
\text{Fe(OH)}_2 + 2 \ \gamma - \text{FeO(OH)} & \rightarrow \text{Fe}_3\text{O}_4 + 2 \ \text{H}_2\text{O} \\
\end{align*}
\]

Due to the electrochemical nature of the process, rust-bonding is sensitive to ore type. Magnetite has high conductivity and good bonding, while hematite, pyrite, limonite, and goethite display variable to poor bonding. The hydrated ores (limonite and goethite) have the lowest conductivity and are least effective for rust-bonding.

Various additives can be used to affect the rust-bonding process. Salts can be added to affect the corrosion process, although their presence is not desirable during reduction. Starch has been added at doses ranging from 0.2% to 0.5% with 2% to 8% sponge iron powder. The starch acts as a plasticizer or pelletizing aid and improves the pelleting process (Heinrich and Schierloh 1973).

**Organic Binders**

Iron ore concentrate pellets can be cold bonded using certain organic binders (Halt and Kawatra 2013). The iron concentrate and organic binder mixture are ballied using traditional drums and disks, and then cured at ambient or relatively low temperatures. Effective organic binders for cold bonding include wheat and corn starches (Graham 1983; Osmundson 2011), wheat flour (Igawa et al. 2008), dextrin (Agrawal et al. 2000, 2001), lignosulphonates (Chellan, Pocock, and Arnold 2004), and caustic lignite (Qiu et al. 2003a, 2003b, 2004a, 2004b). Typical pellet strengths using organic cold bonding binders are shown in Table 1.

Raw starch and flour are added at doses ranging from 1% to 10%. After pelletization, the green-balls are dried in a controlled manner to gelatinize the starch before moisture is evaporated from the balls. When all moisture is removed from the resultant gels and the balls are completely dried, a strong, adhesive film forms at grain contact points which bonds the pellets. Reported drying temperatures are 150–200°C (Igawa et al. 2008). Bentonite clay (0.1%–0.3%) and sodium hydroxide (0.01%–0.03%) have been added in addition to the organic binder to increase pellet strength at higher temperatures. Osmundson (2011) reported that age- ing the balling feed mixture for 0.5–4 h prior to pelleting increased green ball quality.

Dextrin, derived from starch by acid hydrolysis, has been used as a cold binder at a 4% dose (Agrawal et al. 2000, 2001). Laboratory pellets were cured for 3–4 days for full strength development, while pilot scale pellets were air cooled for 4–7 days. Long curing cycles would require that large open areas (protected from freezing temperatures) be available for pellet storage. A composite binder composed of dextrin (3%) and bentonite (1%) was used to bind chromite pellets following a 1 h, 150°C cure (Dwarapudi et al. 2013).

A lignosulphonate-based material was used as a binder for magnetite-coal composite pellets (Chellan, Pocock, and Arnold 2004). The binder dose was 1%, and the binder increased the wettability of the naturally hydrophobic coal particles. Pellets were thermally treated at temperatures ranging from 500–900°C. At these temperatures, the coal may lose volatile matter and help form additional bonds between particles (Takano and Mouro 2003).

A caustic soda (NaOH)-treated lignite coal was used as a cold bonding binder for magnetite pellets. Optimal binder dose was reported to be 1.5%. Pellets were hardened or cured under heated blowing air (200–250°C).

**Cold Bonding Process Considerations**

Cold bonding processes generally use high binder doses and long curing cycles instead of the low binder–high-temperature recipes followed during heat induration. This leads to a number of tradeoffs that must be considered.
when evaluating each type of cold bonding process, and when choosing between cold bonding and heat induration. Some of the important advantages and disadvantages to consider are discussed here.

**Disadvantages**

Cold bonded pellets are cured for long periods of time, and will require extensive floor space and equipment needed for managing large amounts of hardening pellets. High binder doses (in cement bonding) increases pellet contamination with silica (Eisele and Kawatra 2003).

The hydrothermal processes produced strong pellets, but were batch processes subject to mechanical issues, and had difficulties with non-uniform pellet feeds. Blast furnace testing of 5000 tons of hydrothermal pellets was successful (Goksel and French 1979), although there was concern with higher zinc contents in the furnace introduced from the cold bonded pellets. Due to low temperatures in hydrothermal and other cold bonding processes, volatile impurities such as lead (Pb) and zinc (Zn) in pellets are not removed, and then must be dealt with in another unit or in the reduction furnace.

As shown in Table 1, pellet strengths can also be quite low, especially when pellets contain high quantities of reducing agents. This may be problematic for shaft furnaces, but not for rotary hearths and kilns. Rotary hearths and rotary kilns are fed low quantities of pellets (layers are 1–2 pellets deep in rotary hearths) and pellets have low strength requirements compared to blast furnaces and other shaft furnaces. Pellet strength requirements for rotary hearths and kilns range from 20–65 lbs/pellet.

**Advantages**

Cold bonding processes may be attractive for economic reasons. Sah and Dutta (2003) reported a study that estimated cold bonding capital and operating costs to be 2/3 that of heat induration. Considering production levels, traditional induration furnace capacities range from 350,000 to over 7,000,000 tons per year, and are increasing, while the generation of dust, sludge, waste oxides, and refractory ores may be much lower. Have induration furnaces been designed for smaller operations? Are they economical on a smaller scale? Should be considered when choosing an appropriate bonding process.

**Conclusions**

A variety of cold bonding methods have been developed to agglomerate self-reducing pellets, refractory ores, and waste materials from iron and steelmaking. Cement and organic materials have been the most popular cold bonding binders. Both are easy to use, and do not present major difficulties during agglomeration or curing. Simple air curing agglomerated pellets suffices for both binders, although cements can be hardened more quickly using steam treatments. Further research should be conducted into alternative cements, as some references indicated improved high temperature pellet properties using aluminate cement compared to Portland cement. Feed quality requirements for alternative iron-making operations should be reviewed in order to understand which cold bonding methods are suitable for each process.

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