Polyacrylamide as an agglomeration additive for copper heap leaching

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1. Introduction

Heap leaching is a method used to recover precious metals such as gold and copper from low grade ores. In copper heap leaching, the ore is stacked in approximately 6.1 m (20 ft) ‘lifts’ and an acidic leach solution (raffinate) is sprayed on the top of the heap. As the raffinate percolates through the heap, the copper is solubilized and retained in the liquid phase. The flowing liquid can also cause migration of fine particles within the ore bed. The migration of fines clogs the natural flow channels, and forms impermeable layers within the heap which the raffinate cannot penetrate easily. When this happens, solution flows around sections of the heap, leaving them un-leached or only partially leached, which lowers overall recovery. Agglomeration is one method which is being used to resolve this problem. Agglomeration causes the smaller particles to adhere to the surfaces of the coarser ore particles, which prevents fines from migrating. However, current practice is to agglomerate the ore by moistening it with raffinate. This procedure does not bind particles together very strongly, resulting in agglomerate breakdown, which causes fines migration. Binders are a potential solution to this problem since they will form stronger, more stable agglomerates which will resist breakdown. Not only should an effective binder have a strong affinity for the particle surfaces, it also must withstand the extreme acid environment which is found in a heap. In the past, in other heap leaching operations, binders were added without any systematic reasoning. The majority of common binders do not perform well in an acidic environment as would be experienced in a leach heap. The soak test was developed to do this. With use of this testing procedure, a variety of binders for agglomeration could be compared to determine which type produced the best results. Once a binder had been determined, it was important to investigate how and why it was working.

2. Theory

Attraction forces are forces which can act between ore particles and a binder, giving an agglomerate strength. Attraction forces between solid particles are mainly molecular, electrostatic, and magnetic (Lewandowski and Kawatra, in press; Pietsch, 2002). At small distances the effect of these forces can be great, although they decrease quickly with distance. These forces may also enhance the forces due to the other binding mechanisms, such as adhesion and cohesion forces, solid bridges, surface tension, or capillary pressure.

Molecular forces include (i) van der Waals forces, (ii) valence forces, and (iii) non-valence association.

i. van der Waals forces are physical forces of attraction and repulsion existing between molecules which occur due to polarization induced in each particle by the presence of others. Drying induces van der Waals interactions, causing the polymer chains to become irreversibly adsorbed to the ore.

ii. Valence forces arise when the bonds between atoms or molecules are broken, creating new surfaces with unsatisfied valences. If the newly created surface area is large, the valences themselves may recombine if newly created surfaces come close to each other.

iii. Non-valence association includes hydrogen bonding. Hydrogen bonding is an attraction interaction between an electronegative atom and a hydrogen atom (hydrogen bond donor) which is bonded to another electronegative atom (hydrogen bond acceptor), shown in Fig. 1. The hydrogen bond acceptor does not
need to be attached to a hydrogen atom. The electronegative atom is almost always fluorine, oxygen, or nitrogen. Hydrogen bonds are typically stronger than van der Waals forces, but they are weaker than covalent or ionic bonds. Due to the fact that hydrogen bonds are stronger than van der Waals forces, it was expected that hydrogen bonding would be occurring between the binder and ore surfaces would lead to more stable agglomerates. The strengths of hydrogen bonds vary depending on the bond donor and bond acceptor atoms, as shown in Table 1.

If a binder has hydrogen bond donor sites, it will increase the ability for hydrogen bonding to take place between the ore and polymer, giving additional strength to the agglomerate. If a binder does not have any donor sites, hydrogen bonds cannot take place, leaving the agglomerates with lower strength than those with binders which have donor sites.

Electrostatic forces may exist due to unsatisfied electrostatic fields. When surfaces are immersed in water, ion exchange with the liquid causes electrical double layers to form. One way binders would be attracted to the surfaces of the particles is through electrostatic attraction (Nasser and Franks, 2006). This allows them to be attracted to the negatively charged ore surfaces, neutralizing the surface charges of the ore particles. When anionic polymers are subjected to acid, their charges are neutralized, leaving them able to attach to the ore by electrostatic attraction.

Magnetic forces act similarly to electrostatic forces. This mechanism is limited to particles which possess magnetic properties, and are not applicable to this study.

Experiments were to be conducted to determine what types of binder produced the most stable agglomerates. They would also be used to conclude if either hydrogen bonding or electrostatic attraction could be the reason for the improved agglomerate stability.

3. Experimental

3.1. Materials

Two hundred pounds of a low grade chalcocite ore (Cu₂S) which was rich in silica (SiO₂) was received from a copper processing operation. The ore consisted of approximately 0.25% Cu₂S and 42% SiO₂. The ore was crushed to 85% passing 0.635 cm (1/4 in.) in order to be a suitable size for agglomeration tests. Identical samples were needed for experiments that had size distributions and compositions that were as nearly identical as possible. A consistent size distribution was particularly important, since the primary benefit of agglomeration was control of migration of fines, which was dependent on the quantity of fines present. Samples were produced by screening the entire ore sample received from the mine into five size fractions, given in Table 2. Each size fraction was divided into subsamples using a rotary splitter, and the individual subsamples were weighed to ensure that they were all of identical weights. Experimental samples were prepared by combining one subsample from each of the five size fractions. The resulting experimental samples then had size distributions identical to that of the original ore sample. The composition of the sample was analyzed using X-ray diffraction (XRD), near infrared spectroscopy (NIR), and ocular microscopy (OM), to determine the various minerals within the sample. The majority of the sample was found to be silica with trace amounts of copper-bearing minerals, such as chalcocite, covellite, and chalcopyrite. The mineralogical analysis is given in Table 3.

The average weight of each experimental sample was 500 g. The size distribution of the samples used is given in Table 2.

A limited number of experiments were also performed with a pyrrhotite ore (FeS). This ore was predominately pyrrhotite, and did not contain much gangue material. Approximately 3000 g of pyrrhotite was crushed and rotary split into uniform samples. The average weight of each experimental sample was 500 g. The size distribution of pyrrhotite samples used is given in Table 4.
3.2. Procedure

Agglomerate stability was evaluated using an acid soak test, shown in Fig. 2. First, approximately 500 g of a low grade chalcocite ore, which was rich in silica, was placed into an agglomeration drum. The drum was turned while a liquid or emulsion binder and raffinate mixture was sprayed onto the ore over a period of approximately 20 min, to give an even distribution of binder on the ore surface. The raffinate solution was applied with a spray bottle at a dosage of 0.08 mL/g ore. After the agglomeration was complete, the agglomerates were removed from the drum and placed carefully onto a Tyler 10 mesh (1.70 mm) screen. The agglomerates were then allowed to air dry, or cure, on the screen at ambient temperature (20–25 °C) for 24 h.

While the agglomerates were curing, an 18.9 L (5 gal) bucket was filled with a solution of 6 g H₂SO₄/L concentration, resulting in a pH of approximately 1.8. This concentration represented the acidity of the solutions of the leaching operations from which the ore was obtained. The Tyler screen with the cured agglomerates was then slowly lowered into the acid solution, ensuring the ore was completely submersed. The agglomerates were soaked for 30 min, and then the screen and remaining material was carefully lifted from acid solution and allowed to drain under gravity. The material which passed through the 10 mesh screen and remained in the bucket was allowed to settle. The solution was decanted to leave the solids, and the fine material was dried and weighed.

The value of “fines migration” was calculated from the weight of material which had passed through the Tyler 10 mesh screen. The fines migration percentage was calculated using Eq. (1). This test gives a quick assessment for the ability of each binder to retain fines in its agglomerates when subjected to acidic conditions.

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\text{Fines Migration} = \frac{\text{Weight of ore migrated out of the sample}}{\text{Total weight of } 10\text{ mesh fines available in the sample}}
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3.3. Equipment

Zeta potentials were measured by the streaming potential method, using an Anton Parr Electro Kinetic Analyzer (EKA) coupled with a Remote-controlled Titration Unit (RTU). The EKA applies a fluid flow across a stationary bed of particles and measures the voltage drop. Measurements began with an initial pH of about 10, and nitric acid was titrated into the system over time to lower the pH. The zeta potential was then plotted as a function of pH. The limitation to this unit is that the sample must contain particles coarser than 25 μm.

4. Results

To determine which binder produced the most stable agglomerates, a large variety of anionic, cationic, nonionic, and proprietary ionic charge binders were tested using the soak test, producing the results shown in Fig. 3. The binders and dosages were chosen based on studies completed by Lewandowski and Kawatra (in press). When comparing the results from the soak test, it was evident that some binders produced

![Fig. 2. Soak test experimental procedure.](image-url)

![Fig. 3. Soak test results using a range of products with varying ionic charge, categorized by ionic charge. Error bars shown are the variation between two sets of experimental results. For points where error bars are not visible, the symbols are larger than the error bars.](image-url)
a lower percentage of fines migration than others. While the anionic, cationic, and nonionic binder classes all showed significant variations in fines migration, most of the best performing binders were either cationic or nonionic. However, it was necessary to examine the results further to determine which type, and ionic charge, of binder would produce the more stable agglomerates.

When all of the soak test results were sorted in order of performance, as shown in Fig. 4, it was clearly evident that, in general, the polyacrylamide binders resulted in the lowest fines migration.

One reason the polyacrylamide binders produce better results than the remaining binders is due to a much higher molecular weight (Green et al., 2000; Green and Stott, 2001). It is known that higher molecular weight polymers lead to improved flocculation (Michaels, 1954). Comparing just the performance of the polyacrylamide binders with high molecular weights (molecular weights greater than 1 million Daltons), as shown in Fig. 5, eliminates many of the changes in flocculation due to differences in molecular weight. By comparing the same polymer (polyacrylamide) at relatively similar molecular

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**Fig. 4.** Soak test results using a range of products with varying ionic charge, categorized based on performance. Error bars shown are the variation between two sets of experimental results. For points where error bars are not visible, the symbols are larger than the error bars.

**Fig. 5.** Soak test results using a range of polyacrylamide products with varying ionic charge, categorized based on performance. Error bars shown are the variation between two sets of experimental results. For points where error bars are not visible, the symbols are larger than the error bars.
weight, it then becomes evident that cationic and nonionic polyacrylamides perform much better than anionic polyacrylamides, and the best performing binders were all non-ionic, as expected.

5. Discussion

5.1. Surface charge

The improved performance of the cationic and non-ionic binders over anionic binders can be partially attributed to the surface chemistry of the ore particles. The surface chemistry of the ore particles was determined using an electrokinetic analyzer (EKA) to measure the streaming potential across a packed bed of particles. The streaming potential was then used to calculate the zeta potential of the particles. At a pH of 2, the surface of the ore particles was found to have, on average, a slightly negative to neutral zeta potential, as shown in Fig. 6. The smaller particle size fraction has a slightly more negative average zeta potential than the larger size fraction particles, probably due to changes in the relative concentrations of the minerals present due to selective breakage when the ore was crushed. While the bulk zeta potential of mixed minerals is a poorly-defined concept, it does give some suggestion of likely surface reactions. The fact that, on average, the zeta potential is measured to be neutral to slightly negative at acidic pH suggests that cationic binders would tend to be bonded more strongly than anionic binders. However, the magnitude of the average zeta potential is low enough that it may not be a noticeable effect. Other factors, such as hydrogen bonding, were therefore considered to be more important.

It should be kept in mind that there may be another factor causing the anionic binders to behave more poorly in acidic solutions than cationic or nonionic binders. The carboxylate groups are weak acids, and so easily bind to hydrogen cations in acidic environments, causing them to lose their charge. The lack of electrostatic repulsion between the neutralized carboxylate groups then allows the polyacrylamide chain to coil up, reducing its ability to bridge between particles and act as a binder.

5.2. Hydrogen bonding

In addition to electrostatic attraction, binders can also attach to surfaces by hydrogen bonding. Hydrogen bonding occurs when there is an attraction interaction between an electronegative atom, and a hydrogen atom bonded to another electronegative atom. Hydrogen bonding always involves a hydrogen atom and is typically stronger than van der Waals forces, but weaker than covalent or ionic bonds. Due to the fact that hydrogen bonds are stronger than van der Waals forces, it was expected that hydrogen bonding would be occurring between the binder and ore surfaces.

Silica (SiO₂) is the major constituent of the ore that was studied here. When silica is placed in water, hydrolysis occurs to form hydroxyl (OH) groups on the surface of the particles. The surface silanol groups (–Si–OH) are hydrogen bond acceptors, and are maximized at a pH of approximately 2. Hydrogen bond donors can be found on the polyacrylamide chains, as shown in Fig. 7, and the polyacrylamides were the most effective binders. Non-ionic polyacrylamide has the most hydrogen bond donor sites as cationic and anionic polyacrylamides would be diluted by ionized groups. The polyvinyl acetate does not contain hydrogen bond donor sites, as can be seen in Fig. 8, and did not produce as stable of agglomerates compared to the polyacrylamide.

To verify if it was possible that hydrogen bonding was occurring, it was necessary to run a soak test comparing a material which had hydrogen bond acceptor sites and one that did not have any hydrogen bond acceptor sites. When hydrogen bonding is able to take place, it should result in less fines migration and therefore more stable agglomerates. The silica-rich ore (SiO₂) being used in these experiments thus far, have oxygen as hydrogen bond acceptors which would be attracted to the hydrogen bond donors of polyacrylamide.
The polyacrylamide agglomerates will therefore produce more stable agglomerates of silica-rich ore than raffinate alone. Pyrrhotite (FeS) is an example of an ore which does not have any hydrogen bond acceptor sites. One pyrrhotite sample was soaked in an acid solution to ensure that dissolution of the pyrrhotite was not occurring. The weight of the sample before and after soaking did not change significantly, indicating that the pyrrhotite did not dissolve upon contact with the acid solution.

When soak tests were run using pyrrhotite and polyacrylamide, hydrogen bonding was not expected to take place, and should therefore produce results similar to the use of raffinate as a binder. As can be seen in Fig. 9, the polyacrylamide binder produced a large reduction in fines migration for the silica-rich ore with its many hydrogen bond acceptor sites, while it did not significantly reduce fines migration in the pyrrhotite ore, which had no hydrogen bond acceptor sites. Negligible weight change of the sample was observed after soaking in an acidic solution indicating that dissolution of the pyrrhotite sample in acid was not occurring. These results strongly indicate that the primary mode of attachment for the polyacrylamides is hydrogen bonding, although it is possible that other factors, such as the presence of iron in solution due to minor dissolution of the pyrrhotite, may have been responsible as well.

### 6. Environmental safety of polyacrylamide

While polyacrylamides help to reduce fines migration and stabilize agglomerates which can lead to improvements in metal recovery rates, it is important to keep in mind that some polyacrylamides are more toxic than others. Certain non-ionic polyacrylamides are not considered toxic to aquatic organisms and have no known adverse effect on human health, as defined in the products material safety data sheets. Each product is slightly different, so upon use of a polyacrylamide product in agglomeration, it would be necessary to abide by all regulations given.

Environmental concerns with using acidic leach solutions are significant. To address this concern, strict regulations and testing procedures are followed to safeguard against spillage or leakage of the acidic leaching solutions into the surrounding groundwater. Therefore, any binder which may happen to be removed with the pregnant leach solution would have a limited chance of coming in contact with the outside environment.

### 7. Conclusions

The breakdown of agglomerates in heap leaching causes a loss of recovery. The use of binders aids in forming stronger, more stable agglomerates. In the past, binders were used without any systematic reasoning. This study was completed to develop a method which could be used to determine what binders would produce the most stable agglomerates for heap leaching applications and what attraction forces were occurring between the ore particles and the binders. To determine agglomerate stability, low grade chalcopyrite ore, which was rich in silica, from a southwest U.S. mine was agglomerated, and subjected to an acidic environment, at a pH of approximately 2. Agglomerates which were considered stable were those with a low percentage of fines migration.

For this ore, it was found that non-ionic and cationic polyacrylamides reduced the fines migration the best in a novel soak test. These binders increased agglomerate stability through hydrogen bonding and electrostatic attraction.

Hydrogen bonding occurred when the hydrogen bond donor sites on the polyacrylamide chains were attracted to the silanol group hydrogen bond acceptor sites in the ore, leading to more stable agglomerates. Non-ionic polyacrylamides had increased ability for hydrogen bonding, by having a larger number of hydrogen bond donor sites. Although these tests were completed using a low grade chalcopyrite ore, if a different ore was to be used, the soak test and surface charge determination procedures could be carried out on this ore as well, to identify an applicable binder. Hydrogen bonding could be expected to occur with the use of polyacrylamide, as long as the ore to be used in agglomeration had available hydrogen bonding acceptor sites, as are found with silica. Experiments using pyrrhotite, which has no hydrogen bond acceptor sites, showed that the polyacrylamide was a much less effective binder in these conditions.

The cationic binders, determined in this study to create more stable agglomerates, were found to neutralize the negative surface charge of the ore. It could be expected that most silica-rich ores, when subjected to similar acidic conditions as used in this test, would also possess negative surface charges. Therefore, the cationic binders determined in this study could be applicable to other applications, as electrostatic attraction would still be able to occur between the polymers and the ore particles.

It is recommended that soak tests and surface charge analysis be completed on any ore which is to be used in agglomeration for heap leaching operations. This should be done to select the most appropriate binder for the application.

### References


