

Novel Binders and Methods for Agglomeration of Ore

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Abstract

Many metal extraction operations, such as leaching of copper, leaching of precious metals, and reduction of metal oxides to metal in high-temperature furnaces, require agglomeration of ore to ensure that reactive liquids or gases are evenly distributed throughout the ore being processed. Agglomeration of ore into coarse, porous masses achieves this even distribution of fluids by preventing fine particles from migrating and clogging the spaces and channels between the larger ore particles. Binders are critically necessary to produce agglomerates that will not break down during processing. However, for many important metal extraction processes there are no binders known that will work satisfactorily. A primary example of this is copper heap leaching, where there are no binders that will work in the acidic environment encountered in this process. As a result, operators of acidic heap-leach facilities see a large loss of process efficiency due to their inability to take advantage of agglomeration. The large quantities of ore that must be handled in metal extraction processes also means that the binder must be inexpensive and useful at low dosages to be economical. The acid-resistant binders and agglomeration procedures developed in this project will also be adapted for use in improving the energy efficiency and performance of other agglomeration applications, particularly advanced primary ironmaking.

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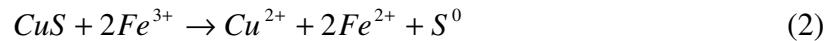
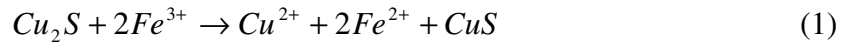
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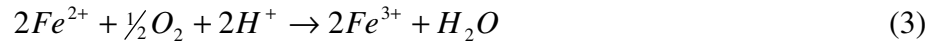
Introduction

As copper mines become depleted of higher grade ore bodies and operation costs increase, it has become necessary for mining companies to re-evaluate the current ways in which they process ore for the recovery of copper. Traditionally, copper sulfide ores have been crushed, milled, concentrated, smelted and refined using high-temperature pyrometallurgical techniques to produce saleable copper. These high temperature techniques are energy-intensive and tend to release toxic emissions into the air, and so more acceptable alternatives are needed. Several copper mining companies have recognized this, and with the advent of new technologies and knowledge these companies have begun moving towards processes based on hydrometallurgical operations. One such example is the Phelps Dodge Mining Company (PDMC), with their Mine for Leach (MFL) program at its Morenci mine site. This same approach is being used at other copper mines in North America as well as South America and Australia.

The basic approach to hydrometallurgical processing of a secondary sulfide such as chalcocite (Cu_2S) is a chemical dissolution process (Bartlett, 1997). The liberation of copper from the mineral is done through a two-step chemical reaction with iron (III), as illustrated in Equations 1 and 2 below.



The iron (III) is then regenerated from iron (II) using the reaction shown in Equation 3, which consumes oxygen and acid:



From these reactions, it can be seen that copper sulfide leaching requires both ready access of solutions with dissolved iron to the ore particles, and also easy flow of air to provide oxygen.

The geometry of the leaching operation consists of crushing the ore to an appropriate size (typically a top size of 0.5 inches) and stacking it in a heap. Then the crushed ore is conveyed into an agglomeration drum where it is wetted with raffinate (barren leach solution) that contains an additional 50 grams liter⁻¹ of sulfuric acid level (acid levels vary from mine to mine). Sufficient raffinate is added to make the ore into an adhesive mass, but not enough to convert it into a plastic or fluid mud. The moistened ore is tumbled in the drum and the smaller particles adhere to the larger particles. This agglomerated ore is conveyed to a stacking system or is trucked to a pad and placed on top of an aeration system to a set height know as a lift (lift heights vary from mine to mine, but approximately 20 feet is typical). The lift is then irrigated with raffinate either by drip emitters or a sprinkler system. The raffinate is then percolated through the heap and air is blown from the bottom allowing the copper to be liberated from the ore via the reactions mentioned earlier. The solution now referred to as PLS (pregnant leach solution) is captured in a pond and is sent to a solvent extraction and electro winning circuit where

the liberated copper is ultimately recovered. The duration of time in which the heap is leached is known as the leach cycle.

During the leaching cycle the agglomerates break down rapidly, and fines begin to migrate. The migration of fines clogs flow channels through the ore in the heap, which leaves areas in the heap void of the necessary reagents to dissolve the copper, resulting in poor recoveries. Due to this, some mines such as Phelps Dodge Morenci are experiencing lower recoveries than what is expected. A cost effective binding agent in the agglomeration step could greatly enhance the overall recovery of the heap by preventing agglomerate breakdown and limiting the migration of fines. In addition, the use of a proper binding agent should result in a more uniform percolation throughout the heap, which may also shorten leach cycles allowing production to increase.

Executive Summary

The objective of this project is to develop and implement binders and agglomeration procedures that will increase the efficiency of heap-leaching operations. This is particularly important in copper leaching operations, where the acidic leaching environment prevents existing leaching binders from working satisfactorily. Improved binders are also needed by the primary iron industry, which needs to efficiently agglomerate iron ore concentrates so that they can be reduced to metal using new, advanced ironmaking technologies. Without binders, agglomerates tend to break down over time as shown in Figure 1, leading to reduced fluid flow through the ore.

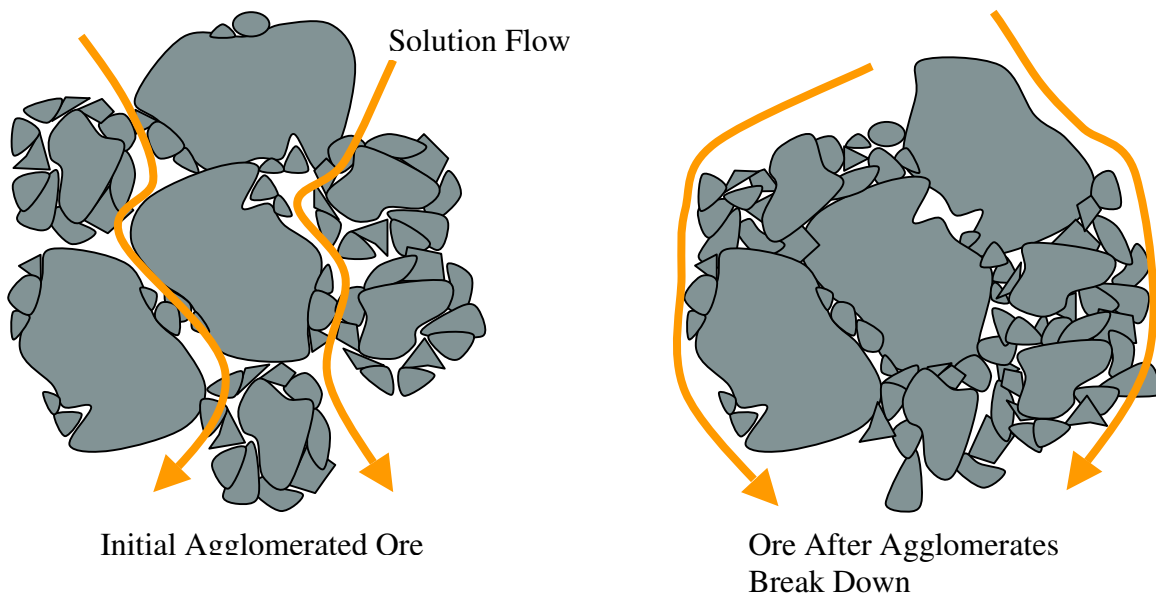


Figure 1: When ore is agglomerated without binder, initially the fines adhere to coarse particles, and solutions or gases can flow through easily. Over time, the agglomerates break down, and fines migrate to clog channels through the ore.

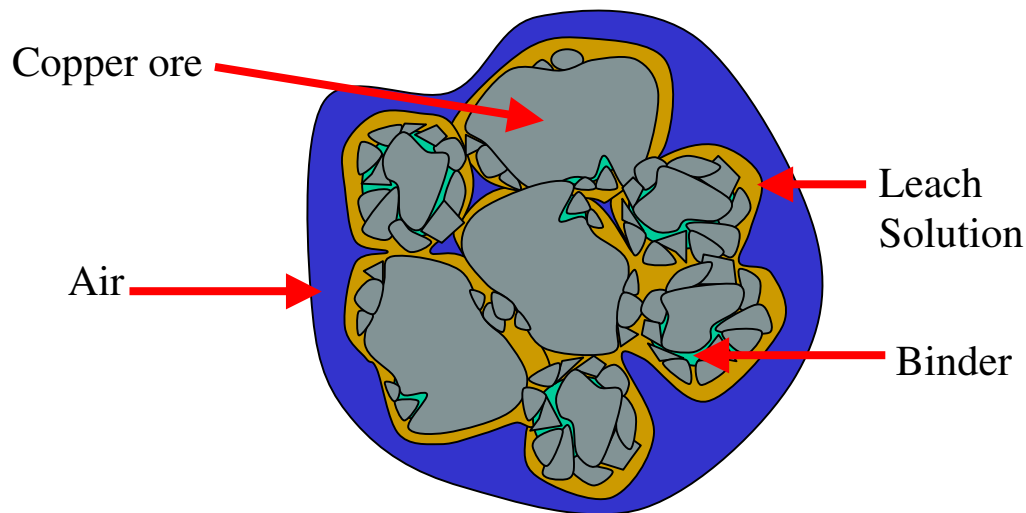


Figure 2: Small quantities of binder hold agglomerates together, allowing both solutions and gases to percolate readily through the ore, without channels being clogged by migrating fines.

To prevent this agglomerate breakdown from occurring, a binder is needed to attach the particles in the agglomerates together. This is done very successfully in many precious metal leach operations, where the use of an alkaline leaching solution makes it possible to use Portland cement and similar materials as binders. (McClelland, 1986; Chamberlin, 1986; Eisele and Pool, 1987). However, these cement-type binders dissolve readily in acid, and so are completely ineffective in an acidic leaching environment.

To date, no binders have been developed that are both effective in an acidic environment, and sufficiently economical to be used on a full industrial scale. The goal of this project is therefore to develop binders that meet these requirements. Binders are being developed based on theoretical considerations and on past experience, and are being evaluated to determine their effectiveness.

Past research in ore agglomeration has been hampered by the lack of a quantitative measurement of agglomerate quality. One of the first concerns in this project has therefore been the determination of a satisfactory set of tests that can be used to evaluate binders. After a thorough review of the literature and extensive discussions with the industrial partners, the following testing protocol has been devised:

1. Initial testing of a binder is conducted using a “soak test”, which consists of immersing agglomerated ore in raffinate and observing the degree of breakdown of the agglomerates with time. This is the simplest test, using only 500 grams of ore per test, and can be conducted rapidly for a number of binders, but the results are only qualitative.

2. Binders which perform well in the soak test are then evaluated in the percolation test, using the apparatus shown in Figure 3. This test gives a quantitative measurement of the permeability of the ore to the leach solution as a function of time, and also provides a measure of the “slump” of the ore.

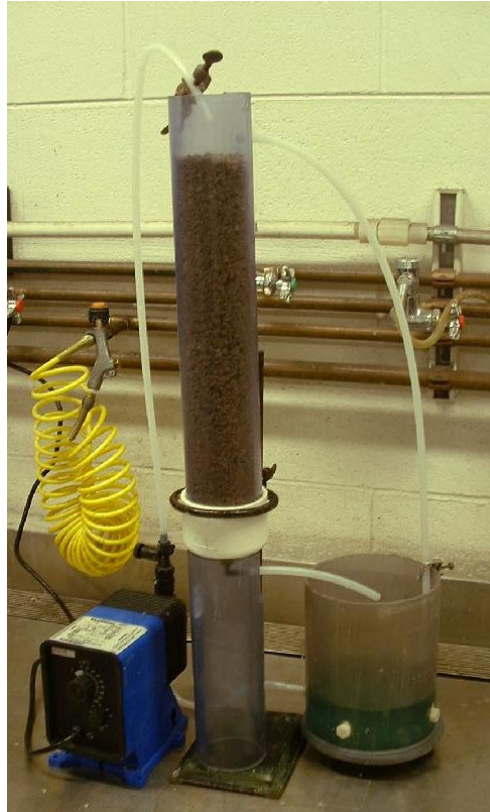


Figure 3: One of the percolation test columns provided to MTU by Phelps Dodge Inc. Agglomerated ore is added to the column, and raffinate is circulated through the agglomerates continuously while the flowrate of raffinate is monitored. The “slump”, or decrease in height of the ore, is also measured, and the quality of the agglomerates over time is monitored visually.

3. Following the percolation tests, the final test for a given binder will be a long-term column leach test, using the leaching columns shown in Figure 4. These columns were constructed by Phelps Dodge specifically to simulate as closely as possible the conditions seen in their industrial leaching heaps. Since long-term column tests typically run for 150 days and require up to 100 pounds of ore per test, only the most promising binders will be tested in this way.

Industrial cost-share for this project is being provided by Phelps Dodge, Inc.; Newmont Mining Co., and Northshore Mining Co. All three companies have already contributed considerable amounts of engineering time to this project, and Phelps Dodge has provided experimental apparatus for conducting percolation and column leaching tests. Phelps

Dodge has also provided several hundred pounds of their Mine for Leach (MFL) ore, and will provide additional ore as needed in the project.



Figure 4: Leaching columns provided by Phelps Dodge set up for leach testing at Michigan Technological University. These columns are used for long-term testing for periods of several months, and provide the closest simulation of actual industrial heap-leaching behavior that can be achieved in the laboratory.

Experimental

Materials

200 lb of Mine for Leach (MFL) Ore was received from the Phelps Dodge Morenci operation for use in soak tests and percolation tests. This ore was crushed to pass ¼ inch in order to be a suitable size for agglomeration tests, and was then divided using a rotary sample splitter to ensure that all samples used in experiments had identical size distributions and compositions.

An analysis of the raffinate composition at the Morenci operation was provided, and a simulated raffinate solution was prepared that contained all of the elements that were present at concentrations greater than 100 ppm, which are shown in Table 1. These elements were added as sulfate salts, along with sufficient sulfuric acid to simulate the Morenci raffinate:

Table 1: Composition of simulated raffinate.								
Elements	Al	Ca	Cu	Fe	Mg	Na	Zn	SO ₄ ⁻²
Concentration (mol/l)	0.254	0.013	0.004	0.056	0.089	0.000869	0.0244	0.0612

Based on theoretical considerations and availability, the first binders tested were sodium silicate, which reacts with acid to form a silica gel that can act as a binder; and calcium hydroxide, which reacts with sulfuric acid to precipitate calcium sulfate dehydrate (gypsum). Additional binders that are expected to perform well in acid solutions, primarily organic polymers, are being obtained from chemical manufacturers.

Test Procedures

Three tests are being used to evaluate binders: the soak test, the percolation test, and the column leach test.

Soak Test is shown schematically in Figure 5. Ore that was crushed to pass $\frac{1}{4}$ inch was first combined with binder. The mixture was then agglomerated in a rotating drum at 35 rpm while spraying it with simulated raffinate over a period of 20 minutes, gradually increasing the moisture content of the ore to no more than 15% moisture. The agglomerates were placed on a 10 mesh screen and allowed to air-dry and cure for at least 24 hours. The screen with the cured agglomerates was then immersed in simulated raffinate solution for 4 hours, and any disintegration of the agglomerates was observed.

The first series of soak test experiments examined the following binders:

1. Raffinate alone (control experiments, simulating current practice at Morenci)
2. Calcium Hydroxide (reacts with sulfuric acid to form gypsum precipitates)
3. Sodium Silicate (precipitates silica gel on contact with acidic solution)

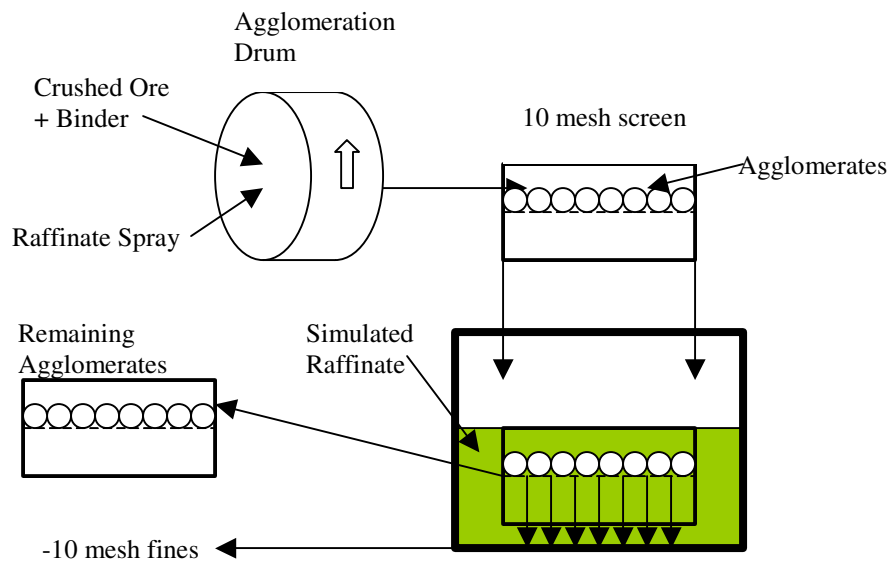


Figure 5: Schematic of agglomerate soak test. The quantity of fines passing through the 10 mesh screen was measured in an attempt to provide a quantitative measure of binder effectiveness.

Percolation Test will be conducted as shown in Figure 6. A 3-inch diameter transparent plastic column is filled with agglomerated ore, and simulated leach solution is added to the top of the column. A portion of the solution percolates through the ore and exits at the base of the column, while any excess circulates back to the holding tank. The flowrate through the exit port is measured to determine the ore permeability. In addition, the height of the agglomerated ore in the column is measured as a function of time. As agglomerates break down, the packing density of the particles in the column increases, and so this “slump” measurement is a direct measure of the degree of agglomerate breakdown.

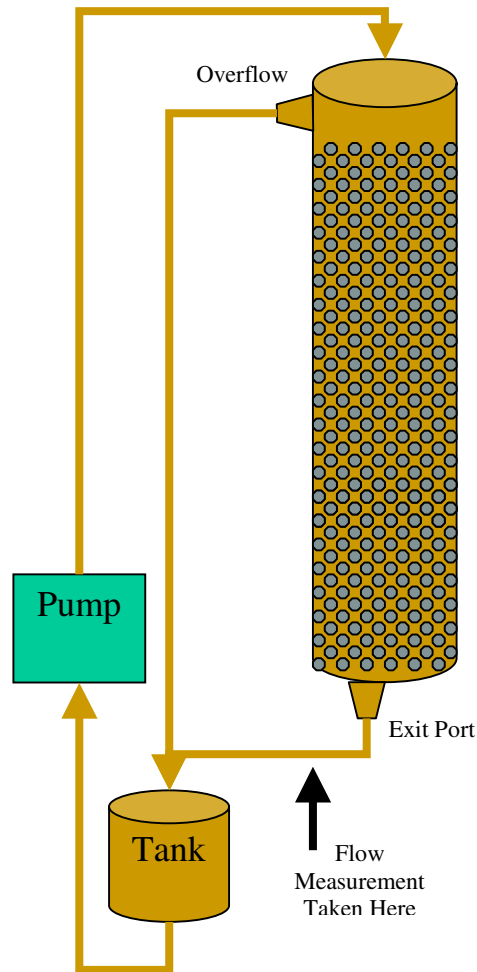


Figure 6: Schematic of percolation test. The degradation of agglomerates over time is indicated by the slump of the ore in the column as it settles and packs more densely, and by the decreased flowrate of solution through the ore.

Leach Test will be conducted using columns designed as shown in Figure 7. This test requires a 150 day leach cycle, and will check for any adverse effects the binders might have on the overall copper recovery that would not be apparent in the percolation or soak tests, such as chemical reaction with the leaching solutions or precipitation of impermeable gel coatings over leachable ore. This test simulates a heap by scaling down

variables such as flow rates, air injection, temperature, etc. The ore is agglomerated with the selected binder, and the agglomerates are loaded into a 5 foot tall 6 inch diameter column. Leach solution is then pumped in at the top of the column at a rate that corresponds to the flowrate per unit area used in the field. After percolating through the column, the solution is then captured at the bottom for chemical analysis. All solutions are analyzed so that any possible adverse effects can be noted. This test is the final laboratory evaluation of a binder, and due to the long time periods involved will only be used for binders that performed satisfactorily in the percolation and soak tests.

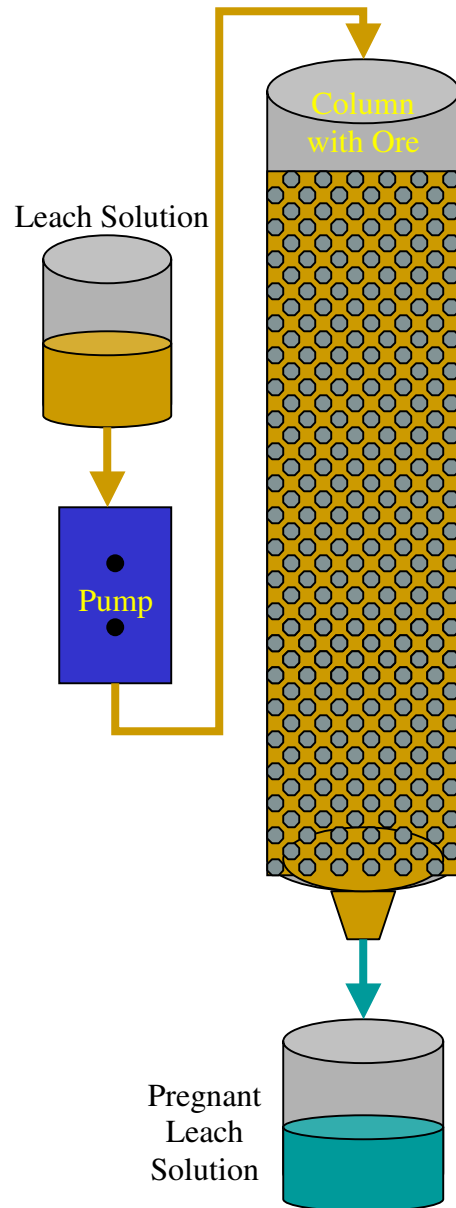


Figure 7: Schematic of leach testing column, designed to simulate leaching behavior expected in a full-scale heap leaching environment as closely as is practical in a laboratory setting.

Results and Discussion

Ore agglomerated with simulated raffinate solution alone is shown in Figure 8. After agglomeration, the ore was allowed to air-dry for 24 hours before immersing it in a simulated raffinate solution for the soak test. The degradation of the agglomerates over time can be clearly seen in Figures 9-11. After removing the ore from the solution and air-drying, the agglomerates had almost completely broken down, as can be seen in Figure 12. This control experiment clearly shows that, in the absence of a binder, the agglomerated ore has only negligible ability to remain agglomerated in the presence of leaching solution. This is in spite of the fact that, before the soak test, the air-dried agglomerates appeared to be strong and durable, and confirms that a binder is very necessary for agglomerating this ore.



Figure 8: Agglomerated ore after air-drying for 24 hours, before soak test in simulated raffinate. These agglomerates were made using only raffinate as binder.

Following the control tests with no additional binder other than raffinate, two candidate binders were examined: Sodium silicate and calcium hydroxide. The binders were both added to the ore at a dosage of 0.5 g binder per 500 g ore, which corresponds to 1.0 kg binder per metric ton ore (kg/mt). Each binder was added to the ore as a dry powder and mixed with the ore before agglomerating. After air-drying and curing for at least 24 hours, agglomerates made with each binder were immersed in simulated raffinate for 4 hours. At the end of this time, the 10 mesh sieve with the remaining agglomerates was removed, and the -10 mesh fines that “dropped” from the agglomerates were filtered from the simulated raffinate and weighed. The results for these two binders are shown in Table 2.

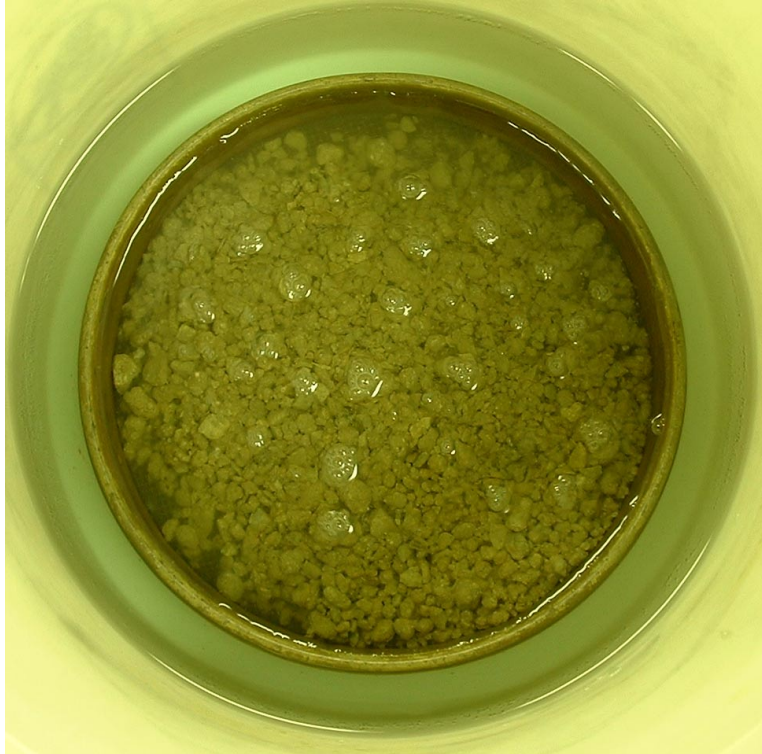


Figure 9: Raffinate-bonded agglomerates after initial immersion

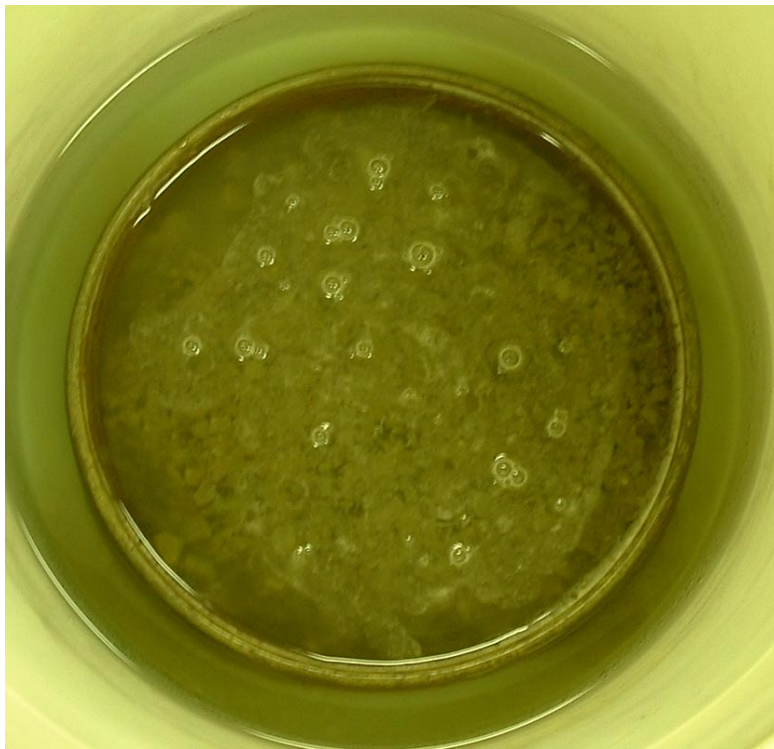


Figure 10: Raffinate-bonded agglomerates after 5 minute immersion.

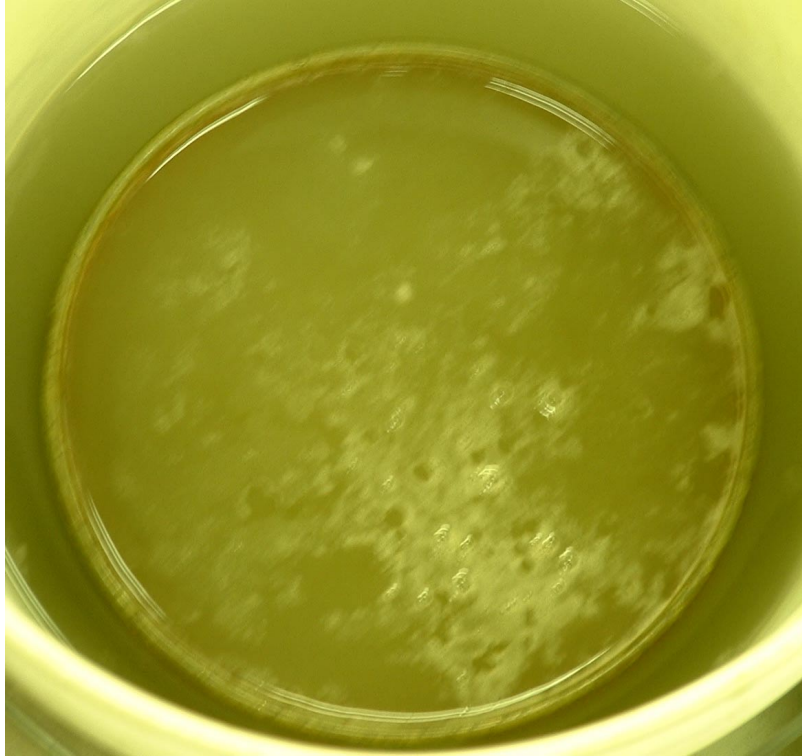


Figure 11: Raffinate-bonded agglomerates after 20 minute immersion.



Figure 12: Raffinate-bonded agglomerates removed from simulated raffinate after 20 minute immersion. The agglomerates have almost completely broken down.

Table 2: Soak test results for calcium hydroxide and sodium silicate binders.			
Binders	Binder Addition, g	Ore Weight (g)	-10 mesh Dropped Fines (g)
Ca(OH) ₂	0.5	580.2	89.755
Na ₂ SiO ₃ .	0.5	552.1	37.96

From the results in Table 2, it can be seen that less than half the quantity of fines dropped through the screen during the soak test using the sodium silicate, showing that it is a more effective binder than the calcium hydroxide, although both binders still allowed a significant degree of agglomerate breakdown. Additional experiments are underway with the sodium silicate to determine the effects of dosage and addition methods on its performance as a binder.

Additional binders to be examined will fall into the following general classes:

1. Inorganic binders. Based on the performance of sodium silicate, inorganic materials with a similar ability to dissolve in alkaline or neutral solution while precipitating on contact with acid will be examined. Different sodium silicate formulations will be examined, as will materials such as alkali-modified fly-ash.
2. Polymeric binders. Long-chain polyacrylamides, gums, and starches that have particular ability to resist the action of acid will be selected. In particular, anionic polymers that can bond to hydrogen ions that adsorb onto the mineral surface will be examined.
3. Bacteria. The action of bacteria, particularly Thiobacillus ferrooxidans, is critical for copper leaching reactions, and they are already present in leaching operations. Since these bacteria attach to mineral surfaces, they have the potential to act as a binder between particles which will not only perform well in acid solutions, but will also naturally grow and become more effective with time.

Conclusions

Agglomeration of copper sulfide ore for heap leaching critically requires a binder, as binderless agglomerates break down rapidly and completely on contact with acidic leaching solution. Based on soak test results, it is evident that sodium silicate is moderately effective as a binder, and will be evaluated further. This binder functions by reacting with acid in the leach solution to form a silica gel that causes particles to adhere together, and other binders that show this behavior will also be investigated.

Additional binders, particularly organic polymers, have been selected based on their expected behavior in acid solutions, and are being obtained for testing. All binders will be evaluated by soak testing and percolation testing to evaluate the quality of the agglomerates that they produce.

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