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. Primary examples of this are copper heap leaching, where there are no binders that will work in the acidic environment encountered in this process. As a result, operators of many 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 a broad range of mineral agglomeration applications, particularly heap leaching.

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Introduction

The high grade ores which were once easily mined have become depleted. This means it is necessary for ore to be ground to a finer particles size in order for it to be liberated. The finer-grained ores is much harder to handle, and is not producing the required recoveries with the current operating conditions. Agglomerating the material into pellets or similar masses or particles that are durable enough to be handled is a solution to dealing with these fine mineral concentrates, allowing them to be more easily processed to extract the valuable minerals at lower costs. Agglomeration is important in the heap leaching of metals such as gold and copper as it allows for easier handling and processing but also increases the availability of transport of the leach solutions throughout the heap.

Heap leaching of copper sulfide minerals requires the access to 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 conveying into an agglomeration drum where it is wetted with raffinate (barren leach solution). Sufficient raffinate is added to make the ore into ad 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 transported to a pad and placed on top of an aeration system to a set height known 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 selectively dissolved from the ore. The solution, now referred to as PLS (pregnant leach solution), is captured in a pond. It is then sent to a solvent extraction and electro winning circuit where the liberated copper is ultimately recovered.

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 that 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 results it a more uniform percolation throughout the heap, which may also shorten leach cycles allowing production to increase. The problem with copper leaching is that it requires a high use of acid solutions which decrease the pH of the heap to very acidic conditions. Most agglomeration binders which are used successfully in other operations require a more neutral pH or alkaline. Acid-resistant binders are needed for these copper operations which will not breakdown in acid, allowing access of air and leach solutions to reach the ore particles.

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 form working satisfactorily. To prevent 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 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 for mineral agglomeration that meet these requirements, allowing for increased processing efficiency. Binders are being developed based on theoretical considerations and on past experience, and are being evaluated to determine their effectiveness in an acidic leaching environment.
Three tests have been developed to determine the quality of a binder to be used in agglomeration in the heap leaching process. These tests are the soak test, percolation columns, and long-term leach columns. The soak test consists of immersing agglomerated ore in an H_2SO_4 solution and observing the degree of breakdown of the agglomerates with time. The percolation columns give quantitative measurements of the permeability of the ore to the leach solution as a function of time, and also provide a measure of the "slump" of the ore. The long-term leach columns simulate as closely as possible the conditions seen in their industrial leaching heaps. It is emphasized that these testing procedures are still not yet confirmed. Duplicate testing is currently being run to verify the accuracy of these testing processes.

The soak test and percolation columns along with the calculations of fines migration, bulk density, and hydraulic conductivity were some factors that went into narrowing down the field of binders to a select few that will be tried in the long-term leach columns.

A total of six large long-term leach columns are planned. The first column, with ore agglomerated with only raffinate, has been started. This column was started to help locate any errors or trouble within the operating procedures. A failure of the agglomerating drum motor was discovered and fixed. The next of the remaining five columns will be filled with non-agglomerated ore, the third will have ore agglomerated with AGG950, the fourth with AGG9250 with Dearcodox, the fifth with ore agglomerated with Tall Oil Pitch, and finally the sixth will have ore agglomerated with Chem-Loc 411.

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.

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

Recently, two 350 gallon totes of industrial raffinate were received from Phelps Dodge. This raffinate was drawn directly from their process lines and will be used in the long-term leach test columns. It will also aid in the simulation of the industrial leaching heaps. The results of the chemical analysis are shown in Table 2. As you can see, these results are similar to the simulated raffinate which had been used prior to receiving the industrial raffinate.

Table 2: Composition of Industrial Raffinate.

Elements	Al	Ca	Cu	Fe	Mg	Na	Zn
Concentration (mol/l)	0.299	0.016	0.005	0.050	0.107	0.000742	0.0271

Equipment

Soak Tests

The soak tests help look at how well the agglomerates hold together after being agglomerated with various binders. A 10 mesh screen is used as a base for the agglomerates while they are being immersed in a sulfuric acid solution. The fines which pass through the 10 mesh screen can then be collected. A screen and fines are shown in Figure 1.

Figure 1: On the right is the 10 mesh screen holding the previously immersed agglomerates. The bucket on the left contains the fines which have been released due to the breakdown of the agglomerates.

Percolation Columns

The percolation columns have been designed to help analyze the effects of various binders on a slightly smaller scale. These columns, shown below in Figure 2, were assembled using equipment provided by Phelps Dodge Inc. Each column has an inside diameter of 3 inches, and a height of 20 inches. The raffinate is held in a container at the base of the columns, and is pumped up to the top where it slowly drips onto the surface of the ore. After percolating through the columns, the solution is passed through a flask where any fines passing through the column are collected.

Figure 2: Percolation test columns assembled at MTU using equipment provided by Phelps Dodge Inc. Agglomerated ore is added to the column, and raffinate is circulated through the agglomerates continuously. The “slump”, or decrease in height of the ore, is also measured. The columns shown each contain agglomerates made with a different binder, and were initially all filled with the same amount of ore.

Long-Term Leach Columns

The long-term leach columns have been assembled to simulate the heap leaching process occurring at the Morenci location of Phelps Dodge Inc. The columns, shown below in Figure 3, were created out of materials received from Phelps Dodge. Our laboratory houses six large PVC columns. These columns are approximately 5 ft in height with an inside diameter of 5.89 in. Each column has recently been equipped with an air flow meter which injects air into the lower part of the column, and a cover containing a pressure release valve. Raffinate is held in the side containers and is pumped into the top of the columns. It then percolates through, and the pregnant leach solution is then collected in the buckets below.

Figure 3: 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.

<u>Test Procedures</u>

The soak test is the first analysis which is performed on a binder. Approximately 500 grams of ore is used in this test. The ore is agglomerated in a rotating drum with raffinate and the binder over a period of 20 minutes. The ore is then transferred to a 10 mesh screen and allowed to air dry or cure overnight, or for approximately 24 hours. The screen is then lowered into a 6 g H_2SO_4/L water solution and left to sit from 30 minutes. After 30 minutes, the screen is carefully removed. The acid solution is decanted, and fines passing through the screen are collected, dried, and weighed.   The procedure is diagramed in Figure 4.

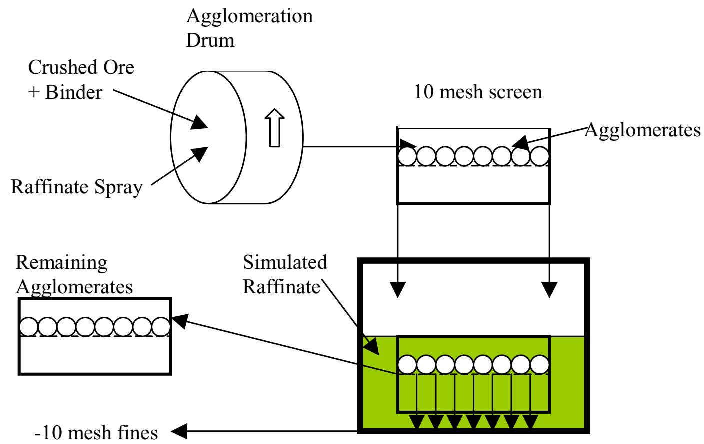

Figure 4: Schematic of Agglomerate Soak Test.

To further test the selected polymer, a percolation column test is performed. Two kg of ore is agglomerated with raffinate and the binder. The ore is then transferred to a 3 inch diameter column. Raffinate solution is dripped onto the ore at the top of the column where it passes through the ore, and exits out the bottom. Figure 5, below, outlines this process. After approximately an hour, the waste acid solution is decanted, and fines which have passed through the column are collected, weighed, and dried. The mass of particles which are collected is a measure of the degree of fines migration that occurs with a given binder. In addition, the height of the agglomerated ore is measured as a function of time. This “slump” measurement is a direct measure of the degree of agglomerate breakdown.

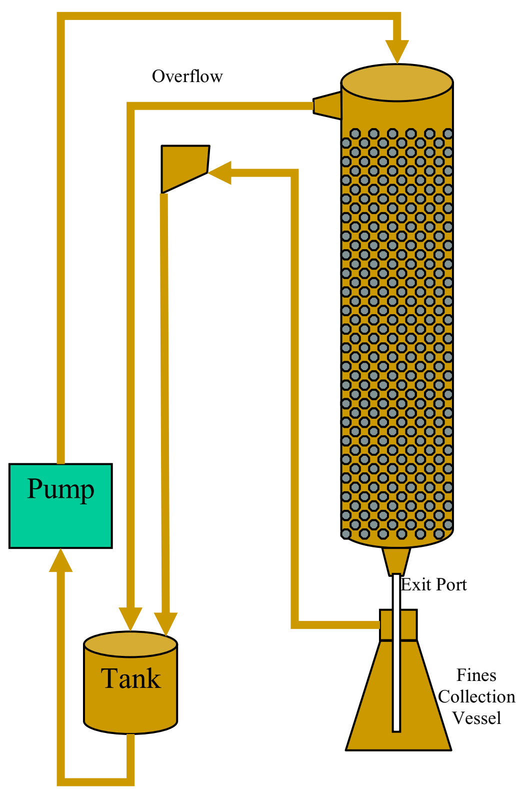

Figure 5: Schematic of Percolation Test.

The best binders will then be tried in the long-term leach columns, as the leach cycle for these columns is 150 days. These columns follow the same general procedure as the percolation columns but on a much larger scale. Here approximately 80 lbs of material is agglomerated with raffinate and a selected binder, in an agglomerating drum. It is then spread out to air dry, or "cure" for at least 48 hours. After dry, the agglomerates are transferred to the column. The column is capped with a cover containing a pressure release valve. This enables tests to be done which may involve subjecting the column to pressure changes. The raffinate is pumped to the top of the column at a flow rate of 27.9 ml/hour. This rate was determined by the rate being used at the plant, scaled down appropriately to these equipment sizes. At this time air is also being injected into the bottom of the column at a flow rate of 16.68 ml/min. The raffinate solution percolates slowly through the column, and is collected in a bucket below, as shown in Figure 6. The solution collected is called the pregnant leach solution, and is later tested for copper and iron recovery along with free acid, pH, oxidation/reduction potential (ORP), and temperature.

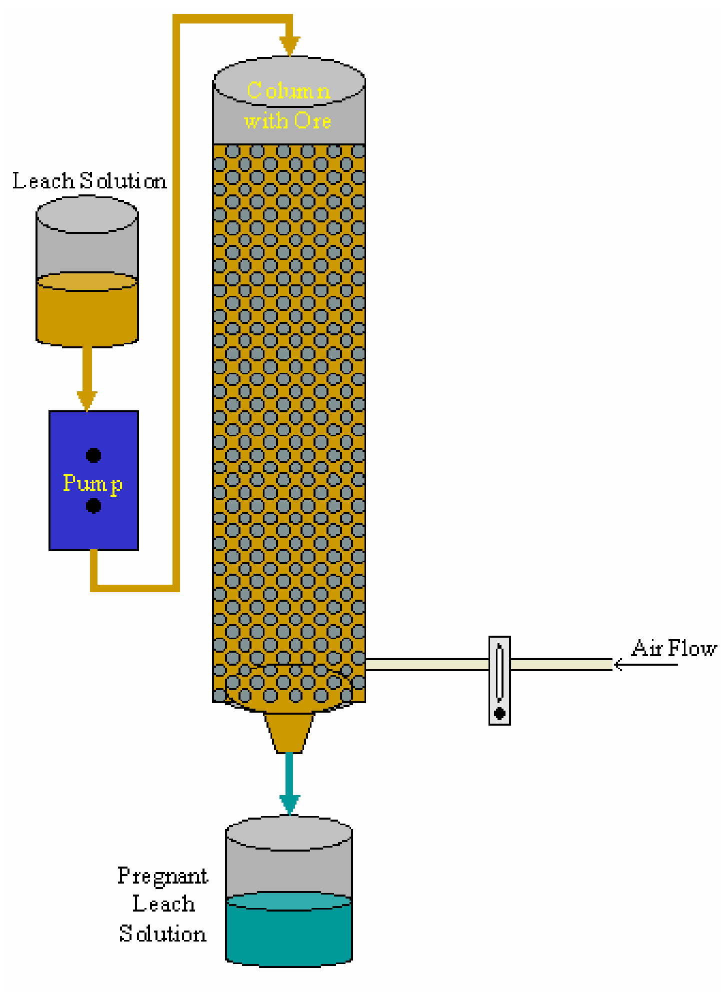

Figure 6: Schematic of Leach Testing Column

Results and Discussion

The development of the soak test, percolation columns, and long-term leach columns are still being refined. Replicate testing is being performed to analyze the accuracy of these tests.

From completed soak tests the binder addition rate is a key factor in determining the overall strength of a particular binder within agglomerates. Table 3 gives an overview of the current soak tests which had been run at different binder addition rates. It can be seen that an addition rate of 5 pounds of binder per ton of ore seems to be the optimal addition point. Further tests will be done to determine the optimum binder addition rate for each particular binder.

Table 3: Variable Binder Addition Rates

Binder	Addition Rate lb/ton	Fines Migration
*Completed without Cure Time		
Percol 351	1	25.17%
Percol 351	2.5	10.17%
Percol 351	5	4.63%
Aerospray 70-A	1	24.43%
Aerospray 70-A	2.5	11.09%
Aerospray 70-A	5	2.90%

The soak tests determined several binders which showed improvement over agglomerating with raffinate alone. The binders which showed the best improvement over the ore agglomerated with raffinate only, are listed in Table 4.

Table 4: Soak Test Results
Comparison of the Best Performing Binders

Binder	Addition Rate lb/ton	Cure Time	% of Grams Passed per Grams Less than 10m Availible in Sample
Baseline	No Binder	Yes	30.06%
Baseline	No Binder	Yes	27.28%
Aerospray 70-A	5	Yes	23.46%
Aerospray 70-A	5	Yes	18.36%
AGG 9250	5	Yes	4.34%
AGG 9250	5	Yes	5.07%
Chem-Loc 411	5	Yes	11.36%
Chem-Loc 411	5	Yes	5.45%
Magnafloc 351	5	Yes	16.95%
Magnafloc 351	5	Yes	23.62%

The Magnafloc 351(formerly Percol 351), Aerospray 70A, Chem-Loc 411, AGG 9250 when used at a rate of 5 lb/ton showed the best improvements in agglomeration stability (least amount of fines released). These binders, along with one other binder, Tall Oil Pitch, were then used in the percolation columns. Figure 7 shows a summary of the ratio of the weight of the fines migrating out of the column to the total weight of -10 mesh fines which were available in the percolation column tests. The Tall Oil Pitch and AGG 9250 show the least fines migration out of all 6 binders tested, indicating the least tendency for the agglomerates to break down.

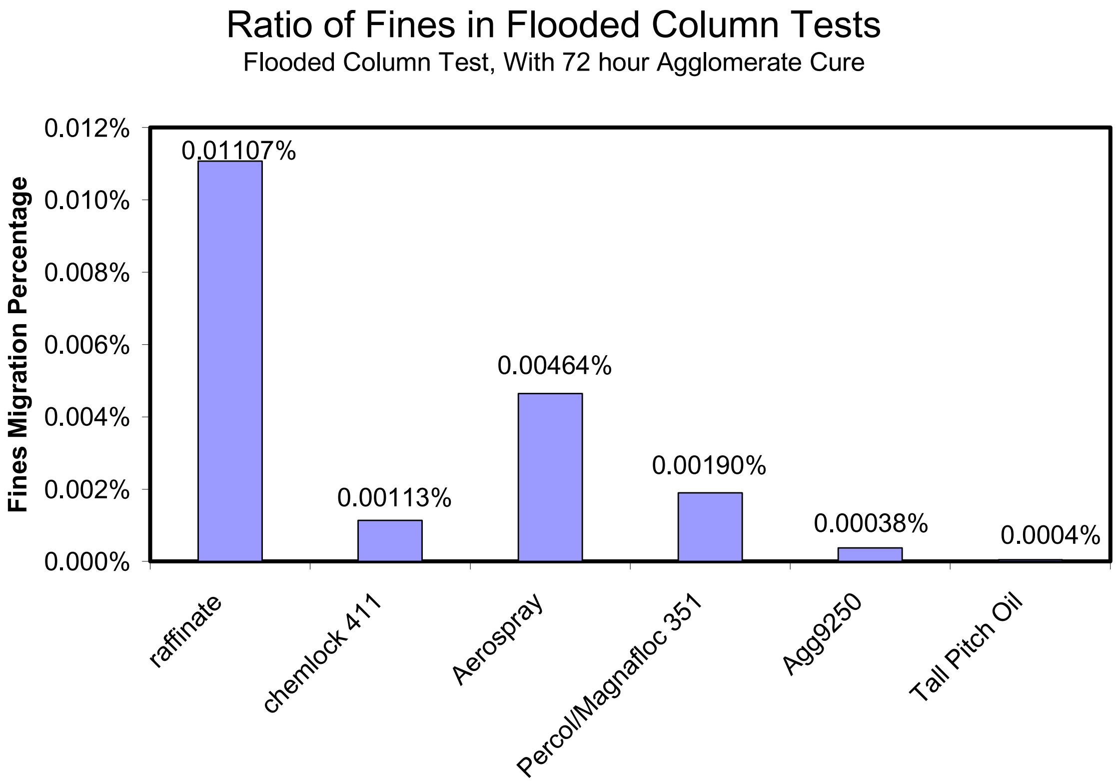

Figure 7: Ratio of Fines in Flooded Column Tests

The ore bulk density also varied for these 6 particular binders. Although the Tall Oil Pitch had the least amount of fines present in the raffinate solution, its bulk density was almost the highest out of those tested. A higher bulk density indicates a decrease in void space and more compaction of the ore in the column due to the breakdown of the agglomerates. Figure 8 shows the ore bulk density with time for the various agglomeration binders.

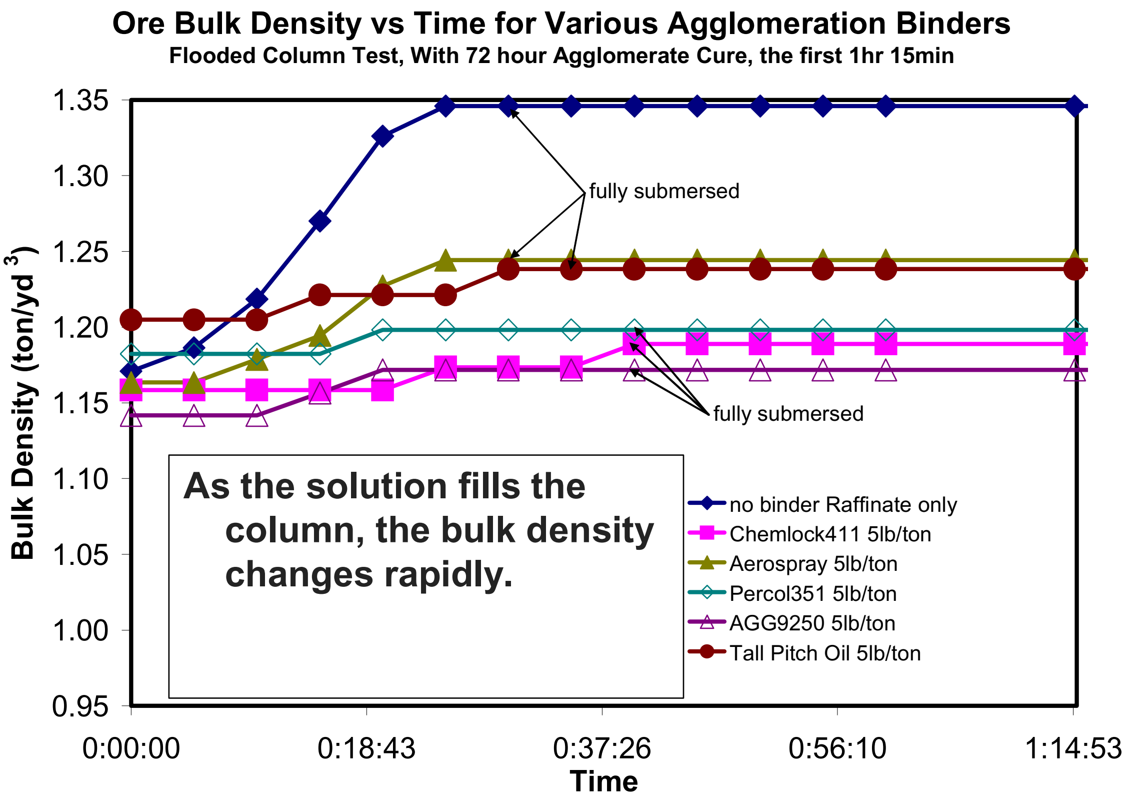

Figure 8: Ore Bulk Density vs. Time for Best Performing Binders

The three binders which had the smallest initial change in bulk density were the Magnafloc/Percol 351, Chem-Loc 411, and AGG 9250. The Tall Oil Pitch bulk density was not as good as the others, but the agglomerates never visually broke down. The agglomerates in the raffinate & Aerospray 70-A columns could be seen breaking down.

The turbidity of the solution in the column also gives an indication of the strength of the agglomerates. A more turbid solution is due to more fines being released into the solution from the breakdown of the agglomerates. The Magnafloc/Percol 351 showed the least turbidity where as Aerospray 70-A and raffinate alone had turbid solutions that could easily be seen.

The availability for solution to flow freely through the heap, or the hydraulic conductivity, was calculated as another measure of agglomeration strength. If a particular binder has a high hydraulic conductivity this means the reagents can be carried through the heap easily, which allows for better kinetics. Measurements to determine conductivity were taken on the same six binders as above. The summary of this calculation are shown in Figure 9. The Magnafloc/Percol 351 shows the highest conductivity, and the Aerospray 70-A produced the worst out of the six. However, all binders had higher conductivities than the test agglomerated with raffinate only.

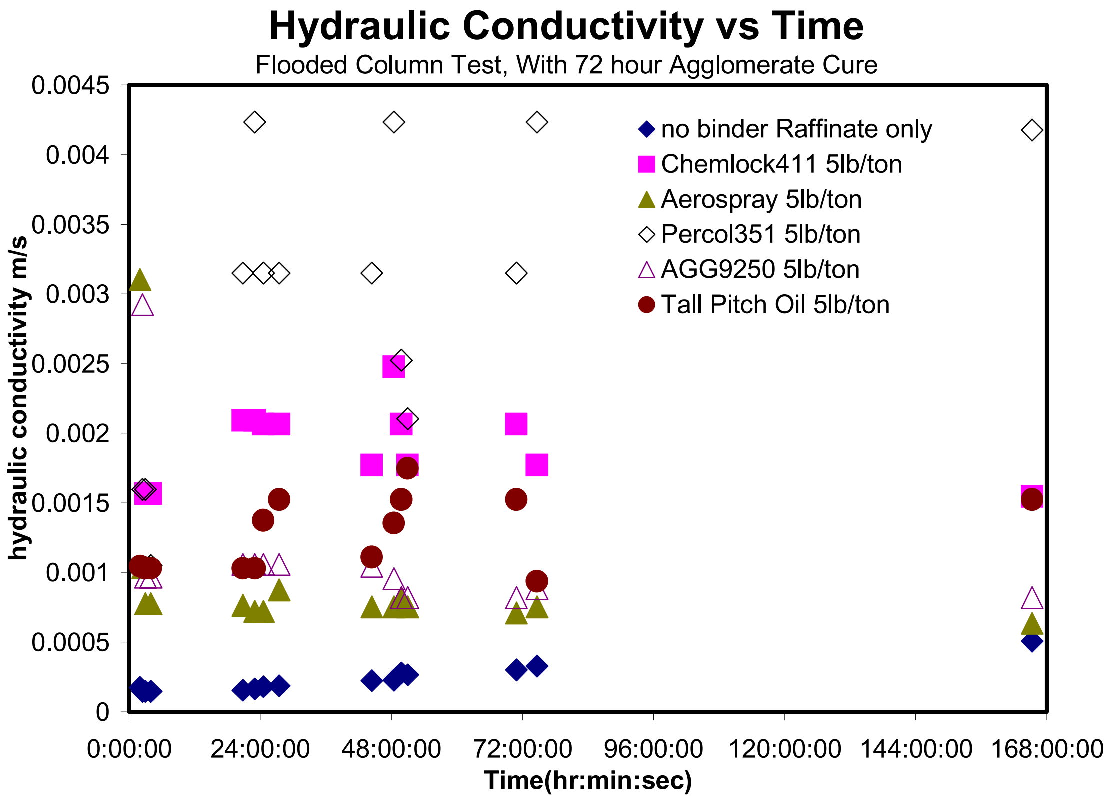

Figure 9: Hydraulic Conductivity for the Best Performing Binders

The fluctuations within the data may be a result of the flow rates cycling up and down slightly due to the pumps heating up and not performing properly. Any future tests will include a flow rate taken immediately after the change in height is taken.

Due to these results the AGG 9250, Tall Oil Pitch, and the Chem-Loc 411 will be the three binders which will be tested in the long-term leach columns. The other columns will include a non-agglomerated ore column, a column with ore agglomerated with raffinate only, and the final column will have ore agglomerated with AGG 9250 with an addition of Dearcodox. The Dearcodox product was a solution that was received with the AGG 9250 binder. This product is said to help aid in copper recovery.

One column agglomerated with raffinate only is currently running. This gives time to locate any errors in the agglomeration process or column operations. It was found that the current agglomeration drum did not have the motor capabilities to hold the 80 pound load required. This motor was then repaired along with other screw fixtures on the drum to leave it in working order. The ore was spread out to dry, for 48 hours to allow for adequate dry time. The ore was loaded into the column without a problem, and the raffinate solution was begun pumping into the top of the column. After approximately one week after the solution was started the first sample was collected. Samples are collected every Monday, Wednesday, and Friday each week. Each sample is tested for copper and total iron concentration, pH, temperature, Oxidation/Reduction Potential (ORP), and acid content. The excess PLS solution is kept in a container provided by Phelps Dodge, which will later be shipped back to their facilities. This way no disposal of the acidic solution will be necessary.

Future and Continuing Test Work

From the results of all tests to this date, it can be seen that the most effective binders are nonionic materials. Research is being done to identify other nonionic or slightly cationic binders that may be tested.

The binder addition rate is shown to have an effect on how well the agglomerates withstand being subjected to acidic conditions. Further tests will be completed with different binder addition rates in the percolation columns. An optimum balance between performance and cost for each binder needs to be defined.

The electrical conductivity probe received from Phelps Dodge is currently being assembled. After assembly control tests will need to be run to determine the reproducibility of its readings.

The first column has already been started. This means that samples are taken three days a week, and need to be tested for copper and total iron concentration, pH, temperature, ORP, and acid content. The copper and total iron concentration analyses will be run weekly, where as the pH, temperature, ORP and acid content will determined each time a sample is collected. In May, the remaining five columns will be started. The same testing procedure will be completed on the PLS of each column 3 days a week.

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 polyacrylamide and vinyl acetate polymers are effective as binders, and will be evaluated further.

Additional binders, particularly organic polymers, have been selected based on their expected behavior in acid solutions, and are being evaluated by soak testing and percolation testing to evaluate the quality of the agglomerates that they produce. Several binders have been identified that perform well in the soak test and percolation testing. These binders will be evaluated in the leaching column tests.

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