Development of experimental procedures to analyze copper agglomerate stability

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Abstract
The efficiency of heap leaching is reduced by poor solution flow characteristics (i.e., channeling and ponding) that result from fines migration. Agglomeration of the ore can immobilize fines, but for agglomeration to be successful in copper leaching, an acid-resistant binder is needed to stabilize the agglomerates. Until now, there has not been a satisfactory method to evaluate whether a binder was effective, other than squeezing a handful to see if it “feels right.” This paper reports on several procedures that have been developed to quantitatively determine whether a binder gives good performance in an acidic solution. These procedures have been used to identify binders that would be suitable for copper heap leaching.

Key words: Agglomeration, Heap leaching, Copper

Introduction
Heap leaching is a method used to recover metal from low-grade ores in a reasonable amount of time at low operating and capital costs (Eisele et al., 1984; Weir, 1984; McClelland, 1985; Dixon, 2003). However, leaching heaps are plagued with permeability problems that result in less than ideal metal recoveries. Poor permeability can be caused by fine particles migrating downwards in the heap with the leach solution, clogging the spaces between the larger ore particles (Chamberlin, 1986; Lipiec, 1998). These fine particles build up and begin to form impermeable layers within the ore bed. The build-up prevents air and leach solution from flowing freely through the heap. Thus, the solution either flows down the path that gives the least amount of resistance (channeling) or tends to pool within the heap (ponding), as shown in Fig. 1. Either of these actions will result in a portion of the ore being poorly contacted by leaching solution, leaving zones that are either unleased or only partially leached by diffusion. Air may also enter the channel in an upward direction, creating similar problems to those associated with solution channeling. As a result, inadequate metal recoveries would be experienced unless the leach times were extended (Wadsworth, 1981; McClelland, 1986; Ortiz, 2003; Trincado, 2003).

Agglomerating the ore would allow the fine material to adhere to the coarser material (Fig. 2) through mechanisms such as adhesion forces, cohesion forces, surface tension forces, capillary forces, electric forces and molecular forces such as hydrogen bonding. Agglomeration would help to increase permeability by preventing fine material from migrating downwards in the heap, thereby lessening the channeling and ponding effects. Increased permeability will lead to a better interface between the leach solution, air and ore, which in turn will result in improved metal recovery rates.

A cost-effective binder is needed in the agglomeration step to prevent agglomerate breakdown when the ore is moistened (McClelland, 1986). However, copper heap leaching requires a highly acidic environment (i.e., a pH of approximately 2) to help the bacteria convert ferrous iron (Fe^{2+}) back to ferric iron (Fe^{3+}), which is needed for the copper extraction to progress. Most agglomeration binders that are used successfully in non-acidic heap leaching are alkaline materials such as Portland cement. They therefore break down in the acidic environment needed for copper heap leaching (Chamberlin, 1986; Efthymiou et al., 1998; Serrano, 2003). Acid resistant binders that will not break down in acid while allowing air and leach solution to reach the ore particles are needed for copper operations.

The use of a proper binder will result in a more uniform percolation throughout the heap. There is now at least one
copper heap leaching facility in the United States that uses agglomeration. However, without an effective acid-resistant binder, they are agglomerating with only raffinate (i.e., the solution used for leaching). The limited binding effectiveness of raffinate allows the agglomerates to break down, and therefore, the full theoretical benefits of agglomeration are not being achieved.

No standardized quantitative method for evaluating agglomerate stability when using binders in agglomeration is described in the literature. Currently, handfuls of agglomerates in industry are often squeezed to see if they “feel right” (McClelland, 2004). Other stability tests that have been conducted include soaking agglomerates in water and observing the breakdown or placing them on a screen and jigging them in and out of water for 10 to 30 seconds (Milligan, 1983; Chamberlin, 1986; Herkenhoff et al., 1987; McClelland, 1988; von Michaelis, 1992). Percolation columns were used by Pautler et al. (1990), among many others, to test agglomerate stability by looking at the “slump” of the ore bed. However, all of these procedures showed significant variations and are not sufficiently controlled to give quantitative results. Therefore, standard, reproducible procedures needed to be developed to quantitatively determine whether using a binder in agglomeration would be able to provide increased stability in acidic solution (Lewandowski, 2006).

Experimental procedure

Binders. The binders chosen for agglomeration fall into three general classes: organic, inorganic and polymer. The binders that were examined in this study are presented in Table 1. Many of the binder compositions were proprietary, and only limited composition information was available. These binders were chosen based on the following factors:

- **Organic binders:** Organic binders, such as modified cellulose and lignin, were chosen based on the fact that they are difficult to degrade. Cellulose is used as a binder in papermaking, as cellulose molecules bond to other cellulose molecules to give strength. Cellulose, in particular, is a very abundant organic compound and is also highly hydrophilic, which allows it to absorb water (Bailey et al., 2000; Water Structure & Behavior, 2006). The ability of the cellulose to absorb water allows the binder to retain some of the leach solution that comes in contact with it, holding it to the ore surface. Several organic binders, including agar, gelatin, gums, sodium carboxymethylcellulose and starch, were previously tested under acidic conditions by Southwood (1985), and they showed poor results.

- **Inorganic binders:** Inorganic binders, such as sodium silicate, were chosen based on their expected ability to react with the acid to form a silica gel that could act as a binder (Southwood, 1985). Several other inorganic binders, including iron (II) sulfate, sodium tripolyphosphate and calcium sulfate were previously tested under acidic conditions by Southwood (1985), and they showed poor results.

- **Polymer binders:** Polymer binders that have the ability to resist degradation by acid liquors were chosen based on availability. Other studies examined the use of polyacrylamides and acrylamide. However, limited information on the performance of these binders in relation to copper ore agglomeration has been published (Gross and Bonin, 1989; Gross, 1990; von Michaelis, 1992; Gonzales et al., 1996; Kerr, 1998; Tramfloc Inc, 2004; Bouffard, 2005). Polymer binders may also have the ability to bond to the hydrogen ions that adsorb onto the mineral surfaces (Sperling, 2001).
The material that had passed through the screen and had been collected in the bucket could then be compared to the total amount of -10-mesh (-1.70-mm) material in the sample. This ratio was defined as the percent of fines migration, as indicated by

\[
\text{Fines migration} = \frac{\text{Weight of ore migrated out of the sample}}{\text{Total weight of -10 mesh fines available in the sample}}
\] (1)

A binder that improves the stability of the agglomerates will have a low percentage of fines migration because the agglomerates will not be breaking down and will not release the fine material from their surfaces. All of the binders were initially tested at a dosage rate of 2.5 kg of binder per metric ton of ore (5 lb/st) for comparative purposes. However, polyacrylamide 1 was too viscous when dissolved in solution and, therefore, was used at a lower application rate of 0.5 kg of binder per metric ton of ore (1 lb/st).

The results for all the binders are presented in Fig. 4. The polyvinyl acetate 2 was also tested for comparative purposes. However, polyacrylamide 1 was too viscous when dissolved in solution and, therefore, was used at a lower application rate of 0.5 kg of binder per metric ton of ore (1 lb/st).

The percolation flooded column tests (Fig. 5) were used to evaluate the permeability of an ore bed agglomerated with the various acid resistant binders identified using the soak test. The following procedure was used in the percolation flooded column experiments. First, approximately 1.5 kg (3.307 lb) of ore was agglomerated in a drum with raffinate and a binder. The ore was then allowed to cure by air-drying at ambient conditions for 24 hours before being transferred into the column apparatus. The leach solution was then dripped onto the top of the column at a controlled rate, where it slowly began to flood the column. Bulk density and hydraulic conductivity measurements were then taken at various increments over a 72-hour period. After 72 hours, the pumps were stopped, and the columns were allowed to drain for one hour. The ore was then emptied from the column and was dried and weighed.

The binders chosen for the percolation flooded column studies included tall oil pitch, polyvinyl acetate 1, waste treatment additive and polyacrylamide 1, all four of which showed good results in the soak tests. Polyvinyl acetate 2 was also tested in the percolation flooded column test, even though it worked poorly in the soak test. This binder was tested to show how, by comparison, poor acid resistance of an agglomeration binder affects the permeability and solution flow of an ore bed.

The bulk density of the ore bed is an indicator of the degree of permeability in the heap. The lower the bulk density, the more void spaces there are within the bed, leaving more room for solu-

Table 1 — Summary of binders that were examined.

<table>
<thead>
<tr>
<th>Type</th>
<th>Binding agent</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic</td>
<td>Lignin derivative</td>
<td>–</td>
</tr>
<tr>
<td>Cellulose derivative</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Methyl cellulose</td>
<td>Nonionic</td>
<td></td>
</tr>
<tr>
<td>Tall oil pitch</td>
<td>Cationic</td>
<td></td>
</tr>
<tr>
<td>Inorganic</td>
<td>Sodium silicate</td>
<td>–</td>
</tr>
<tr>
<td>Polymer</td>
<td>Poly(diallyl-dimethylammonium chloride) polymer</td>
<td>Cationic</td>
</tr>
<tr>
<td>Polyvinyl acetate Emulsion 1</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Polyvinyl acetate Emulsion 2</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Polyacrylamide 1</td>
<td>Nonionic</td>
<td></td>
</tr>
<tr>
<td>Polyacrylamide 8</td>
<td>Anionic</td>
<td></td>
</tr>
<tr>
<td>Polyacrylamide 9</td>
<td>Anionic</td>
<td></td>
</tr>
<tr>
<td>Polyacrylamide 10</td>
<td>Anionic</td>
<td></td>
</tr>
<tr>
<td>Polyacrylamide 3</td>
<td>Anionic</td>
<td></td>
</tr>
<tr>
<td>Waste treatment additive</td>
<td>–</td>
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</tbody>
</table>

Soak test. It was important that the binders chosen for copper heap leaching agglomeration would be able to withstand the acidic conditions that would be experienced in the heap. Therefore, the "soak test" was devised to narrow down a large field of binders to determine which binders would not break down in an acidic environment.

Before any binders could be tested, an experimental procedure needed to be developed. This procedure needed to quantitatively measure how well the agglomerates that were made with raffinate and/or various binders held together while being subjected to acidic conditions comparable to those in a heap. The soak test (Fig. 3) was developed to accomplish this task. First, approximately 500 grams (1.10 lb) of ore was agglomerated in a drum with raffinate and a binder. The ore was then placed on a Tyler 10 mesh (1.70 mm) screen and allowed to "cure" (air dry) under ambient conditions for 24 hours. The screen was then lowered into a bucket filled with a 6 g/L H₂SO₄ solution (pH ~1.8) and allowed to sit for 30 minutes. After 30 minutes, the Tyler screen was carefully removed from the solution. The material that had passed through the screen and collected in the bucket was dried and weighed.

Figure 3 — Soak test experimental procedure.
tion to flow. A high bulk density indicates that there is less void space between the agglomerates, which would impede solution flow. The bulk density in the percolation-flooded columns was determined by dividing the weight of the ore by the volume of the ore bed. The variations in bulk density in the course of each test for the various binders are shown in Fig. 6.

The raffinate had the highest change in bulk density, indicating that the agglomerates in this column were breaking down. While breaking down, fine material was being released from the agglomerates and migrated downward in the heap, clogging the spaces between the other agglomerates. The use of binders in agglomeration helped decrease the bulk density by up to 82% in comparison to using raffinate alone. A decrease in bulk density indicated that the use of a binder in agglomeration provided increased agglomerate stability. Polyvinyl acetate emulsion 2, which had the greatest breakdown in the soak test, had the highest change in bulk density when compared to the raffinate agglomerated test. This binder improved the bulk density compared to using raffinate alone, but performed poorly compared to the other binders tested.

Another measure of permeability is hydraulic conductivity, as it expresses the ease of solution flow through the ore bed. Darcy’s Equation can be used to calculate the hydraulic conductivity in the percolation-flooded columns, using the dimensions indicated in Fig. 7.

$$Q = A \times K \times \frac{\Delta h}{L}$$  \hspace{1cm} (2)

where

- $Q$ is the volumetric flow rate ($m^3/s$),
- $L$ is the flow path length ($m$),
- $A$ is the flow area perpendicular to $L$ ($m^2$),
- $\Delta h$ is the change in hydraulic head ($m$) and $K$ is the hydraulic conductivity ($m/s$).

A high hydraulic conductivity indicates that the solution is able to flow through the ore bed freely due to greater permeability of the bed. If channeling occurs, an increase in the hydraulic conductivity over time would be expected. Other phenomena such as ponding or the build up of impermeable layers would produce a decrease in hydraulic conductivity.
All the binders produced higher hydraulic conductivities than the agglomerates made with raffinate alone (Fig. 8). Polyacrylamide 1, in particular, produced the highest hydraulic conductivities with an increase in the hydraulic conductivity of up to 90% in comparison to agglomerating with raffinate alone. As expected from the soak test results, polyvinyl acetate emulsion 2 once again produced the poorest results of all the binders, but was still an improvement over agglomerating with raffinate alone.

The percent of fines migration can also be determined in the percolation flooded columns using similar calculation as that used for the soak tests (Eq. (1)). As the percolation column test progresses, any fine material that had broken off and migrated through the ore bed was collected in the fines migration collection flask located at the bottom of the column shown in Fig. 5. At the end of the experiment, this flask was removed and its contents were filtered. The weight of material on the filter paper was compared to the original weight of the -10-mesh material originally in the sample. The results for the binders tested are presented in Fig. 9. The raffinate-agglomerated column had the highest degree of fines migration, which is another indication that the agglomerates are breaking down with time. The tall oil pitch and the waste treatment additive had the lowest percentage of fines migration, indicating that those agglomerates were breaking down the least. The polyvinyl acetate emulsion 1 and polyacrylamide 1 also produced lower fines migration than the raffinate column. Polyvinyl acetate emulsion 2 performed poorly again, with the highest fines migration of all the binders tested. Although the fines migration values are low, statistical analysis using a 99% confidence interval confirmed that the raffinate fines migration was statistically different that that of the remaining binders. It was also determined, with the same confidence, that the polyvinyl acetate emulsion 2 has statistically significant higher fines migration than polyvinyl acetate emulsion 1, polyacrylamide, waste treatment additive and tall oil pitch. The remaining binders (polyvinyl acetate emulsion 1, polyacrylamide 1, waste treatment additive and tall oil pitch) had fines migrations that were statistically similar to one another.

Figure 6 — Change in ore bulk density vs. time for best performing binders.

Figure 7 — Parameters applied to laboratory-scale columns.

All the binders produced higher hydraulic conductivities than the agglomerates made with raffinate alone (Fig. 8). Polyacrylamide 1, in particular, produced the highest hydraulic conductivities with an increase in the hydraulic conductivity of up to 90% in comparison to agglomerating with raffinate alone. The addition of polyvinyl acetate emulsion 1, the waste treatment additive and tall oil pitch all increased the ease of solution flow compared to using raffinate alone. As expected from the soak test results, polyvinyl acetate emulsion 2 once again produced the poorest results of all the binders, but was still an improvement over agglomerating with raffinate alone.
The soak test results, in combination with the bulk density, hydraulic conductivity and fines migration measurements in the percolation columns can all be used to narrow down a large field of binders to those that would be able to increase the acid resistance and permeability of the agglomerates. To determine whether the increase in permeability, which was shown in the percolation flooded columns, would lead to improved copper recovery rates, tests using larger columns that more closely represent the conditions in the heap would need to be performed. Such column experiments have been carried out by Milligan et al. (1984), McClelland (1985) and Pautler et al. (1990) among many others. These columns are often much larger than the percolation flooded columns developed in this study, and they would subject the agglomerates to acid leaching conditions over a leach cycle of approximately 180 days. However, these columns experiments are out of the scope of this paper and will be discussed in future studies.

**Conclusion**

Previously there had been no quantitative methods to determine the quality of agglomerates in copper heap leaching. Two tests (the soak test and percolation column test) were developed to test agglomerates so that potential binders could be quantitatively evaluated.

The soak test was developed to show that agglomerates are or are not able to resist acid attack by quantitatively calculating the breakdown of agglomerates through fines migration calculations.
The percolation-flooded columns were designed to test the ability for copper ore agglomerates to maintain their stability when being placed into a 76.2-mm (3-in.) diameter ore bed and subjected to raffinate percolation. The columns allowed for the analysis of agglomerate stability through factors such as bulk density, hydraulic conductivity and fines migration. An improvement in the stability of agglomerates could be quantitatively determined by an increase in hydraulic conductivity, a decrease in the bulk density and decreased migration of fines.

Using the soak tests and percolation flooded columns, it was possible to quantitatively examine several binders that were able to maintain agglomerate stability better than using raffinate alone. The soak test has shown that polymer binders are better able to resist acid attack and to retain fine particles on the agglomerate surfaces, resulting in lower percent of fines migration. The tall oil pitch, polyvinyl acetate emulsion, raffinate alone, the soak test has shown that polymer binders were able to maintain agglomerate stability better than using raffinate alone. The percolation-flooded columns were designed to test the ability for copper ore agglomerates to maintain their stability when being placed into a 76.2-mm (3-in.) diameter ore bed and subjected to raffinate percolation. The columns allowed for the analysis of agglomerate stability through factors such as bulk density, hydraulic conductivity and fines migration. An improvement in the stability of agglomerates could be quantitatively determined by an increase in hydraulic conductivity, a decrease in the bulk density and decreased migration of fines.

The flooded column tests indicated that the use of these binders helped to improve the permeability of the ore bed by increasing the hydraulic conductivity and decreasing the bulk density and fines migration. Other, less acid resistant binders produced higher fines migration results in the soak test, and they also produced high bulk density and fines migration and low hydraulic conductivity in the percolation flooded columns. This indicates that binders with low acid resistance are not able to greatly improve solution flow characteristics in acidic copper leaching.

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