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.

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Introduction

As higher grade ore deposits have become depleted, it has become necessary for mining companies 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 know as a lift (lift heights vary from mine to mine, but approximately 20 feet is typical). The lift is then irrigated with raffinate either by drip emitters or a sprinkler system. The raffinate is then percolated through the heap and air is blown from the bottom allowing the copper to be 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 electro winning circuit where the liberated copper is ultimately recovered.

During the leaching cycle the agglomerates break down rapidly, and fines begin to migrate. The migration of fines clogs flow channels through the ore in the heap, which leaves areas in the heap void of the necessary reagents to dissolve the copper, resulting in poor recoveries. 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 which 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 is 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 as shown in Figure 1, 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, with accompanying loss of product as environmentally-objectionable dust.

The goal of this project is therefore to develop binders for mineral agglomeration that meet these requirements, allowing increased processing efficiency and reduced energy losses. Binders are being developed based on theoretical considerations and on past experience, and are being evaluated to determine their effectiveness in both leaching operations, and in ore concentrate agglomeration for thermal processing.

Heap Leaching Agglomeration

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

1. Initial testing of a binder is conducted using a “soak test”, which consists of immersing agglomerated ore in raffinate and observing the degree of breakdown of the agglomerates with time. This is the simplest test, using only 500 grams of ore per test, and can be conducted rapidly for a number of binders, but the results are only qualitative. To date, over 16 candidate binders have been considered

- based on theoretical considerations, and soak tests have so far identified four binders that are particularly promising for this application.
2. Binders which perform well in the soak test are then evaluated in the percolation test, using the apparatus shown in Figure 1. This test gives a quantitative measurement of the permeability of the ore to the leach solution as a function of time, and also provides a measure of the “slump” of the ore.

Figure 1: Percolation test columns assembled at MTU using equipment provided by Phelps Dodge Inc. Agglomerated ore is added to the column, and raffinate is circulated through the agglomerates continuously. The “slump”, or decrease in height of the ore, is also measured. The columns shown each contain agglomerates made with a different binder, and were initially all filled with the same amount of ore. The difference in slump and solution turbidity for various binders is evident..

3. Following the percolation tests, the final test for a given binder will be a long-term column leach test, using the leaching columns shown in Figure 2. These columns were constructed by Phelps Dodge specifically to simulate as closely as possible the conditions seen in their industrial leaching heaps. Since long-term column tests typically run for 150 days and require up to 100 pounds of ore per test, only the most promising binders will be tested in this way.

Figure 2: Leaching columns provided by Phelps Dodge set up for leach testing at Michigan Technological University. These columns are used for long-term testing for periods of several months, and provide the closest simulation of actual industrial heap-leaching behavior that can be achieved in the laboratory.

Ore Concentrate Agglomeration

This project is also investigating the performance of binders in iron ore agglomeration, with the particular goal of both increasing the efficiency of pellet production for use in the blast furnace, and of producing binders suitable for use in advanced ironmaking processes. This is being accomplished by examining the effects of water chemistry on the performance of bentonite clay binders and determining the effect that this has on binder performance and 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 the most common binder for iron ore concentrate (bentonite clay). Filter cake from two plants was analyzed. The water retained in samples of magnetite concentrate filter cake in Plant 1 contained 5088 ppm calcium and 5995 ppm magnesium, while the Plant 2 filter cake contained 231 ppm calcium and 119 ppm magnesium. These levels were dramatically elevated compared to the water that was removed from the concentrate by filtration for recycle to the plants (9 ppm calcium/15 ppm magnesium for Plant 1, and 11.9 ppm calcium/9.3 ppm magnesium in Plant 2).

The primary concern was to determine methods for releasing the calcium and magnesium that is adsorbed on the particle surfaces so that it could be removed during filtration of the concentrate. 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. 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 3. 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, using the carbon dioxide vaporizer shown in Figure 4.

Figure 3. Rinsing filter cake with pH-adjusted water while filtering in the Northshore plant.

Figure 4. CO₂ tanks and evaporator at the Northshore plant. Liquid CO₂ was vaporized in the evaporator, and injected into the filter slurry as a gas.

The injection of carbon dioxide was found to reduce the slurry pH, as anticipated, and also had the significant additional benefit of increasing filtration rates by up to 23.7%. However, while the energy-efficiency benefits of the increased filtration rate would be adequate justification for carbon dioxide injection, there was no effect noted in the plant on the quality of the pellets made from the filtered concentrate. Laboratory studies are currently underway to determine why it did not improve the pellet quality in the manner expected from theoretical considerations.

Experiments are also underway 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.

Figure 5. Direct reduced iron pellets, which are an intermediate stage in production of iron nuggets, using bentonite clay as 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.

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 5. 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. Studies are therefore planned to improve the performance of the binder used in this application.

Industrial cost-share for this project is being provided by Phelps Dodge, Inc.; Newmont Mining Co., and Northshore Mining Co. All three companies have already contributed considerable amounts of engineering time to this project, and Phelps Dodge has provided experimental apparatus for conducting percolation and column leaching tests. Phelps Dodge has also provided several hundred pounds of their Mine for Leach (MFL) ore, and will provide additional ore as needed in the project. Northshore Mining Co. personnel have been cooperating in carrying out extensive in-plant testwork in their facility, providing invaluable data for this project.

Experimental

Two phases of experimentation were carried out. The first phase examined the performance of binders during hydrometallurgical processing (leaching) of ores, and the second phase studied the effects of pH and ion concentration on iron ore agglomeration.

Leaching Agglomeration

Materials

200 lb of Mine for Leach (MFL) Ore was received from the Phelps Dodge Morenci operation for use in soak tests and percolation tests. This ore was crushed to pass ¼ inch in order to be a suitable size for agglomeration tests, and was then divided using a rotary sample splitter to ensure that all samples used in experiments had identical size distributions and compositions. An analysis of the raffinate composition at the Morenci operation was provided, and a simulated raffinate solution was prepared that contained all of the elements that were present at concentrations greater than 100 ppm, which are shown in Table 1. These elements were added as sulfate salts, along with sufficient sulfuric acid to simulate the Morenci raffinate:

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

Based on theoretical considerations and availability, the binders listed in Table 2 were selected for initial investigation. These were chosen specifically to have the best potential for performing well in an acidic environment at low dosages.

Test Procedures

Three tests are being used to evaluate binders for use in leaching operations: the soak test, the percolation test, and the column leach test. One of the major problems in carrying out research in this area has been that no standardized tests have ever been developed to evaluate agglomeration binders used in leaching, and so these tests are being developed and refined as a critical part of this project. It is important to note that these are new tests still under development, and the reproducibility and sensitivity to operational conditions is being determined. Results from these experiments must therefore be considered to be provisional until they can be completely replicated.

Soak Test is shown schematically in Figure 6. Ore that was crushed to pass ¼ inch was first combined with binder. The mixture was then agglomerated in a rotating drum at 35 rpm while spraying it with simulated raffinate over a period of 20 minutes, gradually increasing the moisture content of the ore to no more than 15% moisture. The agglomerates were placed on a 10 mesh screen and allowed to air-dry and cure for at least

24 hours. The screen with the cured agglomerates was then immersed in simulated raffinate solution, and any disintegration of the agglomerates was observed.

Table 2: Binders initially selected for investigation in this project				
Binding agent	Manufacturer	Polymer Type	Molecular Weight (Daltons)	Charge Density
Aerospray 70A Binder	Cytec	Polyvinyl Acetate Emulsion	750000	No charge
Alcofix 269; formerly Percol 406	Allied Colloids; now CIBA	Cationic poly(diallyl-dimethylammonium chloride) polymer	Low	High
Alcotac Fe8 and Soda Ash	CIBA	Cellulose derivative		
Dow A4M	Dow Chemical	Nonionic Methyl Cellulose Ether	86000	No charge
Percol 155	Allied Colloids; now CIBA	Anionic Acrylamide/Sodium Acrylate Copolymer	Ultra High	Low
Percol 156	Allied Colloids; now CIBA	Anionic Acrylamide/Sodium Acrylate Copolymer	Ultra High	Medium
Percol 351	Allied Colloids; now CIBA	Nonionic polyacrylamide	8 million	No charge
Percol E24	Allied Colloids; now CIBA			
Superfloc N-300	Cytec	Nonionic polyacrylamide	Low	None
Chem-Loc 411	Golden West Industries, Inc.	Polyvinyl acetate emulsion		
Alcotac Fe10	CIBA	Cellulose derivative		
Tall Oil Pitch #300	Entac			
Perform PA8230	Hercules	Anionic Acrylamide/ Acrylic Acid Polymer Powder	12-14 million	30%
Sodium Ligninsulfonate	Crown Zellerbach	Lignin Derivative (paper manufacturing byproduct)		
Sodium Metasilicate	Alfa Aesar	Na ₂ SiO ₃		
Superfloc A-870M Flocculant	Cytec	Acrylic Polymer	500000	70%

Figure 6: Schematic of agglomerate soak test.

Figure 7: Schematic of percolation test.

Percolation Tests are conducted as shown in Figure 7. A 3-inch diameter transparent plastic column is filled with agglomerated ore, and simulated leach solution is added to the top of the column. A portion of the solution percolates through the ore and exits at the base of the column, while any excess circulates back to the holding tank. In addition, the height of the agglomerated ore in the column is measured as a function of time. As agglomerates break down, the packing density of the particles in the column increases, and so this “slump” measurement is a direct measure of the degree of agglomerate breakdown. The mass of particles that accumulates in the fines collection vessel is a measure of the degree of fines migration that occurs with a given binder.

Figure 8: Schematic of leach testing column

Leach Test will be conducted using columns designed as shown in Figure 8. This test requires a 150 day leach cycle, and will check for any adverse effects the binders might have on the overall copper recovery that would not be apparent in the percolation or soak tests, such as chemical reaction with the leaching solutions or precipitation of impermeable gel coatings over leachable ore. This test simulates a heap by scaling down variables such as flow rates, air injection, temperature, etc. The ore is agglomerated with the selected binder, and the agglomerates are loaded into a 5 foot tall 6 inch diameter column. Leach solution is then pumped in at the top of the column at a rate that corresponds to the flowrate per unit area used in the field. After percolating through the column, the solution is then captured at the bottom for chemical analysis. All solutions are analyzed so that any possible adverse effects can be noted. This test is the final laboratory evaluation of a binder, and due to the long time periods involved will only be used for binders that performed satisfactorily in the percolation and soak tests.

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.

Results and Discussion

Leaching Agglomeration

During the development of the soak test for this project, it was determined that, in the absence of a binder, the agglomerated ore has only negligible ability to remain agglomerated in the presence of leaching solution. This is in spite of the fact that, before the soak test, the air-dried agglomerates appeared to be strong and durable, and confirms that a binder is very necessary for agglomerating this ore. Subsequent experiments examined numerous candidate binders with a variety of compositions and characteristics to determine how their performance in the acidic environment would relate to their basic properties.

From the results in Table 3, it can be seen that the quantity of fines released varies tremendously among the binders tested. In some cases, only a few percent of the -10 mesh fines contained in the ore were released by agglomerate breakdown during the soak test, while the majority of the binders produced agglomerates that performed no better than with no binder at all. When the binders are classified by type and the results compared, as shown in Figure 9, it can be seen that the binders that are most effective are the polyvinyl acetate emulsions (PVA) and the nonionic polyacrylamides (Nonionic PAA), with all of the anionic polyacrylamides and the sodium lignosulfonate performing much less well.

From these results, it is clearly seen that the most effective binders are nonionic materials, as they are largely unaffected by acidic conditions. Anionic binders appear to be significantly weakened by the presence of acid, and are of minimal effectiveness. The specific binders that have sufficiently good performance in the soak tests to be evaluated in the percolation tests are the Aerospray 70A, Percol 351, Superfloc N300, and Chem-Lok 411. Soak tests are being continued to identify further candidate binders, particularly low-cost nonionic materials that are produced from natural products, such as tall oil pitch emulsions.

It must be emphasized that this test is a new procedure that has not yet been fully confirmed to be completely reproducible. It has already been determined that the results are sensitive to effects such as time allowed for “curing” between production of the agglomerates and beginning the soak test, as can be seen in Figure 10. Allowing the agglomerates to cure overnight appears to cause a serious degradation in agglomerate quality which can be affected by the binders. The reasons for the sensitivity to curing time are still under investigation. This is an important consideration, since agglomerated

ore in full-scale leaching heaps may “cure” for a period of several days before leaching can begin.

Table 3: Soak test results for binders examined. The last column is a measure of the tendency of the agglomerates to break down and release fine particles, smaller values indicate superior performance.

Sample ID	Binders	Binder, Lb/ton	Percent of -10 mesh particles released
1-3	Superfloc A-870	5	15.77
2-2	Superfloc A-870	5	15.58
3-8	Superfloc A-870	5	19.02
4-8	Superfloc A-870	5	27.90
5-8	Superfloc N-300	5	3.27
1-4	Percol 351	5	4.63
2-6	Percol 351	1	27.72
2-7	Percol 351	2.5	11.76
3-9	Percol 351	5	3.47
4-2	Percol 351	5	4.74
1-5	Percol 406	5	23.51
4-11	Percol 406	5	21.18
5-6	Percol 406	5	8.17
1-6	Sodium Lignosulfonate	5	37.11
3-12	Sodium Lignosulfonate	5	21.28
4-7	Sodium Lignosulfonate	5	28.54
1-7	Sodium Metasilicate	5	25.70
4-10	Sodium Silicate	5	27.21
5-5	Sodium Silicate	5	20.17
1-8	Alcotac FE10	5	25.16
5-9	Alcotac FE10	5	20.44
1-9	Aerospray 70A	5	2.90
2-4	Aerospray 70A	1	24.43
2-5	Aerospray 70A	2.5	11.09
4-1	Aerospray 70A	5	0.62
4-4	Aerospray 70A	5	2.06
2-1	Dow A4M	5	19.53
4-12	Dow A4M	5	14.47
5-7	Dow A4M	5	18.43
2-3	Hercules PA 8230	5	24.66
4-9	Hercules PA8230	5	28.37
5-4	Hercules PA8230	5	18.63
3-4	Percol 155	5	25.63
3-10	Percol 155	5	21.54
4-5	Percol 155	5	25.03
3-5	Percol 156	5	28.45
3-11	Percol 156	5	24.48
4-6	Percol 156	5	27.30
3-6	Percol E24	5	27.81
3-3	Chem-Loc 411	5	1.16
2-8	50% Aerospray 70A + 50% Percol 351	5	5.05

Figure 9. Performance of binders tested by chemical category. PVA = Polyvinyl acetate; PAA = polyacrylamide; Da = Molecular weight, Daltons

Figure 10. Effect of curing time on agglomerate quality. After the agglomerates dry overnight, they tend to disintegrate more readily in acid solution. These results must still be replicated, and the causes of this effect are still under investigation.

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 4 and 5. 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 4--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) (3).

Ion	Filter cake moisture	Filtrate water
Calcium	5088	9
Magnesium	5995	15
Potassium	1680	11
Sodium	725	151
Sulfate	803	54

Table 5 -- Ionic concentrations in water samples from Plant 2. Values are reported as mg/L (ppm)

Ion	Filter cake moisture	Filtrate water
Calcium	231	11.9
Magnesium	119	9.3
Potassium	66	15.5
Sodium	266	147
Sulfate	208	53.4
pH	--	8.4

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 II. 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.

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 1** (4). 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.

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 6 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 (3). 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.

Figure 11. 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 6. 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

	Green Ball Quality			Fired Pellet Quality					
	0.46 m			+6.35			15.2 m		
	Wet	Dry	Wet	+6.35	+6.35		Avg.	Max	Drop
	Crush	Crush	Drop,	mm	mm	"Q"	Crush	Crush	%+6.35
	N	N	# of	B.T.	A.T.	Index	N	N	mm
			drops	%	%				
Laboratory/Washed	4.76	7.38	3.95	99.82	97.08	96.9	2780	4919	99.5
Laboratory/Unwashed	4.62	11.96	4.8	99.34	96.77	96.1	2375	3821	98.3
Plant/Rinsed	--	--	7.2	99.8	95.7	95.5	2090	--	93.3
Plant/Unrinsed	--	--	12.4	99.8	96.0	95.8	2095	--	92.7

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. As an added benefit, lowering pH has been reported in at least some plants to improve filter production rates (5).

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) 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 3, 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 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 CO₂ gas. The filter feed pH was controlled with the evaporator outlet pressure. The CO₂ was injected after the slurry pump into the west-header. As a result, the pH of all of the slurry was adjusted by the CO₂, 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 CO₂ as measured by belt scales and recorded by the process control system. For example, before CO₂ was added, filtering rates were at 84.4 tonnes/hour/filter (t/h/f) on both lines. After CO₂ was added the west line improved to 104.3 t/h/f (a 23.7% increase), while the east line remained at 93 t/h/f. The results for the five tests are summarized in Table 7. The CO₂ addition rate was determined to be about 0.54 kg/t concentrate in these experiments. Additional testing is warranted to optimize the CO₂ addition rates. The pH of the slurry responded to the evaporator outlet pressure according to the results in Figure 12.

Table 7. Effect of CO₂ addition on Plant 2 filtering rates during in-plant studies.

Test Date	CO ₂ feed pres., kPa	# of filters	Production before CO ₂ , tonnes/hour	Production after CO ₂ , tonnes/hour	Production rate increase, %
8/21	75.8	1	88.0	102.5	16.5
9/3	214	1	84.4	104.3	23.7
9/22	145	1.5	141.5	146.9	3.8
9/30	145	1	67.1	82.5	23.0
10/21	317	3	25.3	295.7	16.5

Figure 12. Response of pH to CO₂ 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.

Conclusions

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

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

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 a 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 performance of bentonite binders during balling.

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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