1. Introduction

The term agglomeration is a deceptive term in particle technology. In the case of fine powders (<10 μm) particle adhesion/agglomeration may occur due to attractive surface forces whereas in the case of larger particles, adhesion forces must be produced by the addition of liquids and binders to obtain stable and strong agglomerates as is the case in heap leaching operations. Of course agglomeration for heap leaching results in agglomerates that must have sufficient internal porosity to facilitate which occur during leaching transport processes.

Agglomeration is considered as possible insurance for good recovery in heap leach technology. Improper agglomeration is one of the major causes for reduced recovery and higher costs associated with heap leach operations (Velarde, 2005). Effective agglomeration for heap leaching operations offers numerous benefits such as better heap structure by minimizing channeling and improving permeability, other benefits include higher metal recoveries from low grade ores, improved availability of reactants, increased recovery rate i.e. shorter leach cycles, and better conditions for heap leach closure. Nowadays, agglomeration is considered as a pretreatment option for heap leaching operations (Lu et al., 2007; Bouffard, 2005). Agglomeration pretreatment is required for ores which either contain excessive amounts of clay or an excessive quantity of fines generated during mining and crushing. A feed requiring crushing to a nominal size i.e. 2 inches (19 mm) or finer will need agglomeration, especially if clay constituents are present (McClelland, 1988).

In copper heap leaching, sulfuric acid solution is frequently used to bind the particles together by a liquid bridge, and is thought to react with gangue minerals to render them amorphous and to inhibit silica dissolution. Curing refers to acidic reactions between gangue mineral particles which inhibits the dissolution of silicates, forms bonds between particles and accelerates copper extraction (Lu et al., 2007; Bouffard, 2005). Hence, curing may be required if sulfuric acid solution is used. Curing from 8 to 24 h is considered sufficient in the agglomeration of crushed ores (Bouffard, 2005). The majority of copper operations agglomerate by mixing the ore with concentrated sulfuric acid and water. Solid and liquid bridges are the most common bonding phenomenon in the agglomeration of crushed ore. Due to the weak nature of capillary forces prevalent in agglomerates, slumping is one of the common reasons for low recoveries in heap leaching operations. Garcia and Jorgensen (1997) recommended the need for agglomeration of ore with binder, if the ore contains more than 10–15% – 74 μm (200#) fines. The two key factors for any heap leaching operation are copper recovery and acid consumption.

For heap leaching operations, the use of cost effective binders for agglomeration is being considered to prevent agglomerate breakdown and to limit the migration of fines. Copper heap leaching operations frequently require a high level of acid, which makes the pH of the heap leach solution very acidic. A binder in copper heap leaching should withstand the very acidic environment and should not interfere with maintenance of a high bacterial population survival (Lewandowski et al., 2010). Reactions of the binder and the agglomeration solution may occur during agglomeration,
transport, and stacking prior to irrigation for heap leaching. It is desired that the reagent used as a binder not affect the leach chemistry during irrigation nor the subsequent processes for metal recovery.

Hence, for stable agglomerates, binders are required which can create chemical bonds. Lime, molasses, and wood fibers have been tried but the agglomerates resulting from these binders disintegrated completely within a couple of hours of immersion in water (Bouffard, 2008). Cement provides the best strength because of the formation of calcium silicates hydrates, during curing. However, cement-based agglomerates when allowed to dry immediately after agglomeration disintegrated partially to completely when less than 50 kg/t of cement were added.

The cost for agglomeration, labor and energy amounts to $US 0.10–0.30 per tonne of ore whereas the cost of binder alone is around $US 1.00 per tonne of ore (Bouffard, 2005).

Although the cement has been used in precious metal ore agglomeration (gold ores) for heap leaching in the 1980s, very few, if any, copper heap leaching operations add any binder to the sulfuric acid solution, possibly because of the binder cost, large consumption and curing issues, and limited selection of acid tolerant and microbial resistant binders (McClelland, 1988; Bouffard, 2005).

It is known that adding cement or lime to sulfide ores results in precipitation of gypsum and jarosite (Bouffard, 2005). Very little information has been published on the use of gypsum as a binder. Lastra and Chase (1984) mentioned gypsum and jarosite binders, however, such binders may involve precipitation reactions and corresponding alteration of the system pH. Amaratunga (1995) used gypsum β-hemihydrate only as a binder with pyrrhotite tailings and reported agglomerates of poor strength.

Considering these issues, the potential of the acid resistant stucco binder for agglomeration processes has been given an initial evaluation and the results are reported in this paper. Efforts have been made to determine the optimum amount of stucco and conditions to produce high quality agglomerates for agglomeration of the Zaldivar copper ore.

2. Materials and procedures

The copper ore sample used for agglomeration experiments was from the Zaldivar heap leach operations in Chile. The copper grade and mineralogy of the ore sample are shown in Table 1. The ore consists of copper sulfide, oxide and silicate minerals (chalcolite, brochantite and chrysocolla). The particle size distribution of the feed as shown in Fig. 1 was prepared with 10% by weight finer than 200 mesh. The average grade of the feed was 1.21% copper. The feed was prepared using a jaw crusher, HPGR and a roll crusher. In all experiments, the composition of the acid solution (20% acid and 80% water by weight) was kept constant. Stucco, also known as calcium sulfate hemihydrate (CaSO$_4$·½H$_2$O), was used in the form of fine powder for the binder experiments. In some experiments other reagents were added to accelerate stucco hydration and to enhance gypsum setting as discussed elsewhere (Kodali, 2010).

Drum agglomeration is well suited for ores containing clays or a large amount of fines. Chamberlin (1986) prefers a drum agglomerator when a binder is used. All the agglomerates were prepared in a plastic drum mixer (cement mixer) as shown in Fig. 2 at a fixed rotational speed of 20 rpm and with 5° inclination. In all experiments, the amount of acid solution (80% water and 20% concentrated sulfuric acid) and the amount feed material (10 kg) was kept constant.

3. Experimental results

3.1. Agglomerate size distribution

The newly formed agglomerates were air dried below 30 °C for 24 h to obtain dried agglomerated samples. The dried agglomerated samples were then screened on a ro-tap shaker for 3 min at a very low shaking speed. There was very little breakage of agglomerates during screening. The same procedure was followed to obtain the particle size distribution of agglomerates prepared with 50 g, 100 g, 250 g and 500 g of stucco binder. Also, it was observed that the agglomerates became coarser as the amount of stucco binder amount was increased (Fig. 3). The feed and resulting agglomerate particle size distributions are shown in Fig. 3. The agglomerate size distribution becomes coarser and coarser mainly by the consumption of fines. The adherence of fine particles (10% of the feed) to the agglomerates was also investigated.

![Fig. 1. Particle size distribution of feed for agglomeration experiments.](image-url)
minus 200 mesh) in the feed to the coarser particles was found to be the primary bonding mechanism. The P80 value for agglomerates prepared with 0 g, 50 g and 100 g of stucco binder is about 8.5 mm. Note that the fines are agglomerated at low additions of stucco but the size of coarse agglomerates is unchanged. In contrast the P80 values for agglomerates prepared with 250 g and 500 g of binder increases to 9.5 mm and 11.0 mm, respectively. This increase in agglomerate P80 size is an indication of the effectiveness of the stucco binder to facilitate the formation of larger agglomerates which was not observed at lower additions of stucco.

3.2. Permeability

The coefficient of permeability was determined by a constant head method (ASTM D2434) for laminar flow through a packed bed of agglomerates. The set up details are mentioned elsewhere (Kodali, 2010). The coefficient of permeability was calculated from the experimental data using Darcy’s law\(^1\) as given in Eq. (1).

\[
Q = \frac{A}{K \Delta P} \mu L
\]

\(^1\)Darcy’s law: \(Q/A = (K \Delta P)/\mu L\)

where, \(Q\) is the flow rate (cm\(^3\)/s), \(A\) the area of column (cm\(^2\)), \(K\) the permeability (cm\(^2\)), \(\Delta P\) the pressure difference in g/cm h, \(\rho\) the density of water (kg/cm\(^3\)) = 0.001 (kg/cm\(^3\)), \(g\) the acceleration due to gravity (cm/s\(^2\)) = 982 (cm/s\(^2\)), and \(L\) is the length of the column occupied by the agglomerates (cm).

The permeability values for the agglomerate bed prepared with different stucco binder amounts are shown in Fig. 4. It is observed from Fig. 4 that the permeability of the agglomerate bed increases with the amount of stucco binder addition used in the agglomeration process. In fact, the permeability increases five times when 500 g of stucco binder is used in comparison to agglomerates prepared with 50 g of stucco binder.

3.3. Electrical conductivity tests

Electrical conductivity is a useful tool to monitor changes in moisture content due to variation in feed properties. Electrical conductivity is being used as a guiding parameter for adjusting optimum moisture for agglomeration conditions (Velarde, 2005). The agglomerated ore samples were placed into a resistance measurement device which consists of two equal stainless steel rectangular electrodes (length of the electrodes is equal to the length of the cylinder in which they are placed). The resistance was measured using a multimeter that is clipped to the electrodes (Kodali, 2010). The electrical conductivity of the packed agglomerate bed was calculated using \(K_{\text{cond}} = L/R A\); where \(K_{\text{cond}}\) is the conductivity (1/\(\Omega\) cm), \(L\) is the distance between the two electrodes (cm), \(R\) is the measured resistance (\(\Omega\)) and \(A\) is the longitudinal cross

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\[\text{Fig. 2. Feed, plastic drum cement mixer, agglomerates.}\]

\[\text{Fig. 3. Resulting agglomerate particle size distributions.}\]

\[\text{Fig. 4. Constant head permeability test results.}\]
sectional area of the electrode (cm²). Electrical conductivity values are expected to be directly proportional to the amount of moisture present in the agglomerated sample.

The electrical conductivity results shown in Fig. 5, depict a trend of increase in electrical conductivity with an increase in the amount of sulfuric acid solution and eventually a constant value is reached for no stucco addition. For stucco binder agglomerates, the electrical conductivity values decrease with an increase in stucco binder amount for a constant sulfuric acid solution amount i.e. for 1000 g. The best quality agglomerates as determined by visual inspection were observed between electrical conductivity values of 0.002 and 0.004 (1/Ω cm).

3.4. Visual inspection

The agglomerate quality can be described by agglomerates size, permeability, electrical conductivity tests and column leaching results. But still in the industry, one of the most widely used tests is the glove test which involves visual inspection (Velarde, 2005). Hence, prior to the above mentioned tests, visual inspection was made to gain a rough idea of agglomerate quality. Agglomerate color and shape varies with the acid solution chemistry, amount, and binder dosage. More than 75 agglomeration tests were performed, three agglomerate samples were taken under different agglomeration conditions to better illustrate the significance of visual inspection as shown in Fig. 6. It was observed that the good quality agglomerates were prepared with 3–5 wt.% of stucco binder and 7–10 wt.% acid solution. The agglomerates prepared with other combinations of binder and acid solution were either too dry or too wet as shown in Fig. 6. Conditions are specified in Table 2. The sulfuric acid solution used refers to 20% sulfuric acid and 80% water.

3.5. Column leaching of agglomerates

In addition to all the specified tests i.e. agglomerate size, permeability of agglomerate beds, electrical conductivity and visual inspection, the effect of stucco binder on copper recovery was also considered by column leaching experiments.

Generally, the column tests are used to simulate the heap leaching process in small vertical columns to determine recovery, recovery rate and reagent requirements. The columns were loaded with agglomerates prepared with 500 g of stucco and 0 g of stucco to determine the effect of stucco binder on copper recovery during column leaching. While preparing the agglomerates, the amount of acid solution (80% water and 20% concentrated sulfuric acid) and of amount feed material (10 kg) was kept constant. Leaching columns were 10 cm in diameter and 182.8 cm tall. Columns were loaded with agglomerates by using a torpedo to achieve uniform distribution of the agglomerates. Cloth and polymer screens were placed over the agglomerates in the columns, so that the leach solution would be distributed uniformly. Marbles and a polymer screen were placed at the bottom of the columns to prevent broken agglomerates from blocking the outlet of the column. Intravenous (IV) systems were used to feed the leach solution into the columns at a controlled flow rate of 8 L/m²/h. The columns were leached for 112 days. Pregnant leach solution from column leaching was collected at regular intervals of time.

It was observed that the agglomerates prepared with stucco binder filled the column to a height 5 inches greater than the height without stucco binder. It is interesting to note that the flow rates were equivalent in both cases even though the permeabilities...
are quite different. This situation is probably due to the fact that leaching is under unsaturated flow conditions, whereas, the permeabilities measured are saturated flow permeabilities.

In one set of column leaching experiments (without ferric sulfate) the leach solution consisted of sulfuric acid solution only (6 gpl sulfuric acid). The columns were leached for 33 days. Whereas, in another set of column leaching experiments (with ferric sulfate) ferric sulfate was added as an oxidant in the leach solution (11 gpl of H2SO4, 6 gpl of FeSO4·7H2O and 5 gpl of Fe2(SO4)3).

In the case of column leaching without ferric sulfate, pregnant leach solutions were analyzed using the ICP instrument to determine copper recovery from each of the two columns, with and without stucco. The leaching results in µ g/ml of copper in the leach solution measured at different leaching times are shown in Fig. 7. Copper recovery results show that the stucco binder does not inhibit the recovery but, in fact, improves the rate of copper recovery. It is shown in Fig. 7 that for the initial stages of leaching, more copper is extracted from the stucco binder agglomerated sample. A plot of cumulative copper recovery with respect to leaching time with and without stucco binder is shown in Fig. 8. Copper recovery results without ferric sulfate as shown in Fig. 8 indicate that about 13% of the copper was recovered during 33 days (800 h) of leaching for the agglomerates prepared with and without stucco binder (using 500 g of binder).

In the case of column leaching experiments with ferric sulfate addition, the copper recovery is about 44% as shown in Fig. 8. It is worthwhile to mention, that with addition of stucco there is 5% increase in recovery and hence stucco seems to facilitate the rate of copper release.

Previous studies (Miller et al., 2003) in our group revealed that about 80% of the copper can be recovered from this ore sample in performing column leaching. However, the leach solution chemistry must be adjusted to achieve high copper recoveries. Because the ore contains significant chalcocite, Cu2S, improved leaching would have been possible if bacteria had been added to the leach solution as in previous studies.

4. Discussion

4.1. Effect of water content

From the particle size distributions, it was observed that the agglomerates become coarser when the stucco amount was increased from 0 g to 500 g. Considering this effect, a few experiments were done to see whether the increase in agglomerate size is solely due to stucco addition or due to the water effect. Stucco reacts with water to give gypsum as shown in Eq. (2).

$$\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} + \frac{3}{2} \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$$

Agglomeration experiments were conducted without stucco and by decreasing the water amount (water that is estimated to be consumed by 500 g stucco to form gypsum, 3/2 mol H2O per mole of stucco). It is clear from Fig. 9 that the agglomerates are becoming coarser as the binder amount is increased despite the decrease in water amount. Hence, it was concluded that the increase in agglomerates size is only due to stucco addition and not due to the water effect.

4.2. Effect of gypsum binder on agglomerate quality

Gypsum has been mentioned in the literature as a potential binder for agglomeration (Amaratunga, 1995; Bouffard, 2005). Hence, a few experiments were performed by using gypsum as a binder to examine its effect on agglomerate quality. The gypsum binder amount and sulfuric acid solution amount were selected in correspondence to ideal agglomerates that were obtained when stucco binder is used. When stucco binder is added in the agglomeration process, water reacts with stucco to form gypsum. When gypsum binder is added there is no hydration reaction, so in order to maintain the same amounts of solution the water should be reduced according to the reaction stoichiometry as given in Eq. (2).
Agglomerated samples from 350 g of stucco binder, 1000 g of acid solution (80% water and 20% concentrated sulfuric acid) and 20 lb of ore were compared with agglomerates from 350 g of gypsum binder, 945 g of acid solution and 20 lb of ore. The agglomerates obtained from gypsum and stucco experiments are shown in Fig. 10. It was quite clear that the agglomerates with gypsum binder (left) are too wet. They had a shiny surface due to the free solution at the surface. Whereas, the agglomerates with stucco binder (right) were found to be of much better quality.

4.3. Analysis of stucco binder agglomeration

The use of stucco as a binder extends the solution agglomeration which in the absence of a binder primarily occurs via solution bridges. Stucco binder hydration reactions occur within the bridges and the agglomerate structure is strengthened. As the particles are connected during agglomeration they are bounded by a network of interlocking gypsum crystals, the product of the hydration reaction. The important features of stucco binder agglomeration are shown in Fig. 11. Further details are mentioned in the literature (Miller et al., 2009).

Heap leaching has been practiced for many years, but still lacks a definition of ideal agglomerates. Nevertheless, an attempt was made to construct a phase diagram which incorporates all the test results i.e. agglomerate size analysis, permeability values, electrical conductivity, visual inspection and results from column leaching tests to define agglomerate quality. In this regard a phase diagram as shown in Fig. 12 was constructed to describe the agglomerate quality for Zaldivar ore as a function of sulfuric acid solution addition and the amount of stucco binder. The region defined by the hatched box identifies conditions for high quality agglomerates as 3–5% stucco binder and 7–10% acid solution. Agglomerates prepared with other combinations of binder and sulfuric acid solution were either too dry or too wet. The percentage values reported in the phase diagram refer to kilograms of acid solution (20% sulfuric acid and 80% water) for 100 kg of ore.

5. Conclusions

Numerous binders for acid heap leaching of crushed copper ore have been suggested in the literature (Lewandowski and Kawatra, 2009a,b; Bouffard, 2005) but none of them have been adopted by the mining industry. Among the binders suggested is gypsum, but the effectiveness of gypsum has not been demonstrated. In fact, our experimental results show that gypsum itself is not an effective binder. In order to achieve adhesion of fine particles and the formation of stable agglomerates, stucco (calcium sulfate hemihydrate) looks promising. Stucco serves as an effective binder because of the stucco hydration reaction, which occurs during agglomeration of the ore, immobilizes the fines binding them together with coarser ore particles via the gypsum hydration product which forms in situ and serves to stabilize the agglomerates thus formed. It is expected that both the fine and coarse ore particles act as nucleation sites for the hydration of stucco.

The quality/stability of the agglomerates is revealed from results of various evaluation tests (agglomerate size distribution, permeability, electrical conductivity and visual inspection) and, the preferred conditions for the Zaldivar ore and corresponding particle size distribution have been established. The mix for effective agglomeration should contain about 85–90% ore, 7–10% sulfuric acid solution, and 3–5% stucco. Under these conditions the
The conductivity of the agglomerates is found to be between about 0.002 and 0.004 \(1/\text{(cm)}\). These preferred conditions are expected to change with ore type and particle size distribution. The use of stucco as binder extends the solution agglomeration which in the absence of binders occurs via solution bridges. Stucco hydration reaction occurs within the bridges and the improved agglomerate structure is established. As the particles are connected during agglomeration they are bound by a network of interconnected gypsum crystals, the porous product of the hydration reaction. Hence, a strong bonding mechanism occurs with a porous structure which accounts for the effectiveness of stucco binder. In this way, it is expected fines will be immobilized and the permeability will be sustained during the life of the heap leach operation. Future research will consider economic issues associated with the use of stucco as a binder in heap leaching operations.

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References


