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, and advanced ironmaking processes, where binders must function satisfactorily over an extraordinarily large range of temperatures (from room temperature up to over 1200°C). 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 and advanced primary ironmaking.

This project has identified several acid-resistant binders and agglomeration procedures that can be used for improving the energy efficiency of heap leaching, by preventing the “ponding” and “channeling” effects that currently cause reduced recovery and extended leaching cycle times. Methods have also been developed for iron ore processing which are intended to improve the performance of pellet binders, and have directly saved energy by increasing filtration rates of the pelletization feed by as much as 23%.
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INTRODUCTION

As higher grade ore deposits have become depleted, it has become necessary for mining companies to work with progressively finer-grained ores that must be ground to a fine particle size in order to be liberated and concentrated. Dealing with these fine mineral concentrates requires that they be agglomerated to form pellets or similar masses of particles that are durable enough to be handled and processed to extract the valuable minerals. This allows the fine-grained materials to be treated as if they were much coarser particles, which gives major advantages in handling and processing while maintaining the significant reactivity advantages that result from the fine particle sizes of the particles that make up the agglomerates. Examples of areas where mineral agglomeration are particularly important are: 1) Heap leaching of metals such as gold and copper, and 2) Primary metallic iron production.

The basic approach to heap leaching of copper sulfide minerals 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 conveying into an agglomeration drum where it is wetted with raffinate (barren leach solution). 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 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. Raffinate is 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 and is sent to a solvent extraction and electrowinning 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. Due to this, some 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. Agglomeration will therefore result in greater metal production per unit of energy consumed, and will therefore increase energy efficiency. The problem is that copper leaching requires the use of acid solutions, and the agglomeration binders that have been used successfully in other types of heap leaching, such as gold extraction, only function well when the pH is neutral or alkaline. New, acid-resistant binders are therefore needed, which can bind the ore particles into agglomerates that do not break down in acid while still allowing access of air and leach solution to the ore particles.
Similarly, production of primary iron from iron ore is critically dependent on agglomeration. Concentration of iron oxide minerals requires grinding to very fine particle sizes, frequently smaller than 25 µm, in order to liberate and separate the iron oxides from the silicate gangue. The resulting iron oxide powder is too fine to be processed either by conventional blast furnaces, or by advanced ironmaking processes that are under development. The fines must therefore be agglomerated to form pellets of approximately 1.2 cm diameter. Use of these pellets as feed to a blast furnace requires them to be hardened by heating to 1200°C to sinter the fine particles together. The pellets must then be cooled to ambient temperature for shipping and handling, and all of the energy that was used in the hardening step is lost before the pellets are re-heated in the blast furnace to 1500°C to produce liquid iron. Binders for these pellets must therefore be able not only to bind agglomerates at ambient temperatures, but must also continue to function over a tremendous range of temperatures so that the pellets do not disintegrate while they are being heated.

In order to reduce the amount of energy wasted in the multi-step pelletization/blast furnace techniques that are currently used, new processes are needed that can produce metallic iron from ore directly, in a single step. A particularly promising approach is the iron nugget process, where pellets are made that consist of iron oxide concentrate, powdered coal, flux, and a binder. When these pellets are heated, they self-reduce to form metallic iron droplets that separate from the slag. Since this occurs in a single heating step, considerably less energy is used than in the multiple heating and cooling cycles inherent to the blast furnace operations. However, in order to be fully effective, this process places great demands on the binder used to produce the pellets. It must develop high strength at low temperatures, and hold the pellets together not only during the heating stage, but also during the ironmaking stage where the carbon from the coal reacts with the iron oxides to make metal, while the flux reacts with silicate gangue to produce slag.

Both conventional and advanced ironmaking therefore require the maximum performance from the binders used in order to produce satisfactory pellets that can be processed with the maximum energy efficiency. This requires that the factors that affect binder performance be known and controlled in order to achieve the maximum strength and thermal resistance in the pellets.
EXECUTIVE SUMMARY

The objective of this project was to develop and implement binders and agglomeration procedures that will increase the efficiency of metal extraction processes. This is particularly important in the following situations:

1. Copper leaching operations, where the acidic leaching environment prevents existing leaching binders from working satisfactorily. Without binders, agglomerates tend to break down over time, leading to reduced fluid flow through the ore. 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.

2. Primary iron production, which requires agglomerated iron ore concentrates both for conventional blast furnace processing, and new, advanced ironmaking technologies. Binders are needed that can produce high-quality “green” pellets that can be handled at ambient temperatures, and that can also tolerate subsequent high-temperature processing at up to 1500°C without allowing the pellets to disintegrate, as disintegration causes efficiency losses and generates dust.

The goal was therefore to develop binders for mineral agglomeration that meet these requirements, allowing increased processing efficiency and reduced energy losses. Binders were developed based on theoretical considerations and on past experience to be effective in leaching operations, and in ore concentrate agglomeration for thermal processing.

Heap leaching agglomeration
A series of new evaluation techniques (soak test, percolation test, and compaction column test) were developed in this project to determine performance of acid-resistant binders for heap leaching. Of the numerous types of binders examined, polymer binders (mainly non-ionic and slightly cationic binders) were able to produce the greatest agglomerate strength, indicated by possessing the least amount of breakdown under acidic conditions while maintaining void space and maximizing the ease of percolation of fluid through the agglomerated ore bed (hydraulic conductivity). Long-term column leaching experiments were carried out which demonstrated that the binders would not have harmful side effects on the leaching chemistry.

It was discovered that, in order to replicate the common problems of channeling and ponding which occur in full scale heaps, it would be necessary to examine the effects of compaction on the ore characteristics. A special apparatus was constructed for this purpose, and a patent is being applied for (provisional patent no. US60/750,236). This is
a significant development, as until now there has not been a way for the industry to examine compaction effects in heap leaching without constructing a full-scale test heap.

**Ore concentrate agglomeration**
In agglomeration of iron ore to produce pellets for use in the blast furnace and in advanced ironmaking processes, it is important to determine the effects of water chemistry on the performance of bentonite clay binders and how this impacts the pellet quality. It was determined that the water that remains in the filter cake after filtration in iron ore concentrators can contain several hundred times greater concentrations of calcium ions and other cations, due to surface chemical effects carrying the ions along with the water. This is a serious concern for pellet quality, as calcium ions are known to degrade the performance of bentonite clay binders. Based on the theory of the electrical double layer, it was predicted that reducing the pH of the solution to near the isoelectric point (IEP) of the magnetite particles would cause the bulk of the positively-charged calcium and magnesium ions to be released. Carbon dioxide injection was found to be the best available method for reducing slurry pH to near the magnetite IEP so that calcium and magnesium ions would be removed during filtration. In both, laboratory and plant studies, the carbon dioxide injection produced the significant additional benefit of increasing filtration rates by up to 23.7%.

**Energy Benefits**
In heap leaching, preventing agglomerate breakdown and limiting the migration of fines by the utilization of cost effective binders in the agglomeration step would enhance the overall recovery of the heap. Using agglomeration to achieve a 25% increase in copper recovery is estimated to save $1.64 \times 10^{12}$ BTU per year (Phelps Dodge, 2002). Similarly, increasing the leaching rate will shorten the time for one heap leach cycle. For every week that the leaching cycle is shortened, an additional $1.23 \times 10^{11}$ BTU will be saved, assuming 70% of the leach heaps implements the technology.

In iron ore pelletization, filtration costs are in the range of $0.60 - $1.50/ton, much of which is for the energy to apply vacuum to the system. The energy-efficiency benefits of the 23% increase in filtration rate would be adequate justification for carbon dioxide injection, even in the absence of effects on pellet quality. Improved binder technology will also allow the adoption of advanced single-stage ironmaking technologies, which are approximately 13% more energy-efficient than the conventional pelletization-blast furnace technology. Assuming that 50% of the industry converts to single-stage ironmaking, this will save an estimated $6.51 \times 10^{13}$ BTU/year.

**Industrial Involvement**
Industrial cost-share for this project is being provided by Phelps Dodge, Inc., Newmont Mining Co., and Northshore Mining Co. All three companies have contributed considerable amounts of engineering time to this project. In addition to their engineering contributions, Northshore and Phelps Dodge provided substantial material support, as follows:
Northshore Mining Co. personnel cooperated in carrying out extensive laboratory experimentation and in-plant testwork in their facility, providing invaluable data for this project. This work included pelletization studies, evaluations of pellet quality, laboratory filtration experiments, and full-scale in-plant demonstrations of carbon dioxide injection during concentrate filtration.

Phelps Dodge provided apparatus for conducting flooded and column leaching tests. Phelps Dodge has also provided several hundred pounds of their Mine for Leach (MFL) ore for experimental testing along with several hundred gallons of the raffinate solution from their process. Phelps Dodge has completed analysis on the material which they have sent, such as running assays and x-ray diffraction. They have also provided the use of their labs and employees to run duplicate 180 day leach column testing at their facility along with the testing which was being completed at MTU.

Educational Opportunity
This project has allowed for various educational opportunities in relation to the project itself. Several undergraduate students have been given an opportunity to assist in research and testing. Analysis from soak tests, flooded column tests, and long term leach columns was contributed to by several undergraduate chemical engineering students at Michigan Technological University. This experience gave the students a chance to partake in many aspects of the research rather than just performing manual labor tasks. Students took part in designing or constructing laboratory apparatus, along with carrying out experimental procedures, and collecting and analyzing results. One particular undergraduate student is a co-author of this report, and is one of three inventors that took part in the design, creation, and patenting process of a large compaction column defined under provisional patent serial number US60/750,236.

This project has also lead to the completion of a paper (Eisele, et al., 2005) which was presented at the Society for Mining, Metallurgy, and Exploration (SME) Conference in Salt Lake City, Utah in 2005. This paper covers the determination of the acid resistance of agglomerates in copper heap leaching. A paper (Lewandowski et al., 2006) has been presented at the Sohn International Symposium on Advanced Processing of Metals and Materials: Principles, Technologies and Industrial Practice in San Diego, California in August 2006.
EXPERIMENTAL

Copper Ore Agglomeration

The basic approach to hydrometallurgical processing of a secondary sulfide such as chalcocite (Cu₂S) 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.

\[ Cu_2S + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + CuS \] (1)
\[ CuS + 2Fe^{3+} \rightarrow Cu^{2+} + 2Fe^{2+} + S^0 \] (2)

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

\[ 2Fe^{2+} + \frac{1}{2}O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O \] (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. The iron (III) reacts with the ore (Cu₂S), to produce the desired product, copper. It also requires easy flow of air to provide oxygen. The oxygen reacts with the iron (II) produced from the ore reaction and with the aid of the bacteria reconverts back into iron (III), which is a feed material for the other reactions. It is important that all of the equations continue, to obtain the best copper recovery possible.

In a copper heap leaching process, shown in Figure 1, 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 approximately 20 feet is typical. The lift is irrigated with the leach solution, 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 iron (III) to be regenerated by the bacterial reaction shown in Equation 3. The interaction between the raffinate, air, and ore allow for the copper to be dissolved from the ore as indicated in Equations 1 and 2. The solution which has percolated through the heap, now referred to as pregnant leach solution (PLS), is captured in a pond. From the pond it is sent to a solvent extraction and electrowinning circuit where the liberated copper is ultimately recovered.
In the current heap leaching operations, copper recovery is still not as high as desired in a reasonable amount of time. This means it is necessary for ore to be ground to finer particle sizes in order for it to be liberated. The finer-grained ore is much harder to handle, and is still not producing the required recoveries with the current operating conditions. Poor permeability is one of the main problems which results due to the finer-grained ore. The fine particles migrate downward in the heap with the leach solution, and clog the spaces between the larger ore particles, causing uneven distribution of the leach solution, shown in Figure 2. The fine particles build up and begin to form impermeable layers within the ore bed. The build-up leads to a difficulty for air and leach solution to flow freely through the heap. Thus, the solution chooses to either flow down the path that gives the least amount of resistance (channeling), or tends to pool within the heap (ponding). Either of these actions will result in solution not coming in contact with all the ore, leaving these zones either non-leached, or partially leached only by diffusion. The air may also channel upwards creating the same problems associated with solution channeling. Ore which is not leached or partially leached in the heap means 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.
Ideally, the ore bed would be constructed of an ore distribution as illustrated in Figure 3. Spaces between the particles would create a more permeable ore bed which would allow for solution to flow freely and evenly through the heap, and would allow air to flow upwards. There would be limited free fine particles which would clog spaces and result in permeability problems. Agglomeration can be used to achieve this ideal ore bed distribution. Agglomerating the material into pellets, similar masses, or particles that are durable enough to be handled would entrap the fine particles to enable them from filling the spaces between the larger particles and causing build-up. Agglomerating and entrapping the fine particles, allows for an increase in the availability of the transport of the leach solution throughout the heap. When the leach solution percolates evenly through the heap the reactions within the heap can take place within all the ore. Agglomeration has been shown to be important in the heap leaching of metals, such as gold and copper.

In copper heap leaching processes, after the ore is crushed it is sent to an agglomeration drum, where it is agglomerated with raffinate (leach solution). The agglomerated ore is transported to the heap by conveyor, where it is radially stacked. Currently, there is one copper heap leaching facility in the United States which uses agglomeration; however, they agglomerate using raffinate, the leach solution. This facility is still observing copper outputs below the desired recovery rate, due to the rapid breakdown of the agglomerates. This breakdown is caused by the release of fine material which clogs flow channels in the ore bed. Areas are left either un-leached or partially leached, and 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. An increase in permeability will allow for the leach solution to reach the ore in the entire heap evenly.

The use of a cost effective binder 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 to help the bacteria convert iron (II) back into iron (III). The acidic solutions decrease the pH of the heap to approximately a pH of 1.5-3. Most agglomeration binders which are used successfully in other operations, such as Portland cement and lime, require a more neutral or alkaline pH. These cement-type binders dissolve readily in acid, and are completely ineffective in an acidic leaching environment. Acid-resistant binders are needed for these copper operations which will not breakdown in acid, while allowing access of air and leach solutions to reach the ore particles.

The use of a proper binder 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**

**Copper Ore Agglomeration**

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 have been no standard procedures 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 were no known binders which perform adequately, an array of various products including organic, inorganic, and polymeric binders needed to be tested. Testing a variety of products helped to determine what will help keep agglomerate strength.

**Soak Test**

Before any binders were able to 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 procedure, ore was agglomerated in a rotating drum with raffinate and a chosen binder. The addition of the binder helped to bond the fine particles to the coarser ones. It was then placed onto a Tyler 10 mesh 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 4.

![Diagram of soak test experimental procedure]

**Figure 4: Soak Test Experimental Procedure**

It was unknown which type of binder would be able to withstand the acidic heap conditions while aiding in metal recovery. Soak tests were performed on a variety of chemicals including inorganic, organic, and polymeric, in order to get a better idea of which might give additional strength to the agglomerates when subjected to low pH’s.

The binders were judged on the percent of material which has passed through the 10 mesh screen, and is termed the amount of fines migrated. 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.

\[
Fines \text{ Migration} = \frac{\text{Weight of ore migrated out of the sample}}{\text{Total weight of } -10\text{mesh fines available in the sample}} \tag{4}
\]

Even if the binder were able to withstand the acidic conditions that would be encountered in a leaching heap, this did not necessarily mean that the use of these binders would result in increased permeability within the ore bed. Increased permeability is needed to ensure that the leach solution and air are able to flow evenly throughout the heap. Even flow will allow for all the ore to come in contact with the leach solution and air which will result in improved leaching kinetics and increase in 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 would allow for an increased ability for 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, solid, and gas interface.

$$\rho_{\text{Bulk}} = \frac{\text{weight of ore}}{\text{volume of ore}}$$  \hspace{1cm} (5)

$$\Delta \rho_{\text{Bulk}} = \rho_{\text{Bulk Final}} - \rho_{\text{Bulk Initial}}$$  \hspace{1cm} (6)

Where:
\(\rho = \text{density (ton/yd}^3)\)

A high change in bulk density would indicate that the amount void spaces are decreasing during the leaching test. This would be a result of the agglomerates breaking down and compacting together. If the change in bulk density remains low, this indicates that the void spaces between agglomerates 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.

$$Q = A \times K \times \frac{\Delta h}{L}$$  \hspace{1cm} (7)

Where:
\(Q = \text{volumetric flow rate (m}^3/\text{s)}\)
\(L = \text{flow path length (m)}\)
\(A = \text{flow area perpendicular to } L (m^2)\)
\(\Delta h = \text{change in hydraulic head (m)}\)
\(K = \text{hydraulic conductivity (m/s)}\)

The extent of breakdown of the agglomerates can also be quantified by the percentage of fines which have migrated, Equation 4. 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 addressed these issues by keeping fines bound together, creating a more uniform size distribution and producing minimal fines migration.

Determining the degree of permeability allowed the binders to be compared, to decide whether or not the binders 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 had not been developed. Therefore, the flooded column test was designed and constructed to test these parameters.

The flooded columns test apparatus’, shown in Figure 5, were assembled.

![Figure 5: Flooded Test Columns](image)

The ore is agglomerated with raffinate and a chosen binder. The ore is then allowed to air dry, or cure. After drying, the agglomerated ore is transferred to a column. Leach solution is dripped onto the top of the column, where it begins to slowly flood the column. The solution exits the column through the overflow system. Figure 6 outlines this process.

The flooded column test was 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. Therefore, as the columns would not be used for copper recovery data, they were not equipped with any air injection, which would play a major role in the extent of copper recovery obtained, as described in Equation 3.

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 was developed to perform this task.

A long-term leach column was designed and constructed to carry out this simulation. The columns, shown below in Figure 7, were created to simulate a leach heap. Only the best binders would be tested in these columns, as the leach cycle is 180 days. Six of these columns have been built in the Michigan Technological University Laboratory. 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 was that factors such as channeling, where the solution flows directly down one
path without spreading evenly over the ore body, 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.

![Figure 6: Schematic of Flooded Column Test](image)

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. An 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 8. The solution collected is called pregnant leach solution (PLS), and is later tested for copper and iron recovery along with pH, oxidation/reduction potential (ORP), and temperature.

Five of these columns have been run at Michigan Technological University. These five columns included 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.
Figure 7: Long-term Leaching Columns

Figure 8: Schematic of Leach Testing Column
Although the long-term leach columns are a 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 in an industrial heap can partly be contributed to the weight of the ore alone and by trucks driving on the top surface. Compaction due to these factors was 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 was completed to evaluate the binders under compression. This data was used to compare the different binders. This gave 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 apparatus was 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 was 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.

**Iron Ore Agglomeration**

**Materials**
Iron ore agglomeration studies were carried out using iron ore concentrate (magnetite) provided by Northshore Mining Co. This concentrate was collected from the slurry feed to the plant filters. Analytical results with the Northshore concentrate were compared with those that had previously been obtained from a second plant.

**Test Procedure**
The following procedure was used for analyzing filter cake moisture chemistry, which was necessary in order to determine how the performance of agglomeration binder is affected by the concentrations of various ions in the solution:

1. Obtain a representative sample of 50.00+/– 0.01 grams of the moist filter cake from the filters in an operating plant.
2. Place the sample in a bottle that can be sealed and dilute it with 100.00 grams of distilled water.
3. Seal the sample bottle, and shake it vigorously for 60 seconds.
4. Measure the pH and conductivity of the slurry. If it is above pH=7, adjust the pH of the slurry to 5.5 - 6 with hydrochloric acid. This pH adjustment is intended to ensure that the magnetite is near its Point of Zero Charge (PZC), as this is the pH where the magnetite will have a minimal tendency to attach cations to its surface.
5. Filter the solids from the solution.
Analyze the water for ionic concentrations, particularly Ca\(^{+2}\), Na\(^{+}\), K\(^{+}\), Mg\(^{+}\), and SO\(_4\)^{2-}, by any appropriate standard analytical technique (ICP, AA, etc.).

Pelletizing experiments were also carried out on the filter cake in order to determine the effects of cation levels on pellet quality. Standard laboratory pelletization techniques were followed to simulate pellet production in the plant. Bentonite clay was added as binder at a rate of 0.625% of the weight of the filter cake. The following quality tests were conducted:

- **Fired pellet drop test** - A sample of 5000 grams of fired pellets was dropped from a height of 15.24 m (50 foot). The % + 6.35 mm (1/4 inch) material in the pellet sample was measured after the sample was dropped.
- **Fired pellet compressive strength** – Individual pellets were compressed until they fractured, and the force required to fracture the pellets was measured in Newtons (N) per pellet. This was repeated for a total of 100 pellets for each test.
- **Wet green ball drop test** – Wet green balls were individually dropped repeatedly from a height of 457 mm (18 inch), and the number of drops needed to fracture each pellet was recorded. This was repeated for 20 pellets for each test.
- **Dry green ball compressive strength** – Green balls that had been dried at 105°C were compressed individually until they fractured, and the force required to fracture the pellets was measured in Newtons (N) per pellet. This was repeated for 20 pellets for each test.
- **Tumble** – The % -6.35 mm (-1/4 inch) material in a sample of fired pellets was measured before tumbling (B. T.) and after tumbling (A. T.). The “Q” index was calculated from these values, where higher values of “Q” indicate a greater resistance to abrasion and breakage.
- **Wet green ball compressive strength**, in Newtons (N) per pellet (10 pellets).

In addition to conventional pellets consisting of iron ore concentrate and binder, pellets for use in production of iron nuggets were produced using a mixture of iron ore concentrate, powdered coal, limestone flux, and binder. The same pelletization procedure was used as for the conventional pellets.

**Equipment**

In the course of the studies to date, it was determined that additional analytical equipment would be required for this project, and that personnel expenses would be lower than anticipated due to the high degree of industrial cooperation being provided. Funds were therefore reallocated to purchase the following items:

1. A Varian atomic-absorption spectrometer, for analysis of elements in solution. This is particularly critical for evaluating copper mineral dissolution in the planned column leaching experiments, and for measurement of ionic species that adsorb on the surfaces of magnetite particles. ($28,907.00, 100% paid for by DOE).
2. An Electrokinetic Analyzer for measurement of particle streaming potential. This unit is necessary for measurement of the Zeta potential of particles coarser than approximately 25 micrometers, which cannot be measured using the currently
available equipment. Zeta potential of particles controls their interactions with materials from solution, particularly binder molecules and ionic species, and is therefore a critical parameter for this project. ($56,065.00, 58% paid for by DOE/42% by MTU).

3. A computer for analysis and presentation of data collected in this project.
4. Three used high-temperature furnaces were acquired at a total cost of $3000 for use in producing iron nuggets. These consist of two tube furnaces (one of which is being retrofitted to be a high-temperature thermogravimetric analysis apparatus, and the second of which will be used for controlled-atmosphere experiments), and a box furnace that allows rapid heating and cooling cycles of samples in air.

Zeta Potential Measurement
Calcium and magnesium cations that reduce bentonite effectiveness are retained by the strong negative surface charge on the magnetite slurry particles. The charge on the magnetite particles (the Zeta potential) is a function of pH, becoming more negative as the pH increases. An example of the typical change in magnetite Zeta potential that has previously been reported in the literature is shown in Figure (34). From this data, the pH where the Zeta potential equals zero (the isoelectric point) was expected to be approximately 6.5, and so reducing the pH to near this value was expected to release Ca$^{+2}$ and Mg$^{+2}$ from the surfaces. However, the zeta potential for the Plant 2 concentrate had never been measured. Tests were therefore conducted at MTU to determine the zeta potential for these magnetite concentrate particles.

The Zeta potential was measured using a microelectrophoresis unit, with Plant 2 magnetite particles suspended in two different solutions: plant filtrate water over the pH range 7.09-5.27, and distilled water over the pH range 5.07-2.47. The pH was reduced by injection of carbon dioxide down to a pH of 4.92, and by addition of nitric acid to reach pH values down to 2.47. Carbon dioxide was chosen for pH adjustment because when dissolved in water it is a low-cost weak acid, and it also softens water by precipitating calcium ions as calcium carbonate. It was therefore the primary candidate being considered for pH adjustment in the plant studies.

Plant-scale Testing of Filter Cake Rinsing
Laboratory results showed that filter cake washing improved fired pellet quality, but how could this be achieved on a plant-scale? It is obviously not feasible at the plant-scale to re-slurry the filter cake in clean water just to filter it again. A more practical approach would be to alter the pH during filtration to reduce the strong negative charge on the particle surfaces (as measured by the zeta potential) that attracts and holds the divalent cations. The cations would then be released into the filtrate rather than being preferentially held in the filter cake. Lowering pH has also been reported in at least some plants to improve filter production rates (Larsen, 2003).

The first method attempted to lower the pH in the plant filters was the use of a small amount of rinse water at a pH of 6.0. The first source of mildly acidic rinse water considered was water from Plant 2’s electrostatic precipitator (ESP) emission control water system. The water is warm (which also improves filtering by reducing viscosity)
and has a typical pH of approximately 6 in the underflow. However, the pH of the ESP water was not under control, and the water chemistry was questionable for this application because of high concentrations of various ions. It was therefore not considered suitable for a rigorous study.

A second system was designed where plant recycled water was added to a surge tank that was dosed with a small amount of hydrochloric acid using a reagent pump to produce a rinse liquid with a controlled pH. This water was then pumped into the existing filter panel wash water system. The rinse water system in operation is shown in Figure 9, where it can be seen that the rinse water was being sprayed directly onto filter cake on the disk filters. The rinse water was added at a relatively low flowrate of approximately 12 liters per metric ton of filter cake.

Two approaches for achieving this were examined in plant studies. The first approach consisted of rinsing the concentrate filter cake with sprays of acidic water from the plant’s gas scrubbing system, as shown in Figure 9. However, plant trials showed that this was insufficient to achieve the desired goals, and had the added drawback of introducing the potential for corrosion problems and filter cloth blinding. The second approach considered was therefore injection of carbon dioxide into the slurry as it entered the filters, Figure 10.

![Figure 9](image1.jpg)

**Figure 9:** Rinsing filter cake with pH-adjusted water while filtering in the Northshore plant.

![Figure 10](image2.jpg)

**Figure 10:** CO₂ tanks and evaporator at the Northshore plant. Liquid CO₂ was vaporized in the evaporator, and injected into the filter slurry as a gas.
Pelletization for single-stage ironmaking
Experiments were also launched to examine the ability of binders to maintain pellet integrity while being heated to high temperatures in the iron nugget process, one of the most promising methods for advanced single-step ironmaking from iron ore concentrate. The iron nugget process consists of agglomerating iron oxides together with sufficient coal to reduce the oxides to metal, and sufficient flux to allow the impurities in the ore to melt and form a slag. The binder must therefore form an adequately strong pellet at low temperatures, and then continue to hold the pellet together as it is heated to as high as 1500°C while the coal contained in the pellet reacts with the iron oxides. The combination of high temperatures and extreme heat place tremendous demands on the binder, as can be seen in Figure 11. These pellets were removed from the furnace at the last point where the binder is the primary material holding the pellet together. Later in the process, the iron begins to melt and the binder is no longer necessary. In this case, the binder was able to function well enough for the pellets to roughly maintain their shape during the heating and initial chemical reaction, but it can be seen that the pellets were partially breaking down and losing material in the process. These studies have lead to ongoing work to combine the function of binder with the function of metal reduction. This is being done by using organic binders (such as starches and modified cellulose) that make up as much as 20% of the pellet weight. As the pellets are heated, the organic binders both hold the pellets together, and react with the oxygen present in the iron oxide minerals to convert them to metallic iron. This is a completely novel area of research, and will require considerable further study to ensure that it can be successfully adopted by industry.

Figure 11: Direct reduced iron pellets, which are an intermediate stage in production of iron nuggets, using bentonite clay as a binder. These represent the point in the process where the iron oxides have converted to iron, and are about to begin melting to produce finished iron nuggets.
RESULTS AND DISCUSSION

**Heap Leaching Agglomeration**

Each agglomerated sample was 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 12 & 13.

![Figure 12: Visual Deterioration of Agglomerates in Soak Test](image)

![Figure 13: 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.](image)

The fines migration results are summarized in Figure 14. The numbers of tests performed per binder are listed along with the summarized fines migration results in Table 1. These results lead to the conclusion that the use of polymer binders resulted in better agglomerate strength. The results indicated that the polyvinyl acetate emulsion 1, polyacrylamides, and the waste treatment additive showed the greatest decrease in the amount of fines released when compared to the baseline test where no binder other than raffinate was used. The agglomerates which used organic and inorganic additives all broke down during the soak test, resulting in high fines migration values, and therefore would not help to increase permeability any more so than agglomerating with only raffinate.
Figure 14: Fines Migration using Various Chemical Agents

Table 1: Fines Migration using Various Chemical Agents

<table>
<thead>
<tr>
<th>Binder</th>
<th>Percent of Fines Migration</th>
<th># of Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cure</td>
<td>Dry</td>
</tr>
<tr>
<td>Raffinate</td>
<td>28.67% ± 1.97%</td>
<td></td>
</tr>
<tr>
<td>Cellulose Derivative</td>
<td>22.80% ± 3.33%</td>
<td>2</td>
</tr>
<tr>
<td>Lignin Derivative</td>
<td>24.91% ± 5.14%</td>
<td>3</td>
</tr>
<tr>
<td>Methyl Cellulose Ether</td>
<td>17.48% ± 2.66%</td>
<td>3</td>
</tr>
<tr>
<td>Tall Oil Pitch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Silicate</td>
<td>23.69% ± 4.97%</td>
<td>2</td>
</tr>
<tr>
<td>Acrylamide/Sodium Acrylate Polymer 2</td>
<td>24.06% ± 2.21%</td>
<td>3</td>
</tr>
<tr>
<td>Acrylamide/Sodium Acrylate Polymer 1</td>
<td>23.89% ± 4.91%</td>
<td>3</td>
</tr>
<tr>
<td>Acrylamide Copolymer</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl Acetate Emulsion 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polydadmac Polymer</td>
<td>17.62% ± 8.27%</td>
<td>3</td>
</tr>
<tr>
<td>Polyacrylamide 3</td>
<td>20.83% ± 6.36%</td>
<td>3</td>
</tr>
<tr>
<td>Polyvinyl Acetate Emulsion 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste Treatment Additive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacrylamide 1</td>
<td>20.28% ± 4.72%</td>
<td>2</td>
</tr>
</tbody>
</table>
The rate at which the agglomerates broke down was not only based on the binder being added, but was also found to be related to the moisture content of the agglomerates. 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 15, indicated that the wet agglomerates had better strength and released fewer fines, than the agglomerates which were allowed to dry overnight. The number of tests performed per binder, along with the results of the effect of cure time on fines migration, is summarized in Table 2. All the binders performed better than the baseline test, which contained no binder, when the agglomerates were allowed cure time. It was concluded that some of the bonds between the ore and binder degrade during drying. Therefore, 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.

Table 2: Effect of Cure Time on Fines Migration using Various Chemical Agents

<table>
<thead>
<tr>
<th>Binder</th>
<th>Percent of Fines Migration</th>
<th># of Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cure</td>
<td>No Cure</td>
</tr>
<tr>
<td>Raffinate</td>
<td>28.6%±1.97%</td>
<td>7.41%±3.91%</td>
</tr>
<tr>
<td>Polyacrylamide 1</td>
<td>20.28%±4.72%</td>
<td>2.99%±0.00%</td>
</tr>
<tr>
<td>Polyvinyl Acetate Emulsion 1</td>
<td>8.41%±4.18%</td>
<td>5.75%±2.35%</td>
</tr>
<tr>
<td>Polyvinyl Acetate Emulsion 2</td>
<td>20.91%±3.61%</td>
<td>9.48%±0.14%</td>
</tr>
<tr>
<td>Waste Treatment Additive</td>
<td>4.70%±0.52%</td>
<td>4.88%±0.68%</td>
</tr>
</tbody>
</table>
The polymer binders which improved the strength of the agglomerates under acidic conditions in the soak test were then tested in the flooded column. Fines migration results from the percolation flooded column tests, Figure 16, indicated that the all of the synthetic binders tested had a lower percentage of fines migration than the baseline test. This indicates that the agglomerates that were made with a binder had a lower tendency to breakdown. The tall oil pitch and the waste treatment additive agglomerates had the lowest amount of fines migration.

![Bar chart showing fines migration percentages for different binders](image)

**Figure 16: Ratio of Fines in Flooded Column Tests**

The ore bulk densities varied for these five particular binders and raffinate. A higher change in bulk density indicated there was a decrease in the amount of volume that the mass of ore in the flooded columns occupied. A higher bulk density indicates that there is more compaction of the ore in the column due to the agglomerate breakdown. This compaction leads to a decrease in void space within the ore bed. Solution and air flow is impeded if there is not enough void space within the heap. 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 17 shows the ore bulk density with time for the various agglomeration 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. This was shown quantitatively by high changes in bulk density and a high percentage of fines migration.

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 leach kinetics.

Measurements to determine conductivity were taken on the same five binders and raffinate, as analyzed for bulk density and fines migration. The summary of the results are shown in Figure 18. The polyacrylamide showed the highest conductivity, which means the solution had an easier time flowing through the ore bed. The polyvinyl acetate emulsion 2 produced the lowest hydraulic conductivities out of the five binders. It also had the highest fines migration rate and the highest change in bulk density out of all the binders. This indicates that the agglomerates were deteriorating, causing compaction of the ore bed and an increase in bulk density. This along with the fine material which was released from the agglomerates resulted in solution not being able to flow easily. However, all binders had higher conductivities than the ore agglomerated with raffinate only.
Initially, one flow measurement was taken at the beginning of a test. However, the flow rates of the pumps cycle up and down slightly due to the pumps heating up and not performing consistently. The hydraulic conductivity measurements are based off of the solution flow rate resulting in a fluctuation within the data. All remaining tests included a flow rate measurement taken for each hydraulic conductivity point to eliminate the variation.

For comparison purposes all the agglomerates were 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 1, waste treatment additive, and tall oil pitch, have been optimized.

The optimum dosage was determined by looking at the binder dosage rate when the hydraulic conductivity first began to reach a state where there was no longer a significant increase in hydraulic conductivity with increasing binder addition. The change in bulk density also showed a leveling trend around this same addition rate. The optimum binder dosages were determined from the hydraulic conductivity and bulk density results shown for the four binders which have been tested in Figures 19 through 26.
Figure 19: Flooded Column Hydraulic Conductivity Evaluation for the Polyvinyl Acetate 1

Figure 20: Flooded Column Bulk Density Evaluation for the Polyvinyl Acetate 1

Figure 21: Flooded Column Hydraulic Conductivity Evaluation for the Polyacrylamide 1

Figure 22: Flooded Column Bulk Density Evaluation for the Polyacrylamide 1

Figure 23: Flooded Column Hydraulic Conductivity Evaluation for the Waste Treatment Additive

Figure 24: Flooded Column Bulk Density Evaluation for the Waste Treatment Additive
From these results it was determined that the polyvinyl acetate 1, polyacrylamide 1, 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, as this is where the change in bulk density began to become stable with increasing binder dosage.

The copper recoveries, shown in Figure 27, indicated that there was no adverse effect to the leaching process by using these binders in agglomeration.

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 were duplicated concurrently at our industrial partners copper heap leaching operation in Arizona. Both the Arizona location and Michigan Technological University (MTU) ran columns using the same binders and ore from the same split from the Arizona industrial process circuit.

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 indicated a greater concentration of ferrous iron in the system. A higher ORP indicated there was 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 would show there was 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 28, 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. At the beginning of the leach cycle the ORP’s are low. As the leach cycle goes on, the ORP increases. At this point the amount of iron (III) in the system increases accordingly. This means the use of the binders does not interfere with the bacterial populations, in fact they seem to promote bacterial growth over the raffinate and non-agglomerated columns. High bacterial populations are necessary to make sure there is enough feed material to enable the leach kinetics to progress.

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 meant the amount of ferric iron in the system was decreasing and the amount of ferrous iron was increasing. If the low ORP’s were experienced for a long period of time, this would begin to affect the leaching kinetics, given in Equations 1, 2, and 3, and eventually result in a decreased copper recovery.

The stability of the agglomerates throughout the long-term leach column tests were evaluated by comparing the bulk density, or slump, of the ore bed in each column. Figure 29 shows the overall change in bulk density results for the long-term leach columns.
Figure 28: Oxidation/Reduction Potential results from MTU long-term leach columns

Figure 29: Total change in bulk density for various binders over the entire leach cycle
The polyacrylamide had the lowest change in bulk density measurements of the binders tested. This indicated 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 change in bulk density of the raffinate agglomerated column was the highest. In the column the agglomerates deteriorated more.

Experiments were performed on ore agglomerated with raffinate, and ore agglomerated with the four binders used in the compaction flooded leach columns. The trial where the ore was agglomerated with only raffinate yielded some interesting results, illustrated in Figure 30, when comparing bulk density as a function of leach time for the three raffinate agglomerated columns. The paths taken to achieve these bulk densities are somewhat different. Three distinct scenarios can be realized within this set of data.

![Bulk Density as a Function of Time](image)

**Figure 30:** 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 completely 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 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 31, 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 32 indicates that the use of the binders resulted in lower bulk densities than the average column agglomerated with raffinate. This signified that there was less of a breakdown of the agglomerates with time with the use of a binder.

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 33. The polyacrylamide 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. The hydraulic conductivity results for the waste treatment additive are not shown in Figure 34. This is due to the fact that the column became plugged over time, and a build up of solution resulted. Due to the fact that there was no solution flow, the hydraulic conductivity was unable to be measured.
Figure 31: 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 32: 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.

Figure 33: 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 indicated that under compaction, the use of a binder helps to increase the strength of the agglomerates when compared to using raffinate alone. This was shown by a decrease in bulk density, meaning that fine particles from the agglomerates were not breaking off. It was 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 has been 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.

**Economic Analysis**

The polyacrylamide had consistently performed well throughout the various testing procedures including, soak tests, percolation tests, long-term leach columns, and compaction testing. It was necessary to determine whether the use of this product would be economical on an industrial scale.

It was determined that at the current copper selling price of approximately $3.00 per pound of copper, the use of the polyacrylamide could be justified by only a 2-4% increase in copper recovery from the heap or by a decrease in the length of the leach cycle. This increase in copper recovery was based off of the price quoted from the manufacturer, if the polyacrylamide was used at a dosage rate of 1 lb/ton of ore. However, if the dosage rate was able to be dropped to 0.5 lb/ton, the use of the product could be justified with only a 1-2% increase in copper recovery from the heap or again by a decrease in the length of the leach cycle.

The polyacrylamide also offers the benefit of leaving process equipment free of residue during agglomeration. This would help eliminate the clogging of shoots which results in downtime in the operation. This type of benefit along with others, have not been included in the current economic evaluation of the polyacrylamide product. This evaluation was completed using a base cost for the product only. It does not include installation, application equipment, storage, etc.

**Iron Ore Agglomeration**

The results of water analyses for the filtrate water and filter cake moisture removed from iron ore concentrate are shown in Tables 3 and 4. It is particularly notable that the calcium was 500 times more concentrated in the remaining filter cake moisture than in the filtrate water. At the normally high slurry pH in this plant (above 10), the magnetite
particles have a highly negative Zeta potential, and thus adsorb and concentrate, at the particle surface, the cations remaining in the filter cake moisture.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Filter cake moisture</th>
<th>Filtrate water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>5088</td>
<td>9</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5995</td>
<td>15</td>
</tr>
<tr>
<td>Potassium</td>
<td>1680</td>
<td>11</td>
</tr>
<tr>
<td>Sodium</td>
<td>725</td>
<td>151</td>
</tr>
<tr>
<td>Sulfate</td>
<td>803</td>
<td>54</td>
</tr>
</tbody>
</table>

Table 3: Ionic concentrations in water samples from Plant 1. The pH of the filter slurry in this plant was greater than 10. Values are reported as mg/L (ppm)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Filter cake moisture</th>
<th>Filtrate water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>231</td>
<td>11.9</td>
</tr>
<tr>
<td>Magnesium</td>
<td>119</td>
<td>9.3</td>
</tr>
<tr>
<td>Potassium</td>
<td>66</td>
<td>15.5</td>
</tr>
<tr>
<td>Sodium</td>
<td>266</td>
<td>147</td>
</tr>
<tr>
<td>Sulfate</td>
<td>208</td>
<td>53.4</td>
</tr>
<tr>
<td>pH</td>
<td>--</td>
<td>8.4</td>
</tr>
</tbody>
</table>

Table 4: Ionic concentrations in water samples from Plant 2. Values are reported as mg/L (ppm)

In Plant 2, the natural pH range of the slurry is from pH 8 to pH 9, compared to greater than pH 10 in Plant 1. As a result, simply rinsing the filter cake with distilled water, as was done in Plant 1, did not produce a large change of pH. It was believed that a substantial pH change would be needed to release cations from the magnetite surface. Therefore, a small amount of hydrochloric acid was added to the rinse water to reduce the pH (from 8.8 to 5.9), with the intention of lowering the particle surface charge to free the cations for analysis. The certified laboratory results are shown in Table 5. As was the case in Plant 1, the calcium and magnesium in the Plant 2 filter cake were more concentrated in the filter cake moisture relative to the water in the rest of the plant. However, the Ca$^{2+}$ and Mg$^{2+}$ levels in the filter cake were much lower than those measured in Plant 1. This is likely to be due to fact that the pH in Plant 2 is not as alkaline as in Plant 1, and so the surface charge would be expected to be less negative. The lower magnitude of the surface charge would mean that less positively-charged Ca and Mg would be attracted to the surfaces, leading to the observed lower levels of these ions in the Plant 2 filter cake moisture.

The results of the Zeta potential measurements for the Plant 2 magnetite are shown in Figure 11. Surprisingly, the Zeta potentials measured were all significantly more negative than typical values reported in the literature, and according to this graph the Zeta potential will drop to zero at approximately a pH of 3. It is not clear whether this is due
to the Plant 2 magnetite having a naturally low isoelectric point, or whether the carbon
dioxide is reacting directly with the mineral surfaces to increase their negative charge.

**Laboratory Balling of Washed Filter Cake**
In order to quantify how the high concentration of cations remaining in the filter cake
affects green ball and fired pellet quality, two representative samples of Plant 2 filter cake
were collected for testing. One sample was washed twice with distilled water at 60% solids and re-filtered. Green balls were agglomerated and fired in a mini-pot-grate according to laboratory standard procedures which represent the agglomerating and firing
conditions at Plant 2. Table 5 shows that fired pellet quality increased dramatically, from
2375 N/pellet (534 lbf) to 2780 N/pellet (625 lbf) compressive strength, as a result of
washing the filter cake, although the green ball quality was actually reduced for the
washed sample. The reduction in green ball quality due to washing was unexpected,
because it had earlier been shown using the Plant 1 concentrate that rinsing away the
divalent cations before pelletization lead to an increase in green ball strength (Ripke and
Kawatra, 2002). This difference in behavior between the two plants is believed to be due
to differences in the calcium ion sensitivities of the bentonites used in each case.

![Graph showing Zeta Potential vs pH](image)

**Figure 34:** Microelectrophoresis measurements of the magnetite particle surface
charge. For the magnetite from Plant 2, the pH was progressively lowered by
additions of carbon dioxide down to a pH of 4.92, and nitric acid to pH values of
3.33 and 2.47.
Table 5: Laboratory results showing the effect of washing Plant 2 filter cake. In the laboratory, washing the filter cake resulted in a decrease in dry crush strength and wet drop values, and an increase in the fired pellet crush strength. In the plant, only the wet drop value showed a change between the rinsed and unrinsed material. This difference between the laboratory and plant results occurs because, in the laboratory, it was practical to completely flush cations from the filter cake with clean water. However, the plant was necessarily limited to rinsing the filter cake with small quantities of acidic solution to alter the pH

<table>
<thead>
<tr>
<th>Green Ball Quality</th>
<th>Fired Pellet Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46 m</td>
<td></td>
</tr>
<tr>
<td>Wet Crush N</td>
<td>+6.35 mm Drop, # of drops</td>
</tr>
<tr>
<td>Dry Crush N</td>
<td>% % % % % % % % %</td>
</tr>
<tr>
<td>Laboratory/Washed</td>
<td>4.76 7.38 3.95 99.82 97.08 96.9 2780 4919 99.5</td>
</tr>
<tr>
<td>Laboratory/Unwashed</td>
<td>4.62 11.96 4.8 99.34 96.77 96.1 2375 3821 98.3</td>
</tr>
<tr>
<td>Plant/Rinsed</td>
<td>-- -- 7.2 99.8 95.7 95.5 2090 -- 93.3</td>
</tr>
<tr>
<td>Plant/Unrinsed</td>
<td>-- -- 12.4 99.8 96.0 95.8 2095 -- 92.7</td>
</tr>
</tbody>
</table>

Two separate 12-hour plant tests were conducted with filter cake washing. It was found that the quality of pellets collected from the plant that were made with washed filter cake did not change, as can be seen from the plant test results shown in Table 6. It was also determined in the laboratory that hydrochloric acid was too aggressive for this application and could start to dissolve the magnetite concentrate. In addition, hydrochloric acid has been known to cause filter bag blinding in other installations, and so it is not considered suitable for use in this manner.

**Laboratory-Scale CO₂ Testing**
Since hydrochloric acid was too aggressive, CO₂ was selected as an alternate to reduce pH. During the hydrochloric acid tests, no changes in pellet properties were seen to result from adding acid to the filter cake as a direct spray, but the CO₂ could be used to adjust the pH of the entire slurry stream as it entered the filters. Since there was some concern about the effects of pH adjustment on filter performance, the CO₂ tests were conducted to determine any effects on the filtration rate, using a filter leaf cart specifically designed to represent the conditions at the pellet plant. The laboratory-scale testing with this filter leaf cart showed that when a sufficient quantity of CO₂ was injected into the slurry to reduce the pH from 7.6 to 7.0, the filter production rates improved by 11%. This immediately suggested that, even if pH adjustment of the filter cake did not affect the pellet quality, it had the potential to significantly improve filtration rates. It was therefore decided to further investigate the effects of CO₂ on filtration.

**Plant-Scale CO₂ Testing**
Since laboratory results showed CO₂ addition could improve filtering rates by 11%, plant-scale tests were conducted to determine whether this would be a useful procedure on a full scale. It was estimated that one filter producing 90.7 tonnes of filter cake per hour would require about 22.7 kg of CO₂ per hour. Evaporating liquid CO₂ with the
system shown in Figure 4 provided the CO$_2$ gas. The filter feed pH was controlled with the evaporator outlet pressure. The CO$_2$ was injected after the slurry pump into the west-header. As a result, the pH of all of the slurry was adjusted by the CO$_2$, as opposed to the previous filter rinse tests with HCl solution where a mildly acidic solution was sprayed directly onto the face of the filter cake as the filter panel emerged from the slurry.

During most tests, only one filter was fed from the west header and that filter’s production was isolated on an individual conveyor (#11), feeding one pelletizing furnace. The other header fed the remaining filters and their production was combined on a separate conveyor (#111). Therefore, production rates could be compared simultaneously for filtering with and without CO$_2$ as measured by belt scales and recorded by the process control system. For example, before CO$_2$ was added, filtering rates were at 84.4 tonnes/hour/filter ($t$/h/f) on both lines. After CO$_2$ was added the west line improved to 104.3 t/h/f (a 23.7% increase), while the east line remained at 93 tph/f. The results for the five tests are summarized in Table 6. The CO$_2$ addition rate was determined to be about 0.54 kg/t concentrate in these experiments. Additional testing is warranted to optimize the CO$_2$ addition rates. The pH of the slurry responded to the evaporator outlet pressure according to the results in Figure 35.

<table>
<thead>
<tr>
<th>Test Date</th>
<th>CO$_2$ feed pres., kPa</th>
<th># of filters</th>
<th>Production before CO$_2$, tonnes/hour</th>
<th>Production after CO$_2$, tonnes/hour</th>
<th>Production rate increase, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>8/21</td>
<td>75.8</td>
<td>1</td>
<td>88.0</td>
<td>102.5</td>
<td>16.5</td>
</tr>
<tr>
<td>9/3</td>
<td>214</td>
<td>1</td>
<td>84.4</td>
<td>104.3</td>
<td>23.7</td>
</tr>
<tr>
<td>9/22</td>
<td>145</td>
<td>1.5</td>
<td>141.5</td>
<td>146.9</td>
<td>3.8</td>
</tr>
<tr>
<td>9/30</td>
<td>145</td>
<td>1</td>
<td>67.1</td>
<td>82.5</td>
<td>23.0</td>
</tr>
<tr>
<td>10/21</td>
<td>317</td>
<td>3</td>
<td>25.3</td>
<td>295.7</td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 6: Effect of CO$_2$ addition on Plant 2 filtering rates during in-plant studies.

![PH response to CO2 feed pressure](image.png)

Figure 35: Response of pH to CO$_2$ feed pressure during plant-scale tests.
Binder in Iron Nugget Production

Pellets made from iron oxides combined with powdered coal and limestone, using bentonite clay as a binder, were heated to 1425°C over a period of 16 minutes, then removed and rapidly cooled before they could completely transform to nuggets. It was seen that under these conditions, the binder could not completely maintain pellet integrity, as can be seen from Figure 5. A significant fraction of the pellet mass was lost due both to combustion of the coal component and loss of solids as dust. Quantitative measurements of mass loss of the pellets will require the use of a high-temperature thermogravimetric analysis apparatus, which is currently under construction. Once this is completed, it will be possible to evaluate the ability of different binders to prevent loss of dust from the pellets during heating.

Energy Benefits

Copper heap leaching energy benefits

Increasing copper recovery in heap leaching by the use of binders and agglomeration would result in a significant decrease in the amount of energy consumed. Assuming that 70% of all the leaching heaps would convert to using agglomeration technology, as much as 1.64*10^{12} BTU per year would be able to be saved if a 25% increase in copper recovery was experienced. This is the equivalent to saving approximately 18% of the energy currently being used in leaching heaps.

Our industrial partner, Phelps Dodge Corp., is the largest copper heap leaching operation in the United States. Therefore, predicted energy savings were based off of data received through personal communication with Phelps Dodge Corp. in May of 2002. These energy saving values are also applicable to other heap leaching operations, as long as it is noted that the increase in recovery due to agglomeration will vary considerable depending on the nature of the ore in any given situation.

In 2002, approximately 601,000 tons of copper were produced in the United States by heap leaching processes. This was 1/2 of the total 1.14 million tons of copper produced that year. The Phelps Dodge Morenci operation alone was responsible for producing 410,000 tons of the copper produced in the United States at that time. It is assumed that each unit, or leach heap, produces 2000 tons of copper per year. There were 301 units in the United States in 2002. The Phelps Dodge Corp. is responsible for 205 of the 301 units.

In 2002, Phelps Dodge consumed a grand total of 3.04*10^{10} BTU/unit/yr between diesel fuel and electricity, as shown in Table 7 (Personal Communication with Phelps Dodge in May 2002). Diesel fuel consumed the greatest amount of energy at 5.71*10^{9} BTU/unit/yr and electricity at 2.47*10^{10} BTU/unit/yr.
It was estimated that at the Phelps Dodge Morenci operation, every 1% improvement in copper recovery would result in savings of 1.1 million kW-hr per year in electricity and 400,000 gallons/yr of diesel fuel (Personal Communication with S. Rick Gilbert of Phelps Dodge in May 2002). Energy savings with the use of binders and agglomeration in heap leaching were calculated using Equation 8 and 9. The energy savings for increasing percent of copper recovery are listed in Table 8 along side the energy consumption which would be associated with the implementation of the proposed agglomeration technology.

\[
\text{Energy Savings in Diesel Fuel (BTU/yr/Unit)} = \left((400,000 \text{ gal/yr/1\% Inc. Cu Rec.}) \ast (130,000 \text{ BTU/gal}) / (205 \text{ units})\right) \ast (% \text{ Inc. in Cu Rec.})
\]  
\[
\text{Energy Savings in Electricity (BTU/yr/Unit)} = \left((1.1 \ast 10^6 \text{ kW-hr/yr/1\% Inc. Cu Rec.}) \ast (10,500 \text{ BTU/kW-hr}) / (205 \text{ units})\right) \ast (% \text{ Inc. in Cu Rec.})
\]

Cumulative energy savings are based off of the assumption that in 10 years an estimated 70% of the current 301 copper leaching units would be able to use or implement the agglomeration and binder technology. Total cumulative energy savings are calculated using Equation 10.

\[
\text{Cumulative Energy Savings (BTU/yr)} = (\text{Energy Savings (BTU/yr/Unit)}) \ast (\text{No. of Units})
\]

Increasing the percent of copper recovery from a heap, results in a decrease in the amount of energy consumed by heap leaching processes, Figure 36. The current technology has not allowed for an increase in copper recovery. Therefore, the energy consumption of the current heap leaching process is shown in Figure 36 by a horizontal line for all increases in copper recovery, for comparison purposes. Energy savings from a decrease in the amount of diesel fuel makes up the greatest fraction of the total amount of energy which will be saved with the use of agglomeration.

Cumulative energy savings, Figure 37 and Table 8, take into account the total amount of energy which will be saved assuming that 70% of the 301 heap leaching units convert to using the agglomeration technology. As much as $1.64 \ast 10^{12}$ BTU per year will be able to be saved if a 25% increase in copper recovery was experienced. This is the equivalent to saving the energy of approximately 54 copper heap leaching units per year, or approximately 18% of the energy currently being used in leaching heaps.
Table 8: Energy Savings with Percent Increase in Copper Recovery with Proposed Agglomeration Technology

<table>
<thead>
<tr>
<th>Increase in Cu Recovery (%)</th>
<th>Proposed Technology (BTU/Yr/Unit)</th>
<th>Energy Savings (BTU/yr/Unit)</th>
<th>No. of Units</th>
<th>Cumulative Energy Savings (BTU/Yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diesel Fuel</td>
<td>Electricity</td>
<td>Total</td>
<td>Diesel Fuel</td>
</tr>
<tr>
<td>1</td>
<td>2.44E+10</td>
<td>5.66E+09</td>
<td>3.01E+10</td>
<td>2.54E+08</td>
</tr>
<tr>
<td>2</td>
<td>2.42E+10</td>
<td>5.60E+09</td>
<td>2.98E+10</td>
<td>5.07E+08</td>
</tr>
<tr>
<td>3</td>
<td>2.39E+10</td>
<td>5.54E+09</td>
<td>2.95E+10</td>
<td>7.61E+08</td>
</tr>
<tr>
<td>4</td>
<td>2.37E+10</td>
<td>5.49E+09</td>
<td>2.91E+10</td>
<td>1.01E+09</td>
</tr>
<tr>
<td>5</td>
<td>2.34E+10</td>
<td>5.43E+09</td>
<td>2.88E+10</td>
<td>1.27E+09</td>
</tr>
<tr>
<td>10</td>
<td>2.21E+10</td>
<td>5.15E+09</td>
<td>2.73E+10</td>
<td>2.54E+09</td>
</tr>
<tr>
<td>15</td>
<td>2.09E+10</td>
<td>4.87E+09</td>
<td>2.57E+10</td>
<td>3.80E+09</td>
</tr>
<tr>
<td>20</td>
<td>1.96E+10</td>
<td>4.59E+09</td>
<td>2.42E+10</td>
<td>5.07E+09</td>
</tr>
<tr>
<td>25</td>
<td>1.83E+10</td>
<td>4.30E+09</td>
<td>2.26E+10</td>
<td>6.34E+09</td>
</tr>
</tbody>
</table>

*One unit is equal to one leaching heap extracting 2000 tons of copper per year

Figure 36: Energy consumption comparison between the current energy consumption at a copper heap leaching facility and the energy consumption associated with the increase in copper recovery due to the proposed agglomeration technology changes.

Even if the copper recovery may not be able to be increased, the desired recovery may be achieved but with a shortened leach period. Shortening the leach cycle of a heap leach unit by one week allows for energy savings of 5.84*10^8 BTU/Week/Unit or a total of 1.23*10^11 BTU/Week assuming 70% of the total 301 units implement the technology. Achieving increased copper recovery along with a decrease in leach time will only amplify the energy saving results expected from either one of these alone.
Iron ore agglomeration energy benefits
In conventional ironmaking, iron ore concentrate must be combined with binder and flux, pelletized, heated to approximately 1200°C, then cooled, shipped to the blast furnace, and re-heated. The sintering operation requires 950 MJ per metric ton to heat the pellets (Aise, 1999), and all of this energy is lost. In contrast, the single-step iron nugget process only heats the ore concentrate once to produce metal, and therefore completely eliminates the need for heating to sinter the pellets.

In addition, the reduction reactions in the iron nugget process are more efficient than in the blast furnace, due to the elimination of the cokemaking step (Fruehan et al., 2000) and to the improved contact between the reducing agent and the iron oxide particles. Blast furnace operation requires 23,360 MJ/metric ton of hot metal produced, while the iron nugget process reduces this to 21,030 MJ/metric ton, for an additional savings of 2,330 MJ/metric ton (McClelland, 2001).

Introduction of new binders that are appropriate to the needs of the single-stage iron nugget process will allow it to replace a large fraction of the existing blast furnace infrastructure. Conversion of 50% of the iron and steel industry to the iron nugget process is expected to save $6.51 \times 10^{13}$ BTU/year.
CONCLUSIONS

Ore agglomeration is of great value for saving energy in heap leaching operations (potential savings of $1.27 \times 10^{12}$ BTU/year) and in the processing of iron ore to produce metallic iron (potential savings of $6.51 \times 10^{13}$ BTU/year). In order to achieve these substantial energy savings, it is necessary to develop novel binders that can function under the extremes of acidity, temperature, and chemical attack that are commonly encountered in these metal extraction operations.

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, 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. 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 five long-term leach columns. The duplicate columns were able to be used to show that the long-term leach column results were reproducible. They also helped determine whether our industrial partners would progress with additional larger scale test work. 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.

The use of a binder in addition to agglomeration will help to allow for better solution
flow through an ore bed and result in increased copper recovery rates. Previously, there
were no standard tests developed to determine which types of binders will perform best.
A binder needs to be able 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 binders 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. The use of
polyacrylamide, in particular, has shown improved results in comparison to using
raffinate alone in agglomeration, especially under compacted conditions. An economic
analysis of this product showed that only a small increase in heap recovery, or a decrease
in the leach cycle, would justify the use of this product. Any additional recovery, or
benefits of this product, would only add to the profit resulting from the heap. Constant
communication with our industrial partners has allowed concurrent testing to be done at
MTU and at a copper leach facility in Arizona. Meetings with the industrial partners to
discuss MTU’s results have allowed possible future testing to be considered.

In iron ore processing, the moisture remaining in the magnetite filter cakes from two
different plants had a much higher concentration of divalent cations (Ca$^{2+}$ and Mg$^{2+}$)
compared to the filtrate water removed from them. Plant 1, which feeds highly alkaline
slurry to the filters, had much higher levels of calcium and magnesium retained in the
filter cake than was seen in plant 2. Since the preferential retention of cations in the filter
cake is a result of the negative surface charge on the magnetite, this is consistent with the
more negative surface charge expected on the magnetite as the pH becomes more
alkaline.

In Plant 1, it was observed that laboratory green ball quality improved when the cations
were removed from the filter cake by washing. However, the green ball quality measured
in the laboratory for Plant 2 filter cake decreased with washing, although the fired pellets
were stronger for the washed Plant 2 filter cake than for unwashed. The reason for this
difference between filter cake from the two plants is not definitely known, but it is
believed to be due to differences in sensitivity to calcium ions for the bentonites used in
each plant.
The laboratory washing procedure was obviously not practical for removing cations from filter cake on a plant scale due to the quantity of clean water required. Tests in the plant were therefore limited to pH adjustment, which was a much less effective method for removing cations and was not seen to have a significant effect on pellet quality in the plant.

It was determined that carbon dioxide was a suitable method for reducing pH of slurry in the filters, as it is chemically mild and does not have the drawbacks of hydrochloric acid. In addition to lowering pH, which reduced particle surface charge and allowed divalent cations to be released from the surfaces, it also precipitates calcium as highly insoluble calcium carbonate, preventing the calcium from interfering with the water absorption of the bentonite.

In the plant studies, reducing the pH of the filter slurry was not observed to change the quality of the fired pellets. However, carbon dioxide addition was found to be very beneficial in improving filtration rates, increasing the filter production by as much as 23.7%. Since filtration is a major expense, this is an effective method for improving plant performance in the filtration/pelletization section.
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