Novel Binders and Methods for Agglomeration of Ore

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Abstract

The state of agglomeration of ore has a strong impact on the energy efficiency of processing. Ore agglomeration gives following processing advantages over unagglomerated ores: (1) Improved handling characteristics; (2) Better permeability to gases and liquids; and (3) Easier solid/liquid separation. Based on information provided by the industrial co-sponsors, the following conservative estimates were made of energy savings possible by improving ore agglomeration:

- Improved copper leaching efficiency from agglomeration would save at least 1.27 x 10^{12} BTU/year .
- Advanced agglomeration will allow iron and steel industry to adopt technologies that would save 6.51 x 10^{13} BTU/year .

In the second budget period of this project, work is concentrating on using agglomeration to improve energy efficiency of copper ore leaching. Currently, unagglomerated ore has poor permeability to leaching solutions, leading to low leaching rates and poor copper recoveries. Agglomeration of ore into coarse, porous masses prevents fine particles from migrating and clogging the spaces and channels between the larger ore particles. Currently, there is one copper extraction facility in the United States which uses agglomeration. This operation agglomerates their ore by moistening it with their leach solution (raffinate), but they are still experiencing undesirable levels of agglomerate breakdown. The addition of a binder during agglomeration would help to produce agglomerates that did not break down during processing. However, there are no known binders that will work satisfactorily in the acidic environment of a heap, at a reasonable cost. As a result, operators of many facilities see a large loss of process efficiency due to their inability to take advantage of agglomeration. This project has identified several acid-resistant binders and agglomeration procedures. These binders and experimental procedures will be able to be used for improving the energy efficiency of heap leaching.

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Executive Summary

As a result of decreasing ore grades, stringent environmental regulations, and the need to produce metal with the lowest possible energy inputs, there is a general trend in the copper industry towards producing copper by heap leaching. This method allows copper to be recovered from low grade ores in a reasonable amount of time, at low capital, and with low operating costs (Dixon, 2003). In the current secondary sulfide heap leaching operations, with ores containing minerals such as chalcocite (Cu_2S), the liberation of copper from the mineral is done through a two-step chemical reaction involving oxidation by iron (III), with the iron (III) becoming iron (II). The iron (III) is then regenerated from iron (II) using a bacterial oxidation reaction. For these reactions to occur in heap leaching of copper sulfide minerals, it is necessary for the solution carrying the dissolved iron and dissolving the copper to maintain contact with the ore particles, while at the same time allowing easy flow of air to provide oxygen for re-oxidizing the iron (II) to iron (III). The primary energy efficiency issues are to dissolve the copper at the highest practical rate (minimizing the energy inputs needed to complete a leaching cycle), and to increased the copper recovery (maximizing the amount of metal produced for a given energy input).

In order to maximize the copper dissolution rate and increase the ultimate copper recovery, it is necessary for the ore to be crushed, which is an energy-intensive process. When the crushed ore is placed in a leaching heap, the finest material migrates downward and clogs the spaces between the larger ore particles. It is the migration of fines that leads to poor permeability, the main problem in heap leaching, which limits the available contact between the ore and leach solution. The limited contact between the ore and leach solution slows the speed at which the chemical reactions take place, and results in not being able to achieve the desired copper recovery rates. This decreased recovery, in turn, increases the amount of crushing energy that must be expended per pound of metal extracted.

Agglomerating the material into pellets, masses, or granules is a solution to dealing with these fine mineral particles. The agglomerates would help to increase permeability in the heap by binding the fine particles to the larger particles. This would limit the amount of free fine particles, preventing them from migrating in the heap and clogging the spaces between the larger particles, limiting solution flow.

There is only one copper extraction facility in the United States which currently uses agglomeration. They agglomerate ore by using raffinate (the leach solution) to moisten the ore, so that fine particles will adhere in agglomerates. Even with agglomeration, this facility is still observing copper outputs below the desired recovery rate, due to the rapid breakdown of the agglomerates due to the weak bonding of particles by the raffinate. This breakdown results in the release of fine material which clogs flow channels in the ore bed. To get the desired copper recovery rates, the agglomerates need to be made stronger and more resistant to disintegration by the leaching solution so that fines migration and ore compaction can be prevented.

The use of a cost effective binding agent in the agglomeration step would greatly enhance the overall recovery of the heap by preventing agglomerate breakdown and limiting the migration of fines. The result would be an increase in the permeability of the heap. However, copper leaching 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 or alkaline pH. Acid-resistant binders are needed for these copper operations which will not breakdown in the acidic conditions, while allowing access of air and leach solutions to reach the ore particles.

This project has explored the development of acid-resistant binders for mineral agglomeration that allows for increased processing efficiency. A variety of types of binders were initially examined based on theoretical considerations and on past experience. However, there were no standard procedures to test the performance of a binder for agglomeration in heap leaching. It was therefore necessary to first develop an agglomeration procedure which could be used to evaluate the performance of the chosen binders. Once agglomerates were made in the laboratory, the first concern was whether the binders would be able to withstand the acidic conditions that would be experienced in a heap. The soak test was developed as a quick and easy test to determine which types of binders would or would not be able to withstand the acidic environment of a heap. The results of the soak test showed that the great majority of binders, including inorganic, organic, and silicate binders, all deteriorated under acidic conditions. Polymer binders, mainly non-ionic and slightly cationic binders, were better able to produce the greatest agglomerate strength.

After narrowing down the field of possible binders, it was necessary to determine whether the polymer binders would interfere with the solution flow through the ore bed. There was a possibility the addition of a binders could raise the viscosity of the solution enough to where it would not be able to flow freely. Again, no standard testing procedures to do this were in place, and so methods needed to be developed. A flooded column experiment was developed to test the degree of void space between ore particles and measure the ease of solution flow with the use of the selected binders. Both of these factors allow quantitative measurements of the permeability of the ore to the leach solution as a function of time. Results from the flooded column tests proved that the polymer binders were able to increase the strength of the agglomerates by maintaining void space, and helped to increase solution flow when compared to using raffinate alone as an agglomerate binder. These factors are important, as they aid in the ability of the solution to come in contact with the ore, and lead to increased metal recovery rates.

After several binders had been determined to be able to withstand an acidic environment and to help increase the ease of solution flow by maintaining void space, it was crucial to determine if these binders would have any adverse effects on copper recovery during an actual leaching operation. To analyze the effect of the use of the binders on copper recovery and bacterial growth, the long-term leach column was developed. These columns are as close of a simulation to an actual industrial heap as it is possible to perform at this time. Six long-term leach column test, comparing ore agglomerated with four different binders to ore agglomerated with raffinate, and to unagglomerated ore, have been completed at Michigan Technological University (MTU). The use of the binders has showed no negative effects on copper recovery or bacterial growth, indicating that these binders can be used in full-scale heaps. These columns were also duplicated at a copper heap leach facility in Arizona. The leach cycle at this location has not yet been completed, however current results shows that the long-term leach column results for the different binders are reproducible.

It is important to note that these columns are only able to reproduce what is occurring within the top 5 feet of an industrial ore heap leach bed. Compaction which occurs due to the weight of the ore in the heap may be partially responsible for the fine particle buildup which is found within the industrial leaching heaps. Compaction causes a breakdown of the agglomerates, which leads to a decrease in void space in the ore bed and increased liberation of fines from the agglomerates. The migration of fines in these compacted areas leave dead zones in which solution cannot flow, leaving them partially or completely un-leached. To determine the effect of binders under compaction a special apparatus, adapted from the flooded column set-up, has been designed and constructed. The investigators of this project at Michigan Technological University are currently in the process of fully patenting this apparatus (provisional patent serial number US60/750,236). Work is being done to introduce the idea of compaction and its importance to industry, help gather industrial interest in continuing development of the compaction column.

The initial compaction column is based on a 3-inch diameter column. A scaled-up model of the long-term leach column which incorporates compaction is also being developed, which will make it easier to study the effects of blinding, ponding, and the development of dead space in the column. This scale up will allow for the effect of the binders on copper recovery to be tested under simulated compaction conditions that correspond to the full depth of the heap in the laboratory without using an excessive amount of ore. In the future, multiple long-term leach compaction columns could be connected together to simulate all the compaction levels of an entire heap without having to run a full test heap, which would require hundreds of tons of ore. Large-scale lateral effects in the heap will be one of the only things which will not be able to be simulated due to the limitation of laboratory column width.

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 flooded 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.

Introduction

The high grade ores which were once easily mined have become depleted. The lower grade ores are able to be recovered by heap leaching. Heap leaching is a method that is used to recover lower grade ores in a reasonable amount of time, at low capital, and with low operating costs (Dixon, 2003).

In a heap leaching process the ore is crushed to an appropriate size, typically a top size of 0.5 inches. It is then 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 20 feet is typical. The lift is irrigated with the leach solution (referred to as "raffinate"), either by drip emitters or a sprinkler system. The raffinate then percolates through the heap while air is being blown from the bottom, allowing the copper to be dissolved from the ore. The solution, now referred to as pregnant leach solution (PLS), is captured in a pond. From the pond it is then sent to a solvent extraction and electrowinning circuit where the liberated copper is ultimately recovered.

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.

$$Cu_2S + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + CuS \quad (1)$$

$$CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^0 \quad (2)$$

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

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \quad (3)$$

From these reactions, it can be seen that heap leaching of copper sulfide minerals requires the ability for solution, with dissolved iron, to maintain access to the ore particles. It also requires easy flow of air to provide oxygen.

In the current heap leaching operations, copper recovery is still not as high as desired. This is due to poor heap permeability. Ideally, the ore bed would be constructed of a homogenous ore distribution which would lead to superior solution and air flow, as shown in Figure 1. However, in a heap the fine particles clog the spaces between the larger ore particles causing uneven distribution of the leach solution, as shown in Figure 2. The lack of space between particles, due to fine particle build-up, leads to a difficulty for air and leach solution to flow freely through the heap. This build up results in the solution flowing down the path that gives the least amount of resistance. When the solution flows in this manner it does not come in contact with all ore surfaces, leaving areas which are partially-leaching. Partially leached zones in the heap mean there is still available metal which is left un-recovered. To recover the metal, the heaps have to be run for an extended period of time, which leads to a loss in profit or an increase in the amount of energy needed to extract the un-leached metal.

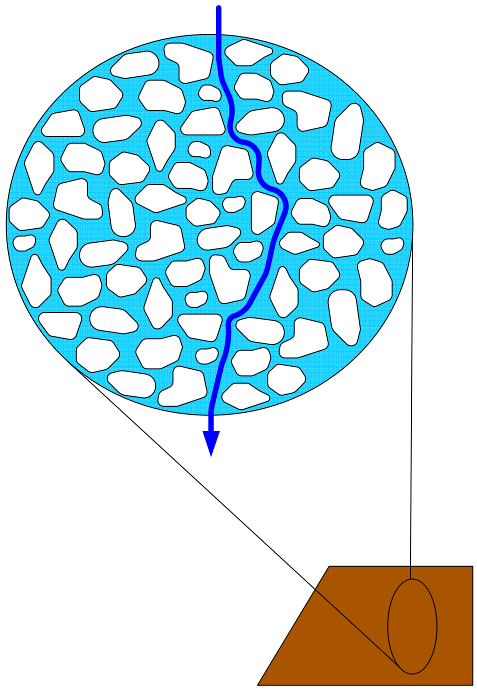


Figure 1: Ideal homogeneous ore bed size distribution

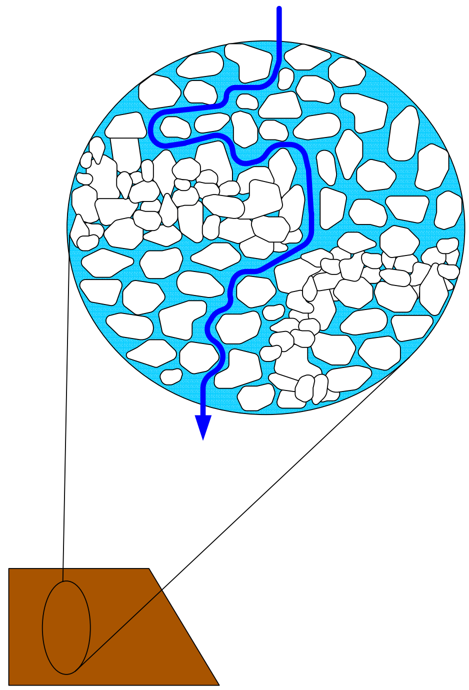


Figure 2: Actual heterogeneous ore bed size distribution

Agglomerating the material into pellets, masses, or granules 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 increases the availability of transport of the leach solutions throughout the heap by entrapping the fine particles to unable them from filling the spaces between the larger particles and causing build-up. In the heap leaching process, after the ore is crushed it is then sent to an agglomeration drum, where it is agglomerated with raffinate (leach solution). The agglomerated ore is transported to the heap as before.

Currently, there is only one copper extraction facility in the United States which uses agglomeration; however, they agglomerate only with raffinate, the leach solution, which produces relatively weak agglomerates that break down easily when they are wetted. This facility is still observing copper outputs below the desired recovery rate, due to the rapid breakdown of the agglomerates. This breakdown results in the release of fine material which clogs flow channels in the ore bed, leaving areas in the heap void of the necessary reagents to dissolve the copper. Thus, resulting in lower recoveries than what is expected. To get the desired copper recovery rates, there needs to be an even greater increase in permeability within the heap. The use of 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. The result would be an increase in the permeability of the heap. However, copper leaching 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 or alkaline pH. 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.

The use of a proper binder agent will result in a more uniform percolation throughout the heap, which will help to decrease the amount of energy used by shortening the number of days the ore needs to be leached.

Binder Evaluation

One of the primary problems in using a binder or additive for copper heap leaching agglomeration is due to the acidic environment, which needs to be maintained to ensure high bacterial populations. Under the highly acidic conditions, most binders break down. Previously, there had been no standard procedure in which to test the selected binders. There is also no known economically feasible binder or additive which will work satisfactorily in an acidic environment. Due to the fact that there are no known binders which perform adequately, an array of various products including organic, inorganic, silicates, and polymeric agents need to be tested. Testing a variety of products will help to determine what will help keep agglomerate strength.

Before the selected binders may be tested an experimental procedure needed to be developed. This procedure needed to give insight as to how well the agglomerates held together after being agglomerated with raffinate and/or various binders while being subjected to acidic conditions which would be found in a heap. The soak test was developed to accomplish this task.

For the soak test, ore was agglomerated in a rotating drum with raffinate and a chosen binder. It was then placed onto a screen and left to air dry, or cure. The screen was lowered into a sulfuric acid and water solution, simulating the acidic conditions which would be found in a heap. After 30 minutes, the acid solution was decanted and the fine material which had passed through the screen was collected, dried, and weighed. The procedure is diagramed in Figure 3.

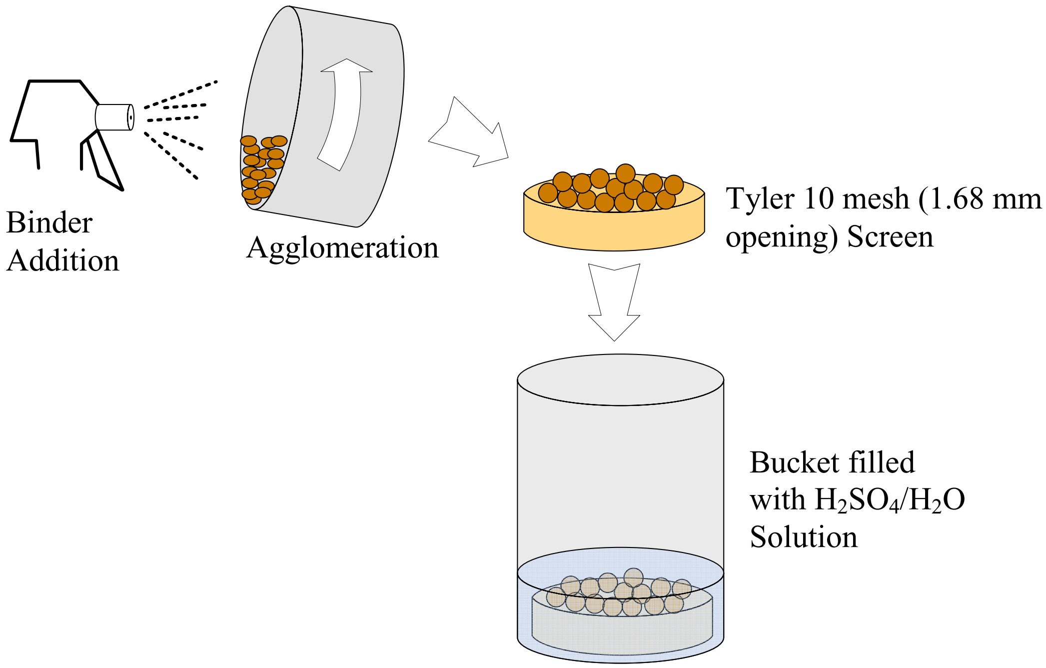


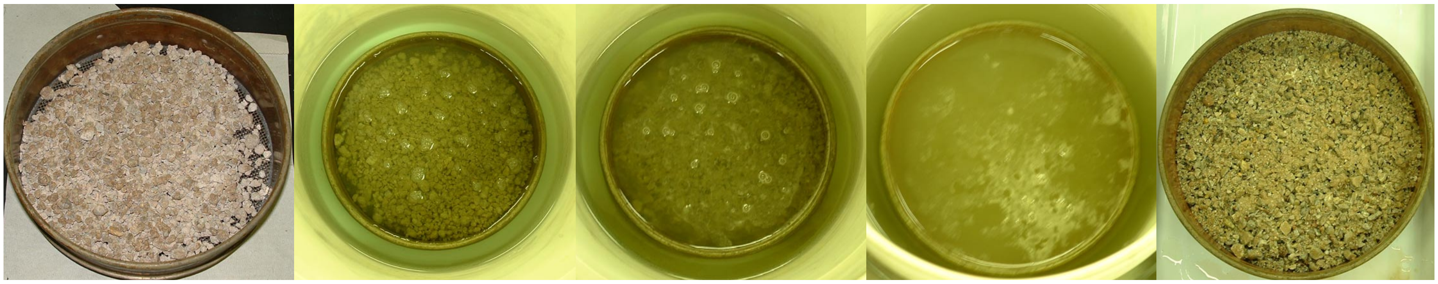
Figure 3: Soak Test Experimental Procedure

It was unknown which type of binder reagents would be able to withstand the acidic heap conditions while aiding in metal recovery. Soak tests were run on a variety of binders including inorganic, organic, silicate, and polymeric compounds, in order to get a better idea of which might be beneficial.

The agglomeration aids were judged on the percent of migrated fines collected. Fines migration is the only quantitative measurement which is able to be recorded from a soak test. The fines migration percentage can be calculated using Equation 4.

$$Fines\ Migration = \frac{Weight\ of\ ore\ migrated\ out\ of\ column}{Total\ weight\ of\ -10 mesh\ fines\ available\ in\ column} \qquad (4)$$

Each agglomerated sample was also analyzed visually to give a comparison between tests. A visual progression of agglomerate deterioration in a soak test and the final fines collection are shown in Figure 4 & 5.



Agglomerates after 24 hours of cure time, before soak test | **Agglomerates after initial immersion** | **Agglomerates after 5 minutes of immersion** | **Agglomerates after 20 minutes of immersion** | **Broken down agglomerates after 30 minutes of immersion in soak test**

Figure 4: Visual Deterioration of Agglomerates in Soak Test

Figure 5: On the right is the Tyler 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.

The fines migration results are summarized in Figure 6. The results indicate that the dust control agent, polyacrylamide, polyvinyl acetate emulsion, and waste treatment additive show the greatest decrease in the amount of fines released when compared to the baseline test where no binder other than raffinate was used. These results lead to the conclusion that the use of polymer binders result in better agglomerate strength. The agglomerates which used organic, inorganic and silicate additives all broke down during the soak test, resulting in high fines migration values.

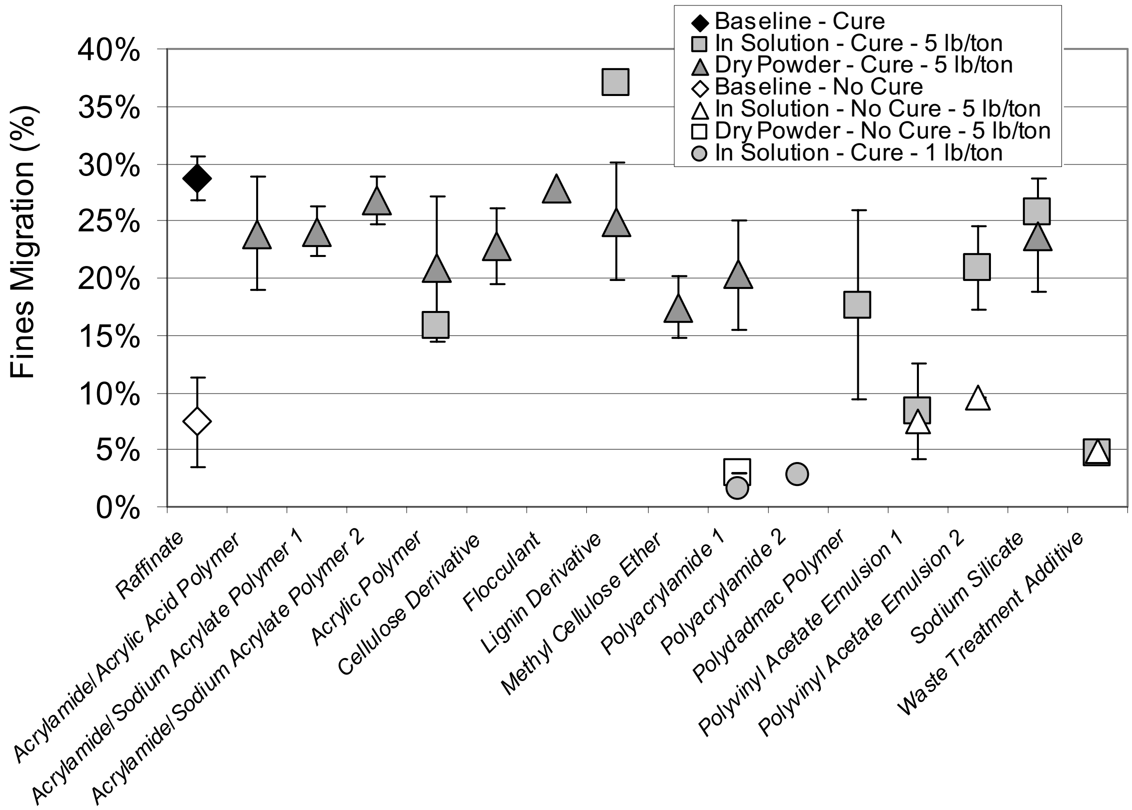


Figure 6: Fines Migration using Various Chemical Agents

The effect of moisture content of the strength of agglomerates is an important factor on the rate at which the agglomerates deteriorate. Several of the binders, which resulted in the least amount of fines in the soak tests, were tested again to determine the effects of moisture content. The results, shown in Figure 7, indicated that the wet agglomerates had better strength and released fewer fines, than the agglomerates which were allowed to dry overnight. All the binders performed better than the baseline test, which contained no binder, when the agglomerates were allowed cure time. Therefore, in can be concluded that binders should not be tested while completely moist, as this is unrepresentative of what will be occurring in the heap, given that drying will occur during the lift stacking.

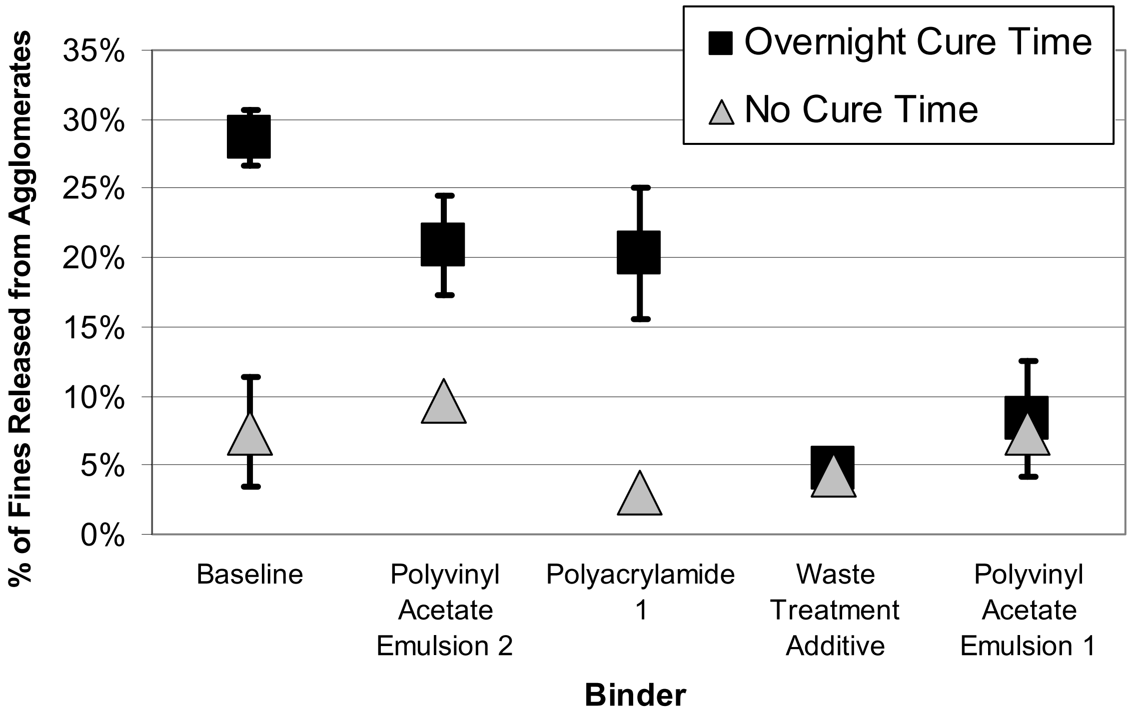


Figure 7: Effect of Cure Time on Fines Migration using Various Chemical Agents

The soak test results indicated several binders which were able to withstand the acidic conditions that would be encountered in a leaching heap. However, this does necessarily mean that the use of these binders will result in increased permeability within the ore bed. Increased permeability is needed to ensure that there is good contact between the air, leach solution, and ore. This contact results in improved leaching kinetics, and increased metal recovery.

The degree of permeability within the ore bed can be related to the amount of void space within the heap. A greater void space will allow for an increased ability for the solution to flow freely through the heap. The change in amount of void space can be determined by calculating the bulk density of the ore bed, Equation 5. Reporting the change in bulk density, Equation 6, eliminates differences due to variables such as differences in agglomerate size or differences in column loading. The void space within an ore body is important to obtain optimum kinetics of the leaching process by providing the area necessary for good liquid and gas interface.

$$\rho_{Bulk} = \frac{weight\ of\ ore}{volume\ of\ ore} \tag{5}$$

$$\Delta\rho_{Bulk} = \rho_{Bulk\ Final} - \rho_{Bulk\ Initial} \tag{6}$$

Where:

- ρ = density (ton/yd^3)

A high change in bulk density would indicate that the amount void spaces are decreasing during the leaching test. If the change in bulk density remains low, this indicates that the void spaces are maintained, however, it does not verify that the solution is able to flow freely through the ore bed. The ability for the solution to flow freely through the ore bed can be determined by calculating the hydraulic conductivity. Darcy's Equation, Equation 7, is used to determine the hydraulic conductivity of the system.

$$Q = A * K * \frac{\Delta h}{L} \quad (7)$$

Where:

- Q = volumetric flow rate (m^3/s)
- L = flow path length (m)
- A = flow area perpendicular to L (m^2)
- Δh = change in hydraulic head (m)
- K = hydraulic conductivity (m/s)

The extent of breakdown of the agglomerates can be determined by the percentage of fines which have migrated. This can be concluded by comparing the amount of fine material which has passed through the ore bed with the amount of that same size material which was initially put into the system. A good binder used for agglomeration addresses these issues by keeping fines bound together creating a more uniform size distribution and producing minimal fines migration.

Determining the degree of permeability would allow each binder to be compared, to decide whether they were helping to increase agglomerate strength and the ability for solution to flow through the heap. However, a standard procedure to calculate the bulk density and hydraulic conductivity has not been developed. Therefore, the flooded column test was designed and constructed to test these parameters.

The flooded columns test apparatus', shown below in Figure 8, were assembled.

Figure 8: Flooded Test Columns

The ore is agglomerated with raffinate and a chosen binder. After drying, the agglomerated ore is then transferred to a column. Leach solution is dripped onto the top of the column, where is begins to slowly flood the column. The solution exits the column through the overflow system. Figure 9 outlines this process.

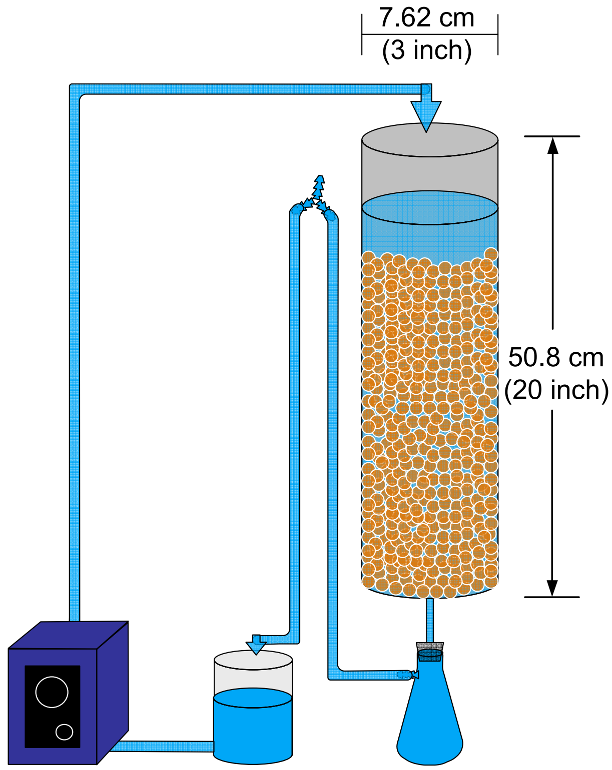


Figure 9: Schematic of Flooded Column Test

The polymer binders which improved the strength of the agglomerates under acidic conditions, where then tested in the flooded column. Fines migration results, Figure 10, indicated that the all of the synthetic binders tested had a lower tendency to breakdown, than the baseline test, by releasing the smaller quantities of fines. The tall oil pitch and the waste treatment additive agglomerates had the lowest amount of fines migration.

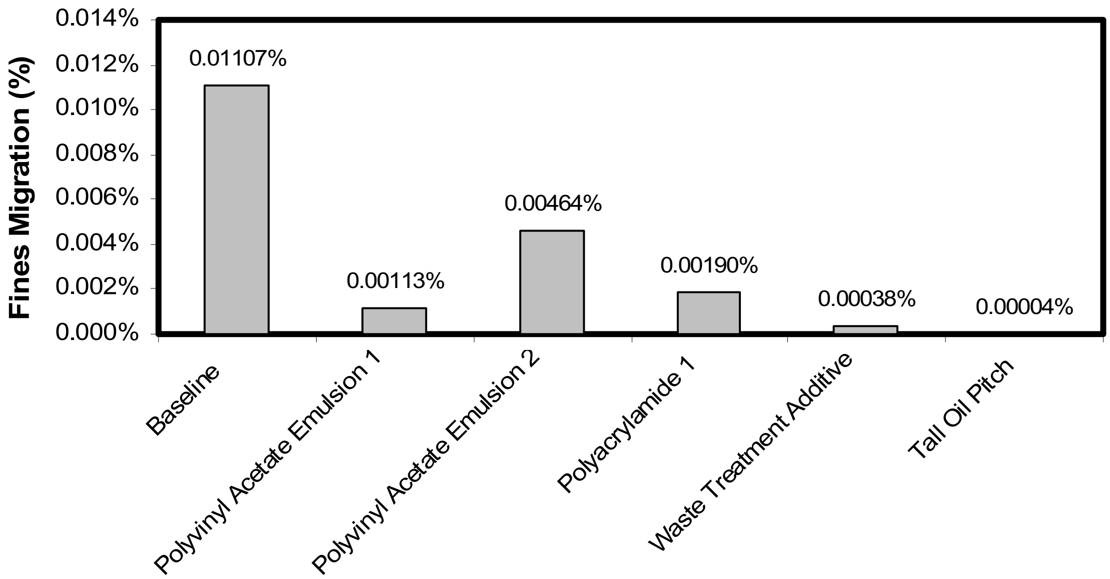


Figure 10: Ratio of Fines in Flooded Column Tests

The ore bulk densities varied for these five particular binders and raffinate. 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. The tall oil pitch had the least amount of fines released. It also had the lowest change in bulk density of the binders tested. Figure 11 shows the ore bulk density with time for the various agglomeration binders.

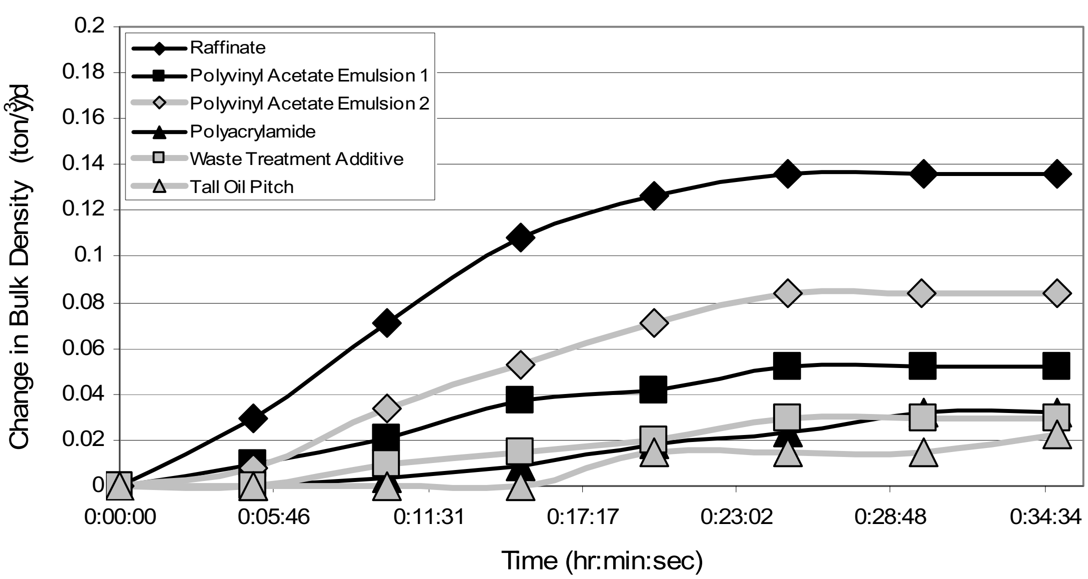


Figure 11: Change in Ore Bulk Density vs. Time for Best Performing Binders

The column agglomerated with tall oil pitch had the smallest change in bulk density. These agglomerates also never visually broke down. The agglomerates in the raffinate & polyvinyl acetate emulsion 2 columns were able to be seen breaking down.

Although the void space is not decreasing as greatly with the use of the binders, the ability for the solution to flow through the ore bed, hydraulic conductivity, still needed to be determined. 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 five binders and raffinate, as above. The summary of the results are shown in Figure 12. The polyacrylamide shows the highest conductivity, and the polyvinyl acetate emulsion 2 produced the lowest hydraulic conductivities out of the five binders. However, all binders had higher conductivities than the trial agglomerated with raffinate only.

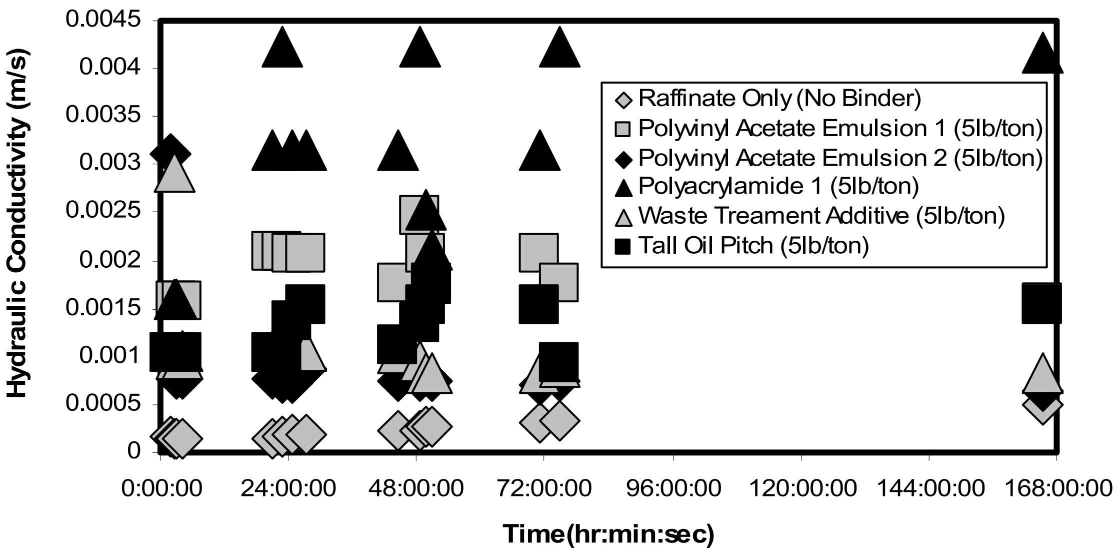


Figure 12: Hydraulic Conductivity for the Best Performing Binders

The fluctuations within the data are a result of the flow rates cycling up and down slightly due to the pumps heating up and not performing properly. All remaining tests include a flow rate measurement taken for each hydraulic conductivity point to eliminate the variation.

For comparison purposes all the agglomerates have been prepared using a binder addition rate of 5 lb of binder per ton of ore. However, this may not be the optimum dosage rate for each binder. A greater or less quantity of binder may actually allow it to produce more stable agglomerates. To determine the optimum binder addition rate, multiple flooded columns were run at various binder addition rates. Hydraulic conductivity and bulk density measurements were used to determine the optimum addition rates. Four binders addition rates, polyvinyl acetate 1, polyacrylamide, waste treatment additive, and tall oil pitch, have been optimized.

The optimum dosage is determined by looking at the binder dosage rate when the hydraulic conductivity first beings to reach a state where there is no longer a significant increase in hydraulic conductivity with increasing binder addition. The change in bulk density also shows a leveling trend around this same addition rate. The optimum binder dosages are can be determined from the hydraulic conductivity and bulk density results shown for the four binders which have been tested in Figures 13 through 20.

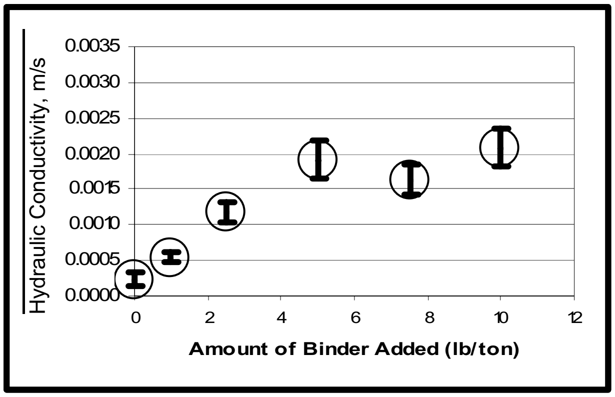


Figure 13: Flooded Column Hydraulic Conductivity Evaluation for the Polyvinyl Acetate 1

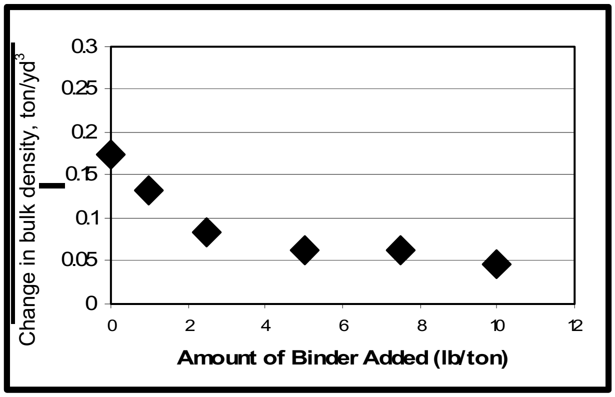


Figure 14: Flooded Column Bulk Density Evaluation for the Polyvinyl Acetate 1

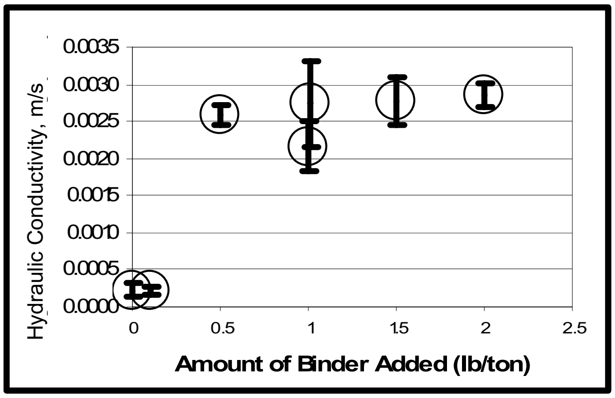


Figure 15: Flooded Column Hydraulic Conductivity Evaluation for the Polyacrylamide

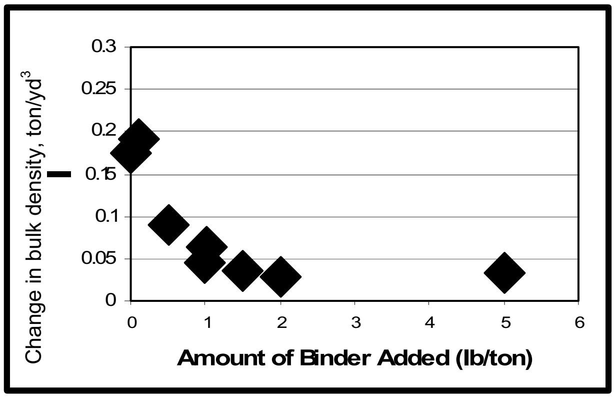
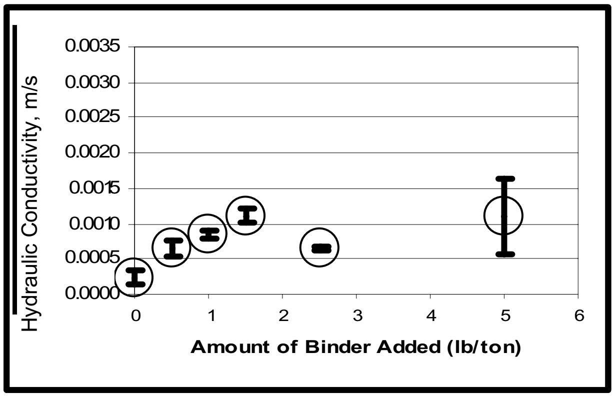


Figure 16: Flooded Column Bulk Density Evaluation for the Polyacrylamide



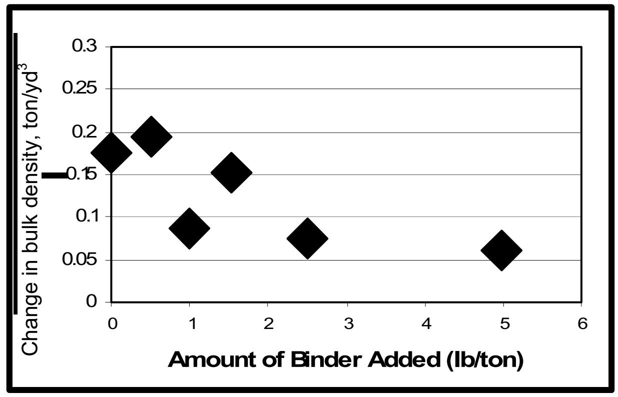
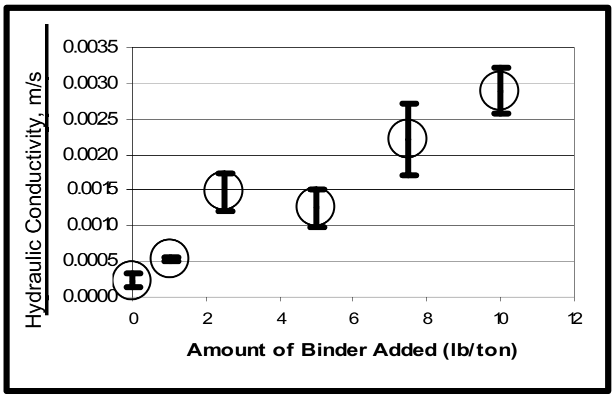


Figure 17: Flooded Column Hydraulic Conductivity Evaluation for the Waste Treatment Additive

Figure 18: Flooded Column Bulk Density Evaluation for the Waste Treatment Additive



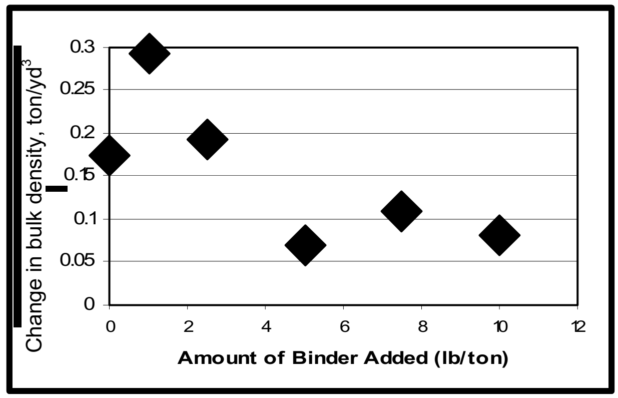


Figure 19: Flooded Column Hydraulic Conductivity Evaluation for the Tall Oil Pitch

Figure 20: Flooded Column Bulk Density Evaluation for the Tall Oil Pitch

From these results we can determine that the polyvinyl acetate 1, polyacrylamide, and the waste treatment additive had optimum binder dosage rates of 5 lb/ton, 1 lb/ton, and 1.5 lb/ton respectively. The ease of solution flow kept increasing with increasing tall oil pitch binder dosage rates. However, the use of this binder will become uneconomical at such high binder addition rates. Therefore, an optimum dosage rate for the tall oil pitch was determined to be 6 lb/ton.

The flooded column test has been used to analyze the changes in solution flow, void space, and migration of fine material with the use of several different binders. However, accurate copper recovery data could not be collected from these columns as factors such as solution flow and ore top size are not accurate as to what would be found in a heap. The flooded columns also did not contain any air injection which plays a major role in the extent of copper recovery obtained.

To determine whether the use of binders showed improved copper recoveries, the industrial heap needed to be simulated on a scaled down laboratory set-up. This would also allow the binder affect on the bacterial populations to be monitored. An experimental apparatus then needed to be created.

A long-term leach column was designed and constructed to carry out this procedure. The columns height, air flow rates, and solution flow rates were all scaled down from the values that were currently being used in industry. One difficulty with this experimental set-up is that factors such as channeling are not accurately represented, as the space for this to occur is limited to 15.24 cm (6 inches) rather than the whole length of a heap. Due to this factor, the tests will only indicate whether the binders are having a negative effect on copper recovery and bacterial growth.

The columns, shown below in Figure 21, were created to simulate a leach heap. Only the best binders are being tested in these columns, as the leach cycle is 180 days. Six of these columns are available in the Michigan Technological University Laboratory.

Figure 21: Long-term Leaching Columns

The ore used is agglomerated and allowed to air dry, or cure, for at least 72 hours. This time is representative of the approximate time it takes for a lift to be created. The ore is then distributed into the column, where it is capped to allow for a controlled environment. The air line is connected to the base of the column. The raffinate is pumped into the top of the column where it is dripped on the ore. Raffinate solution percolates slowly through the column, and is collected in a bucket below, as shown in Figure 22. The solution collected is called the pregnant leach solution (PLS), and is later tested for copper and iron recovery along with pH, oxidation/reduction potential (ORP), and temperature.

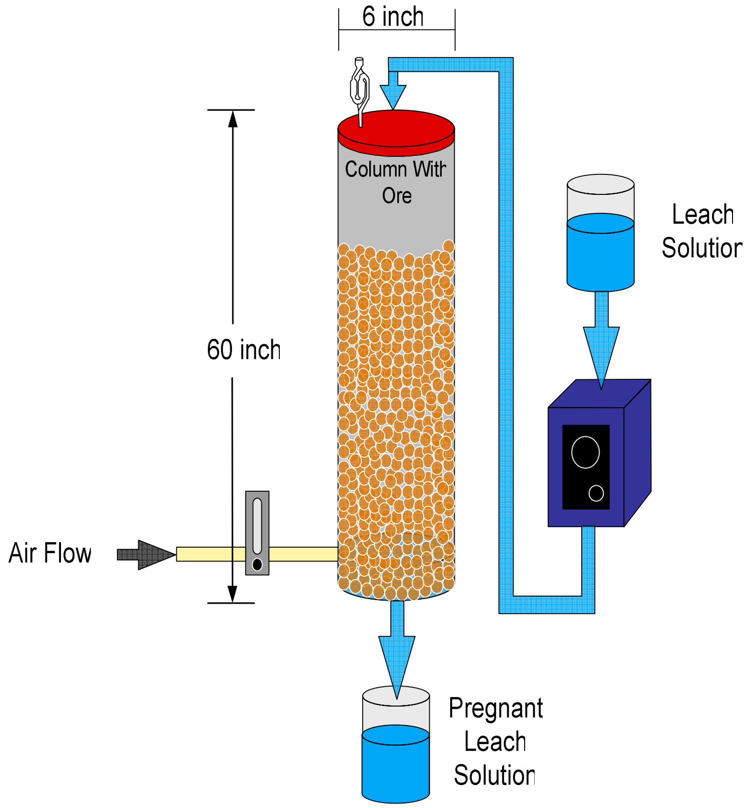


Figure 22: Schematic of Leach Testing Column

Six of these columns have been run at Michigan Technological University. These six columns included one with ore that was not agglomerated, one column where the ore had been agglomerated with raffinate (leach solution) only, and the remaining four had ore agglomerated with the four synthetic binders which have proven to improve agglomerate stability in the soak & flooded column tests. These synthetic binders include the polyacrylamide, polyvinyl acetate emulsion 1, tall oil pitch, and the waste treatment additive.

The copper recoveries, shown in Figure 23, indicate that there is no adverse effect to the leaching process by using these binders in agglomeration.

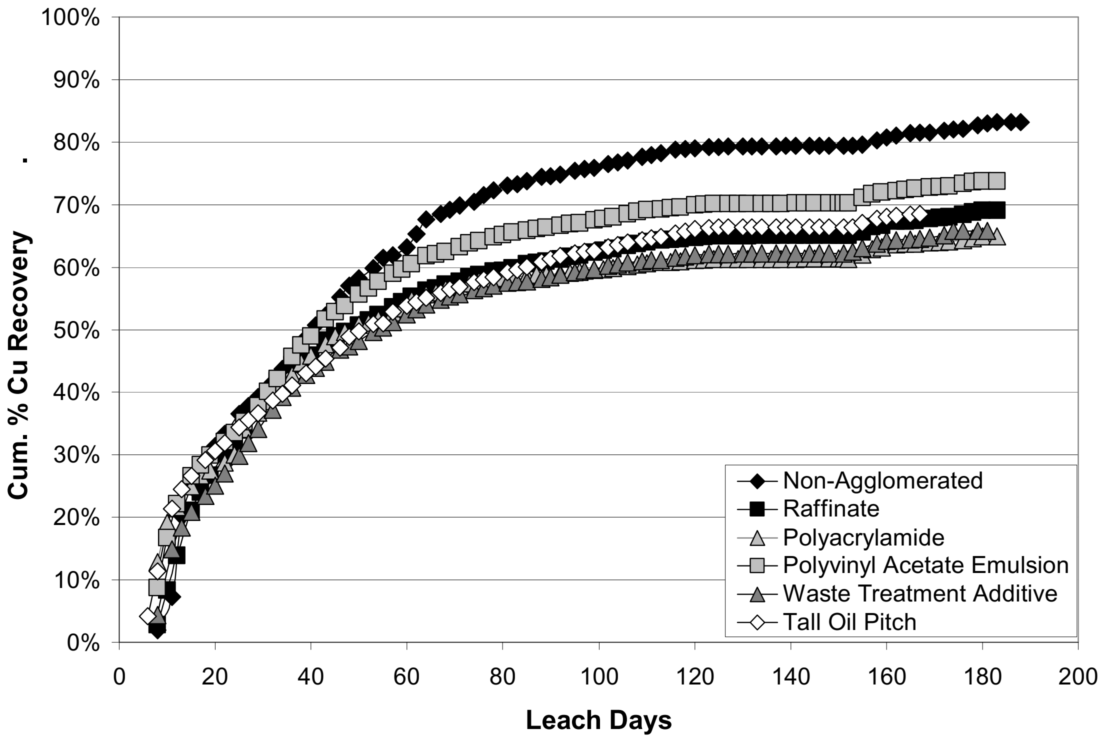


Figure 23: MTU Long-Term Leach Column Copper Recoveries

The copper recoveries of all the columns with ore agglomerated with a synthetic binder were within ±5% of the raffinate agglomerated test. This difference may be contributed by experimental error. The long-term leach columns are being duplicated concurrently at our industrial partners copper heap leaching operation in Arizona. Both the Arizona location and Michigan Technological University (MTU) are running columns using the same binders and ore from the same split from the Arizona industrial process circuit. The columns at the Arizona facility, however, have not completed their full leach cycle. Therefore, more data is still to be collected before a final analysis can take place. Some early comparisons are able to be made between the results from the Arizona operation with the results obtained at Michigan Technological University, shown in Table 1.

Table 1: Comparison of copper recoveries from the long-term leach columns between Michigan Technological University and the industrial partners in Arizona

	MTU	Arizona	
	Copper Recovery		
	(%)	(%)	(%) Difference
Day 40			
Polyacrylamide	46	37	9
Tall Oil Pitch	44	34	10
Day 60			
Non-Agglomerated	62	58	4
Raffinate	55	50	5
Waste Treatment Additive	53	57	4
Polyvinyl Acetate Emulsion	61	62	1

The results comparing the copper recoveries between MTU and the Arizona location show very similar results, especially later into the leach cycle. This indicates that the long-term leach columns are a reproducible way of evaluating copper recoveries from a leach cycle. Results will be analyzed and comparisons drawn once the Arizona location has completed their leach cycle.

The bacteria populations in the column are important. From Equation 3, it is shown that the bacteria helps convert the iron (II) back into iron (III), which is necessary to help with the continuing extraction of copper from the chalcocite ore. The bacterial population can be related to the oxidation/reduction potential (ORP). A low ORP indicates a greater concentration of ferrous iron in the system. A higher ORP indicates there is a greater amount of ferric iron in the system. A high ORP is desired, as this means there is plenty of reactant, or ferric iron, in the system. This indicates there is a high enough bacterial population to convert all the ferrous iron back to ferric, to allow the chalcocite reactions to continue.

The oxidation/reduction potential results from the long-term leach columns, Figure 24, show that the bacterial populations for those columns agglomerated with synthetic binders were greater than the raffinate agglomerated and non-agglomerated columns for most of the leach cycle.

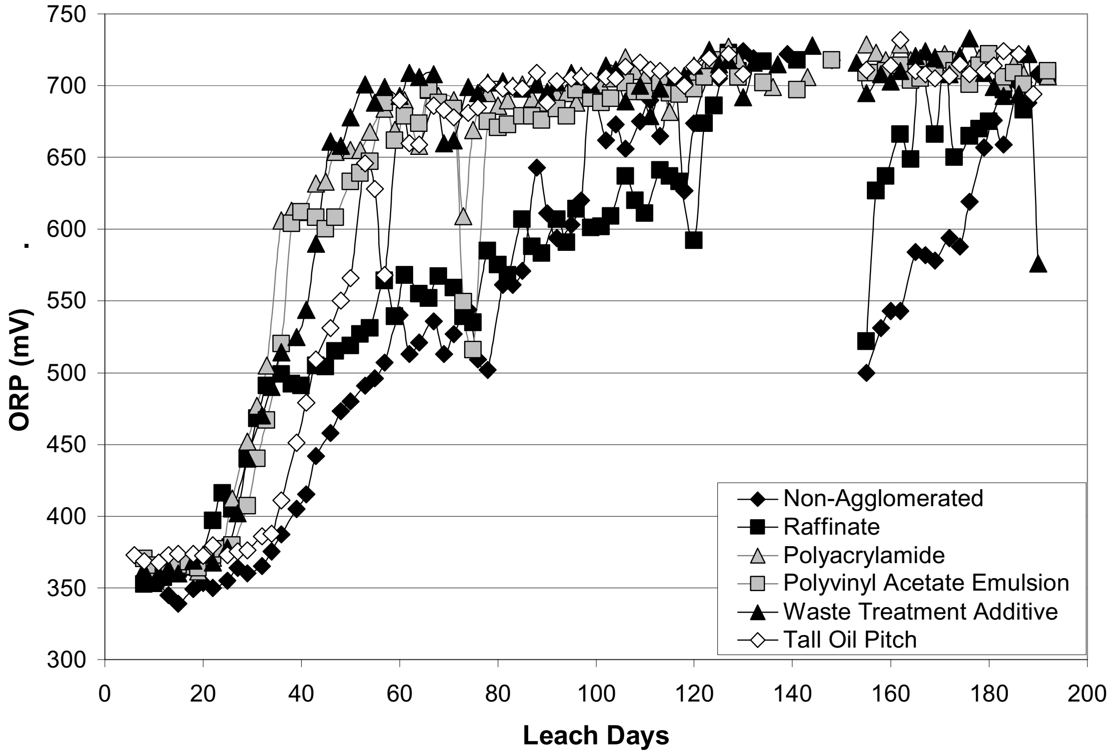


Figure 24: Oxidation/Reduction Potential results from MTU long-term leach columns

The rest period in the leach cycle occurred between days 120 and 150. At this point no leach solution was being added to the columns. At the end of this rest period, the ORP's for the non-agglomerated and raffinate agglomerated columns fell considerably. This means the amount of ferric iron in the system is decreasing and the amount of ferrous iron is increasing. If the low ORP's were experienced for a long period of time, this would begin to affect the leaching kinetics and eventually result in a decreased copper recovery.

The stability of the agglomerates through out the long-term leach column test could be evaluated by comparing the bulk density, or slump, of the ore bed in each column. Figure 25 shows the overall change in bulk density results for the long-term leach columns.

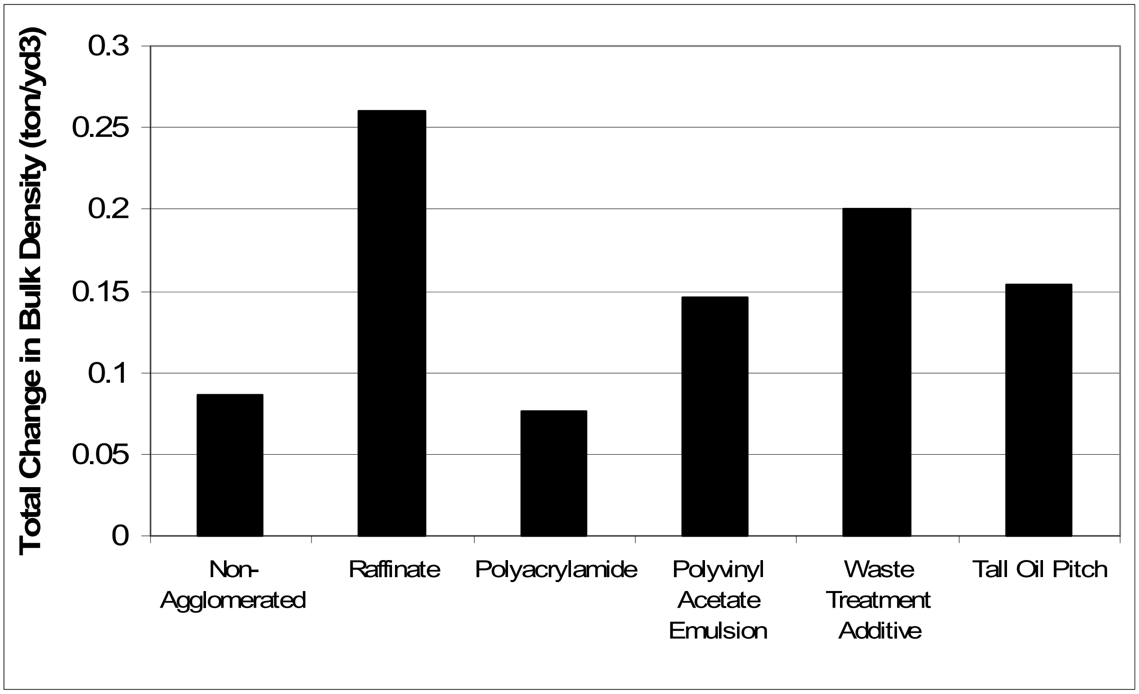


Figure 25: Total change in bulk density for various binders over the entire leach cycle

The polyacrylamide had the lowest bulk density measurements of the binders tested. This indicates that the agglomerates in this column had greater stability, and were less likely to break apart over time. This also means the void spaces within the ore bed were maintained, which in the long run would allow for better solution flow. The non-agglomerated column also had a low change in bulk density, however as this column was non-agglomerated, the change in bulk density was not contributed to agglomerates breaking apart, but from the settling of the ore. It also had the worst initial and final bulk density measurements.

Although the long-term leach columns are useful way to determine if there are any negative effects by agglomerating with a binder, they are unable to take into account all the factors which would occur in an industrial sized heap. In a heap, the ore is stacked into approximately 22 foot high lifts. The long-term leach columns are only taking into account the top 5 feet of ore in the heap. The breakdown in agglomerates and decrease in void space can partly be contributed to the weight of the ore alone and by trucks driving on the top surface. Compaction due to these factors is not able to be taken into account in the long-term leach columns. It is important to determine if the use of a binder will be beneficial when the heap is under compaction.

Testing is currently underway to evaluate the binders under compression. This data will be used to compare the different binders. This will give a better understanding of the additional benefits of each binder in a heap leach setting.

To test the binders under compaction a special apparatus was designed and built. This apparatus is currently in the process of becoming fully patented by the MTU investigators of this project. Currently, MTU holds a provisional patent, serial number US60/750,236 on the apparatus. The first apparatus is similar to the flooded column test, allowing for the same measurements to be made, but under a pressure that would simulate what an actual heap is likely to have at a distance of 10 feet under the surface. The flow rates used for these test were more than 10 times that of the normal field flows. The high flow rates gave a much harsher environment showing longer term effects in a shorter period of time. The compaction, however, is far less than what an actual heap would be placed under.

Experiments were performed on non-agglomerated ore, ore agglomerated with raffinate, and ore agglomerated with the four binders used in the long-term leach columns. The trial where the ore was agglomerated with only raffinate yielded some interesting results, illustrated in Figure 26, when comparing bulk density as a function of time for the three raffinate columns. The paths taken to achieve these bulk densities are somewhat different. Three distinct scenarios can be realized within this set of data.

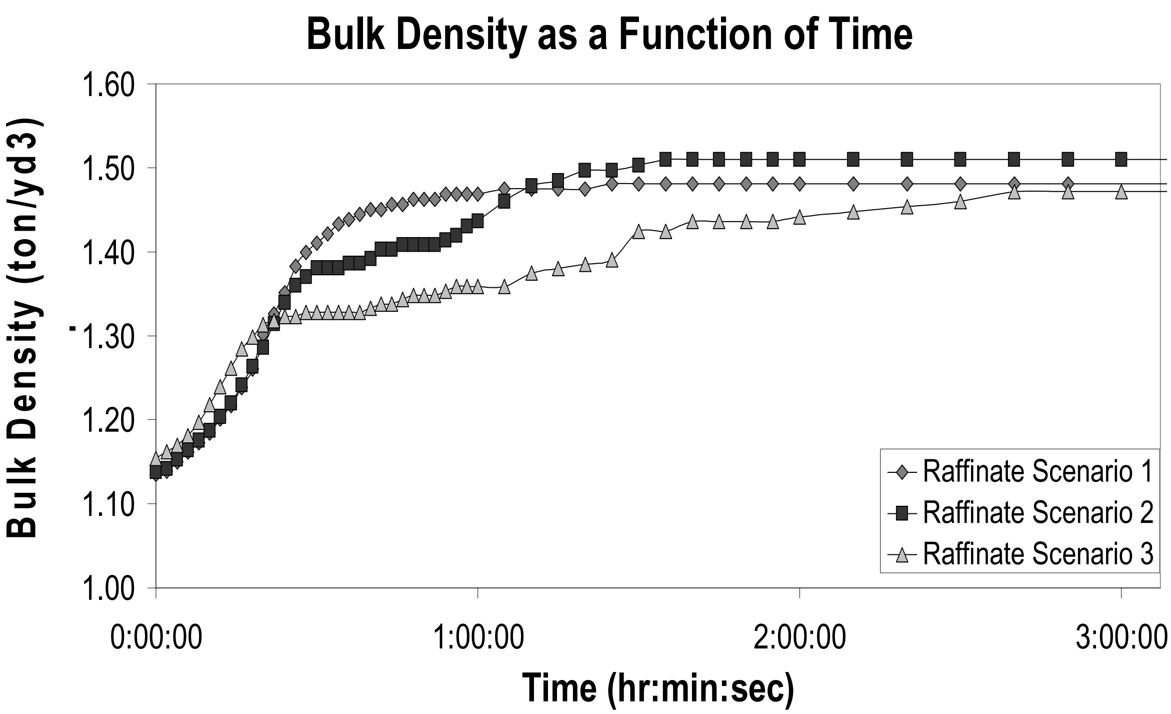


Figure 26: This graph illustrates the bulk density as a function of time for the columns containing raffinate only agglomerated samples. Three different paths exist but lead to a similar overall bulk density.

Scenario 1 had an ideal bulk density change over time curve. This scenario yielded the highest hydraulic conductivity of the raffinate trials for the first eight hours of the test. While comparing the raffinate trials, several points of significance were determined. In scenario 1 the ore in the column began wetting as expected. Fines migration could be seen occurring in the column as the solution wetted. At 28 minutes into the test, the solution in the overflow tube could be seen rising slowly and then dropping rapidly. This surging suggested pressure would build and then drop in the ore bed. At 42 minutes, the solution level in the column was above the compression piston and air bubbles were released from the ore bed corresponding to a drop of solution height in the overflow tube. This continued until the ore become completely wetted at 58 minutes. The void spaces in the ore bed that still remained were filled with air until the end of the test. The measurable fines migration percentage was 0.43% for this scenario.

Scenario 2 resulted in a non-ideal curve of bulk density change over time. This scenario yielded the second highest hydraulic conductivity of the raffinate trials for the first 8 hours of the test. During the atypical part of the curve, the pressure within the column surged as solution slowly wetted the remainder of the ore. The column became completed wetted after 68 minutes into the test.

Scenario 3 has a non-ideal curve of bulk density change over time. This scenario yielded the worst hydraulic conductivity of the three trials for the first 8 hours of the test. Scenario 3 is quite different than either of the first two scenarios. The column was now equipped to measure the pressure buildup in the ore using a manometer. The ore did not become completely wetted until 230 minutes into the test.

What occurred in this column, during scenario 3, was an interesting phenomenon. The fines migration had effectively sealed off a portion of the column from downward solution flow. The result was the creation of a dead spot. The dead spot can be seen in Figure 27, as well as the great amount of hydraulic head that had built up above the ore.

After 24 hours, the area remained saturated with solution. However, the fines had not migrated because there was no appreciative solution flow. This corresponds to the measurable migration of fines being 0.30% which is less than the consistent 0.43% the other two columns yielded. With no appreciative solution flow, the time it would take for any reaction to occur and the solubilized copper to migrate back to the higher flow area would be extensive. This would result in a longer leach cycle or a loss of recovery.

The addition of a binder in agglomeration helped to decrease the bulk density of the system resulting in better solution flows. Figure 28 indicates that the use of the binders resulted in lower bulk densities than the average column agglomerated with raffinate. This signifies that there is less of a breakdown of the agglomerates with time with the use of a binder.

Figure 27: This photograph shows the ponding effects due to fines migration in scenario 3. A large amount of solution can be seen in the column above the ore and the overflow break over point (the Y fitting at the upper left corner).

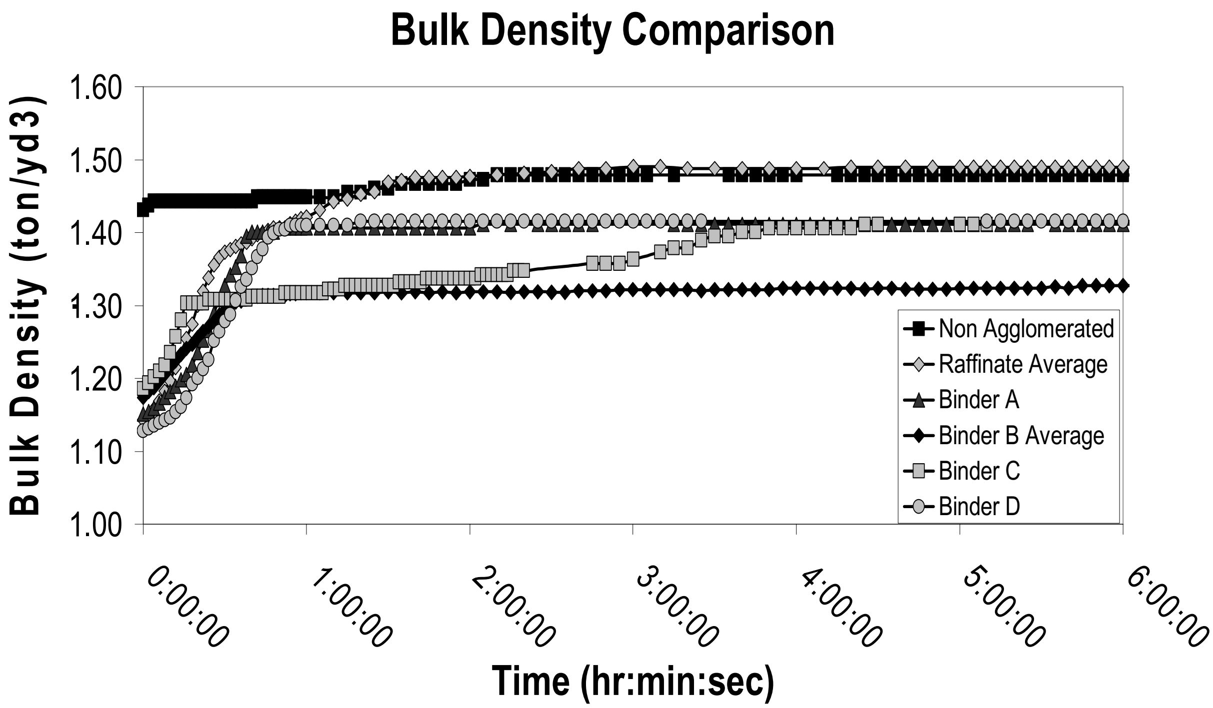


Figure 28: This graph illustrates the bulk density as a function of time for the columns containing raffinate and for the columns containing ore agglomerated with various binders. These results indicate that the use of a binder helped to decrease the bulk density, which will lead to an increase in solution flow.

The addition of a binder in agglomeration helped to increase the hydraulic conductivity, the ability for solution to flow within the heap, compared to using raffinate alone as a binder. These results are shown in Figure 29. Binder B had the lowest bulk density, along with the highest hydraulic conductivity. This leads to the conclusion that the lower the bulk density, the greater the availability for solution to flow through the heap.

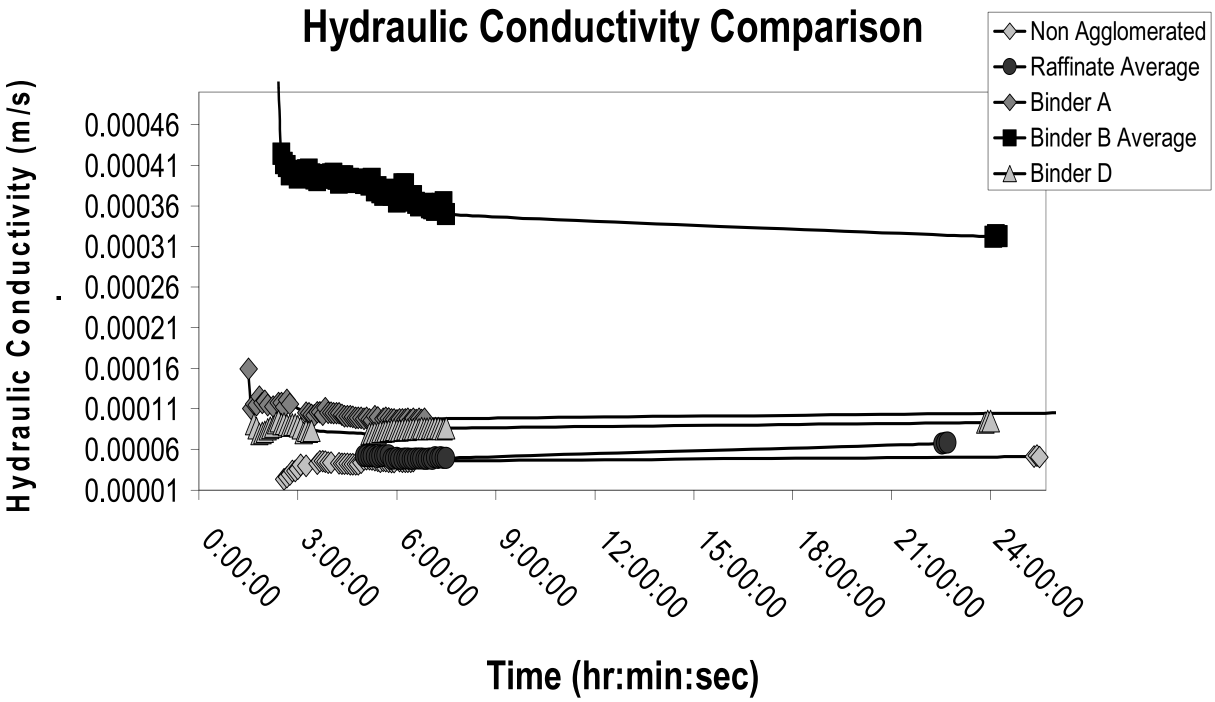


Figure 29: This graph illustrates the hydraulic conductivity as a function of time for the columns containing raffinate and for the columns containing ore agglomerated with various binders. These results indicate that the use of a binder helped to increase the hydraulic conductivity, which indicates an increase in solution flow.

These results indicate that under compaction, the use of a binder helps to increase the strength of the agglomerates when compared to using raffinate alone. This is shown by a decrease in bulk density, meaning that fine particles from the agglomerates are not breaking off. It is also shown by an increase in hydraulic conductivity, the ease of solution flow. The use of the binders resulted in the solution having an easier time flowing through the ore bed. This will lead to the availability for better contact between the solution and the ore, ending in better copper recovery rates.

A scale up of the compression apparatus is currently being constructed. This is also a specially designed apparatus which falls under the provisional patent, serial number US60/750,236, held by the investigators of this project at Michigan Technological University. This scaled up column will allow copper recoveries to be determined at various compaction levels within the heap. This apparatus will hopefully bring to light various conditions which have been discovered in the flooded column compaction test, and there influence on copper recovery. In the future, multiple columns could be conjoined to simulate and entire heap within the laboratory setting.

Summary

Permeability is a problem in copper leach heaps. This permeability problem is due to the buildup of fine particles in the spaces between the larger particles. The build-up of particles results in poor solution flow and in turn decreased metal recovery rates. Agglomeration helps to eliminate the problem of fine material by adhering particles together. However, the use of a binder will help to increase the benefits of agglomeration by adding additional strength to the agglomerates. It will help to increase recovery rates which improve energy efficiency.

A wide variety of binder choices were available including inorganic, organic, silicate, and polymer binders. Although there were no standard tests in place which would determine which binder type would be beneficial. The soak test was developed to determine which binder would be able to hold together in the acidic environment of a heap. The polymer binders, mainly non-ionic and slightly cationic binders, were able to withstand the acidic environment which would be experienced in a leach heap.

The flooded column test was designed to assess the binders' ability to allow solution to flow through the ore bed. All the binders tested showed an increase in solution flow over using raffinate as a binder. The use of the binders also maintained void space in the ore bed better than the raffinate agglomerated ore. These factors are important, as the ability for the solution to come in contact with the ore is critical for good metal recovery rates.

The effect of the binder on copper recovery rates was able to be analyzed by the design and construction of the long-term leach columns. These columns subjected the agglomerated ore to an environment which simulated a leach heap as closely to its actual performance as is possible at that point in time. At this point a meeting was held with our industrial partners. After a review of the results and experimental procedures accomplished, both MTU and the Arizona location decided to concurrently run six long-term leach columns. The duplicate columns were able to be used to show that the long-term leach column results were reproducible, even with or without the use of a binder. They will also help determine whether our industrial partners would like to progress with additional larger scale test work. Currently, the six long-term leach columns have shown that the use of the binders does not have any negative effects on the copper recovery.

The long-term leach columns are able to simulate the heap by scale down factors; however, they are unable to simulate factors such as compaction due to the weight of the ore in the heap. Therefore, a compaction leach column has been designed, constructed, and patented to assess the performance of the binders on solution flow and void space within a compacted heap. The results of these tests have shown there is a tremendous difference in the behavior of compacted ore verses non compacted ore. A large increase in the evenness of solution flow was discovered. This experimental procedure also brought to light other factors, such as channeling, which occur in an ore bed under compaction. A larger scale compaction column is also falls under the provisional patent held by the MTU investigators. This column will help determine the effect of the binders on copper recovery with compaction conditions similar to what would be occurring further down in the heap.

Conclusions

The use of agglomeration in copper heap leaching has been found allow for better solution flow through an ore bed, which is expected to result in increased copper recovery rates in full-scale leaching operations. Currently, there are no standard tests developed to determine which types of binders will perform best. A binder needs to not break down in an acidic environment, allow for good solution flow, and not inhibit copper recovery.

Several tests have been developed which allow each binder to be analyzed, to determine which types of agents will result in improved copper recovery rates. Overall, polymer binders have been found to have the greatest strength when used in agglomerates and subjected to an acidic environment. The binders help to increase solution flow and maintain void space which results in better contact of the leach solution, air, and ore. The use of these binders also has not adversely affected copper recovery. Constant communication with our industrial partners has allowed concurrent testing to be done at MTU and at a copper leach facility in Arizona. Meetings to discuss MTU's results have allowed possible future testing to be considered.

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