Repurposing mine tailings: Cold bonding of siliceous iron ore tailings

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Abstract
The formation of geopolymers from mine tailings using cold-bonding processes is known to be possible. Numerous cold-bonding methods exist, but the hydrothermal processes involving high temperatures and pressures in the presence of steam have been found to be the most ideal. This paper presents the results of successful preliminary studies to apply hydrothermal bonding processes to mine tailings agglomerates. Particle-size analysis revealed the particle size of the tailings waste to be 80 percent passing at 35 μm. The compressive strengths of the tailings pellets were shown to increase with time in the curing vessel, closely approaching the 400 lb. of standard iron ore concentrate pellets. These strengths are sufficient to allow use of the tailings pellets as aggregate materials for asphalt and cement. Additional applications may be possible, including reprocessing to extract more valuable materials and usage as agglomerated road-bed materials, backfills for building foundations, and replacements for sand and lime in cement.

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Introduction
Mine tailings are a waste byproduct of ore concentration and are available in large quantities across the world. Despite their abundance, they have received little attention or consideration for beneficial use. One reason is that the chemical nature of the material is not well known. Another factor that has hindered direct usage is the fine particle size. This raises the questions: what is the composition of the tailings, and how can such fine solids be beneficially used? Because the mining industry produces concentrates, the tailings may be treated as concentrates and processed in the same fashion, but it would be inefficient to consider full sintering or induration conditions for materials that have little ore content. To achieve sustainable operation, the development of technologies to use these tailings is necessary. Mine tailings should not be considered waste, and an “out of sight, out of mind” mentality does not represent a sustainable solution for the future.

One iron ore mine in Michigan is estimated to have accumulated more than 400 million metric tons of tailings during its last 30 years of operation, with an additional 180 million metric tons accumulated before the ore body is depleted. These mine tailings currently have no practical use, largely due to a scarcity of knowledge of their true physiochemical nature. It is thought that lack of quality control of the waste material prevents its use, but variability in the unprocessed ore prevents a consistent waste stream composition. The fact that the tailings are available in such great quantities makes them an extremely attractive resource. However, developing a sustainable, low-cost means of repurposing the mine tailings waste as a construction material may only be completed once the tailings are physically and chemically understood. Due to the high silica content of the material studied, cold bonding was determined to be the most viable method for processing the tailings into a usable product.

Theory and background
Low-temperature curing techniques operating in the range of 200-500°C, known as cold-bonding processes, have been shown to yield compressive strengths comparable to those of high-temperature firing processes (Halt et al., 2014). The use of cold-bonding technology to polymerize fine wastes at low temperatures to create usable materials is a little-researched area of geopolymers. A geopolymer is an inorganic polymer formed from a solid aluminosilicate and a strong alkali...
hydroxide (Duxson et al., 2007). The network of siliceous matrices formed during cold bonding is similar to that formed in an aluminosilicate material, hence of a geopolymer. Cold bonding uses alkaline hydroxides in the presence of elevated temperature and pressure to achieve the same results as other geopolymerization techniques. It may be argued that cold-bonded tailings fall into the category of geopolymer technology as the materials undergo a similar formation process to that of a typical geopolymer. In the past, mine tailings impoundments have been reacted with reagents to create geopolymers in an effort to stabilize and encapsulate wastes (Van Jaarsveld et al., 2000).

Why consider cold bonding?
Cold bonding has numerous benefits for the processing of fine mine tailings and wastes. First, its curing process consumes a fraction of the energy required for conventional pellet sintering operations. Second, previous research has shown that pellets cured using hydrothermal methods have compressive strength of nearly 400 lb./(Zhu et al., 2000). Third, cold-bonded pellets are naturally porous, allowing moisture dissipation and reducing attrition due to thermal cycling.

Cold bonding relies on the same principles that occur naturally beneath the Earth’s surface, where heat and pressure are used to effect changes in rocks on the molecular level. In a similar way, in cold bonding, agglomerated solids mixed with a chemical reagent and subjected to elevated temperatures and pressures in the presence of water partially dissolve, developing a silicate matrix that hardens quickly when exposed to air. Materials agglomerated with calcium hydroxide (Ca(OH)₂) and left in ambient conditions will undergo the same changes, but at very slow rates. In order to ensure uniform hardening and conversion of soft, agglomerated fines to hard pellets, it is necessary to execute this hardening process at elevated temperatures and pressures of around 200°C and 200 psig.

Cold-bonding techniques
Conventional iron ore pelletization requires considerable energy for the drying process, which occurs in the 300-500°C range, followed by the induration, or hardening, at 1,300°C of pellets. Typically, this energy is provided by the combustion of natural gas or coal. To reduce energy costs, other methods involving low-temperature curing have been pursued for pellet manufacturing. However, this allows for very short cycle times from iron ore to finished pellet. Other methods of pelletization and curing have been investigated, with cold bonding and reduction of binders receiving increased attention over the last few years (U.S. Department of Energy, 2013; Robinson, 2005).

In the cold-bonding process, agglomerated fines are treated so that they harden into pellets at low temperatures, eliminating the need to fire the pellets to increase compressive strength and reduce attrition during transport (Graham, 1983). An effective cold-bonding process can have numerous benefits over conventional pelletization. These include but are not limited to:

- Energy consumption is reduced and the options for types of binders used during agglomeration are increased due to the lower operating temperatures, which in turn allows for higher iron content of pellets (Zhu et al., 2000).
- The average particle size of ore concentrate to use in cold bonding is not required to be as small, due in part to the nature of the curing process (Sah and Dutta, 2010).

Similar to other means of geopolymer synthesis, a strong base is used as a reactant to facilitate the formation of a siliceous matrix (Xu and Van Deventer, 2000). For conventional geopolymers, alkali hydroxides are used to facilitate the necessary reaction, whereas hydrothermal processes typically use alkaline hydroxides to facilitate hardening (Duxson et al., 2007; Halt et al., 2014).

Studies had been conducted on cold bonding using various alternative binders, but they had yielded pellets that either proved to be too expensive to manufacture or had inferior strength properties compared with fired pellets (Graham, 1983). Several of these cold-bonding processes using binders that include cement, starch, and hydrocarbon and synthetic polymers have been patented. Cold bonding allows the use of starches as binding agents, an advantage over normal induration, where starches cannot be used because organic binders have been found to thermally degrade at elevated temperatures. While a large amount of work has been performed using different binding agents, questions remain regarding the reaction mechanisms and operating conditions of cold bonding and curing.

The common element among all cold-bonding processes is the low operating temperatures of the curing step, typically in the 200-300°C range (Goksøyr, 1977). However, numerous other factors, such as duration of cure, temperature profile during cure, and operating pressures, require additional investigation.

Cold bonding has been attempted with only a few types of supplementary binders. These include calcium carbonate, cementitious and pozzolanic materials, iron powder, and dextrin, starch and flour (Graham, 1983; Agrawal et al., 2001). These materials harden agglomerates by forming new phases among the inactive grains in the pellet. For example, in calcium carbonate bonding, calcium hydroxide is mixed into the material to be agglomerated, rolled into balls, and hardened by reaction with carbon dioxide (CO₂) (Liu, 2011). The CO₂ reacts with

| Table 1 — Hematite tailings characterization. (BDL = Below detection limit) |
|-----------------------------|-----------------|
| Analyte     | Concentration (%) |
| Fe₂O₃        | 28.175           |
| SiO₂         | 68.775           |
| Al₂O₃        | 0.8675           |
| CaO          | 0.275            |
| MgO          | 0.745            |
| (Mn)         | 0.125            |
| (P)          | 0.0288           |
| TiO₂         | 0.0633           |
| Na₂O         | 0.0183           |
| K₂O          | 0.0423           |
| (S)          | 0.002            |
| BaO          | 0.0228           |
| Cr₂O₃        | 0.0043           |
| CuO          | 0.0013           |
| NiO          | 0                |
| PbO          | BDL              |
| V₂O₅         | 0.0003           |
| ZnO          | BDL              |
the calcium hydroxide to form a calcium carbonate network among the inactive grains, and a hard agglomerate is formed (Goksel et al., 1968). With cold bonding, the agglomerates are cured in a humid, CO₂-rich environment, which lessens the time required for the hardening reactions to occur.

Curing times using cementitious or hydraulic minerals have been drastically decreased using cold bonding. Traditional cement reactions require 5-30 days for agglomerate strengths to reach appreciable levels (Goksel, 1977; Liu, 2011). Curing agglomerates in humid, warm environments results in a more rapid set, and higher agglomerate strengths after only a few hours to a few days, with reported curing times ranging from 4 to 96 hr. Increasing the pressure of the curing environment up to 300 psig can also increase the agglomerate strength and reduce the required curing time. Researchers have reported that some calcium and aluminum and silicate binding minerals partially dissolve and react under pressure to form gels and hydration products without a detectable crystalline structure (Hassler and Kihlstedt, 1977). The fundamental reactions were not understood, but the results were promising. Agglomerate strengths were achieved that previously could only be met using very high temperatures.

This paper presents the initial results of investigations into the use of hydrothermal cold bonding to pelletize fine iron ore mine tailings. Our preliminary studies indicate that fines may be agglomerated and cured using cold-bonding methods to produce pellets with high compressive strengths.

**Methods and materials**

Mine tailings were obtained from a Lake Superior District hematite facility. Table 1 shows the chemical composition of the tailings as determined by X-ray fluorescence (XRF). Particle-size analysis was performed on a suspension with greater than 1 percent solids concentration, using a Microtrac laser scattering particle-size analyzer. The particle size was found to have a bimodal distribution, and the 80 percent passing size was found to be 35 μm (Fig. 1).

**Pelletization procedure. Design.** The diameter of the pel-

![Figure 1 — Size distribution of hematite tailings.](image-url)

**Figure 2 — Cold-bonding thermal pressure reactor apparatus.**
feed mixture. As seeds formed, more feed material was added to facilitate pellet growth. Intermittent addition of spray water was required for pellet growth and to maintain the proper moisture content in the green balls. Occasionally, the green balls were removed and screened to maintain a uniform size distribution in the pelleting drum. Once the green balls had grown to a size range of 7/16 in. to 1/2 in., they were removed from the drum and proceeded to the testing phase.

**Testing.** Upon completion of balling, 20 green balls were selected at random to test the wet-drop value. In wet-drop testing, the number of times a wet, uncurled pellet can be dropped from a height of 18 in. before fracturing is recorded. Another 20 green balls were then selected at random for wet-compression testing. A Mark-10 compression testing unit with crosshead speed of 40 mm/min was used. Once wet-compression testing was completed, the remaining pellets were dried in a convection oven at 105°C for 24 hr. The dried, uncurled pellets were weighed to determine moisture content. Dry compression testing was completed using the same procedure, selecting 20 pellets at random (Ripke and Kawatra, 2000).

**Cold bonding.** Twenty-five dried green balls were placed in a 1-L pressure reactor on an elevated support screen. To provide steam in the high-pressure environment needed for cold bonding, 100 mL of distilled water were placed below the pellets in the reactor (Fig. 2). After the reactor was sealed, the temperature controller was set to maximum output until the pressure in the reactor reached 165-175 psig. The controller output was then decreased to approximately 20 percent, allowing the reactor to reach steady-state curing conditions of 220 psig (Goksel et al., 1968). Pellet-curing residence time was initiated when the reactor pressure reached 220 psig, independent of ramp time. Cure time was terminated by relieving reactor pressure until ambient pressure was attained. Pellets were cold bonded for periods of 15, 30 and 60 min.

**Bulk density and porosity of cold-bonded pellets.** The bulk density and porosity of the cold-bonded pellets were measured. Bulk density was measured by displacement. A 1,000-mL graduated cylinder was filled with the pellets and the weight recorded. All of the pellets had bulk densities in the range of 1 to 1.05 g/cm³. Porosity was measured using a solvent intrusion technique. The pellets were soaked in a volatile solvent, consisting of acetone, for 3 hr. Their masses when wet, when suspended in the solvent and when dry were recorded, and the porosity was then calculated using:

$$\text{Porosity(%) } = \left( \frac{\text{Mass}_{\text{Wet}} - \text{Mass}_{\text{Dry}}}{\text{Mass}_{\text{Wet}} - \text{Mass}_{\text{Suspended}}} \right) \times 100$$  \hspace{1cm} (1)

**Results and discussion**

Figure 3 shows that most of the compressive strength from cold bonding was achieved during the first 15 min of curing. The reactor residence times in Fig. 3 represent the duration of curing at 220 psig. The values given at time zero are those of dry, uncurled pellets. The 12 w/w percent Ca(OH)₂ tests indicate that the residence time in the reactor has little impact on compression strength past 15 min, as noted by the 60-min residence time. Compressive strength results from this test were within the error of the previous data point. Peak compressive strengths were achieved using a Ca(OH)₂ concentration equal to or more than 10 percent. This agrees with the findings of Goksel et al.’s 1968 research. Cold-bonded pellets produced with 10-14 w/w percent Ca(OH)₂ exhibited compressive strengths within the margin error of one another. Thus, pellet strength is not improved by concentrations of Ca(OH)₂ greater than 10 w/w percent. The relative porosities of the cold-bonded pellets were determined to be in the range of 20 to 25 percent, as seen in Table 2.

Conventional agglomeration technology is extremely applicable to the production of uncurled tailings pellets. Agrawal et al. (2001) showed that all operations conducted on a bench scale may be duplicated with existing infrastructure in a pellet production facility. One major limitation of this work is a lack of quality-control measures at the tailings streams. As there are few feedstock quality controls in place, ensuring a consistent
waste stream becomes increasingly difficult.

Cold-bonding technology, specifically hydrothermal processes, are not well known or understood. Despite the current definition of geopolymers as requiring an alkali hydroxide to react with alumina silicates, the two methods of cold bonding and conventional geopolymerization produce similar results, generating high-strength agglomerates that have properties similar to those of other inorganic polymers. One may argue that cold bonding falls into the category of geopolymer technology.

Generating construction materials from mining wastes will provide a sustainable alternative resource for future construction needs. Once basic material characterization is completed, it will be possible to apply the same process to a wide variety of mine wastes other than those from iron ore processing. Iron ore processing in the United States uses relatively simple ores with few gangue minerals, making it a logical starting point for repurposing tailings. There has been a great deal of interest in iron ore and iron ore waste processing recently (Bolen, 2014; Carlson and Kawatra, 2008, 2011, 2013; Halt, Roache and Kawatra, 2014; Haselhuhn, 2012, 2013; Haselhuhn, Carlson and Kawatra, 2012; Haselhuhn, Swanson and Kawatra, 2012; Kawatra and Halt, 2011; Liu et al., 2014; Manouchehri, 2014; Sandvik and Larsen, 2014; Semborg, Andersson and Bjorkman, 2014). This interest has driven investigations on using similar methods to process ores of different types after the mechanistic has been fully understood for simple feedstocks. An industry that repurposes its waste material will insure a sustainable future and significantly decrease the environmental impact of its operations.

If any tailings are to be used as construction materials in concrete or asphalt matrices, the long-term effects of the tailings on the asphalt and concrete must be understood prior to practical application. Leachate studies will ensure that any deleterious materials present in the tailings agglomerates are successfully sequestered within the matrix. To affirm that the tailings may be used safely and effectively, a lifecycle assessment must be completed to understand the implications of using them. The lifecycle assessment will capture information on the wastes generated in the process of making them usable construction materials as well as the energy demands, and provide insight into how long the construction materials will last before replacement is required.

The methods discussed above may be applied to most types of siliceous tailings, but the individual impact of each source material must be determined independently. New cold-bonding technology holds the promise of decreasing the stockpiling of tailings at concentration facilities and reducing the amount of aggregate, silica and clay mined for cement and concrete production. The purpose of this research is to develop technology for tailings disposal and use. Until a robust method to repurpose them is developed, tailings will continue to accumulate. Once the technology has been sufficiently understood, it will be validated through a cost assessment and lifecycle analysis.

Conclusions

This paper presents the results of initial investigations to determine if tailings can be successfully cold bonded and what the properties of the final agglomerates would be. The hydrothermal processing of high-silica mine tailings was shown to produce pellets with quality close to that of iron concentrate pellets. The compressive strengths of these pellets were shown to increase with time in the curing vessel, closely approaching the 400 lb of a standard iron ore concentrate pellet. These pellet strengths are sufficient for use as an aggregate for asphalt and cement. Additional applications for pelletized tailings may include reprocessing to extract more valuable materials and usage as agglomerated road-bed material, backfills for building foundations, and replacements for sand and lime in cement.

References


Table 2 — Porosity of cold-bonded iron tailings pellets.

<table>
<thead>
<tr>
<th>Ca(OH)₂ (wt %)</th>
<th>Porosity (%)</th>
</tr>
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<tbody>
<tr>
<td>6</td>
<td>20.85</td>
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<tr>
<td>8</td>
<td>22.35</td>
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<tr>
<td>10</td>
<td>22.23</td>
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<td>12</td>
<td>25</td>
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<td>14</td>
<td>24.61</td>
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