ALTA 2017

An effective new leaching aid successfully tested with oxide and mixed sulphide copper ores

First publication at ALTA 2017, Nickel-Cobalt-Copper Sessions

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Abstract

Large scale column testing was performed on oxide and mixed sulphide ores using a novel leaching aid. Approximately 90 kg of an agglomerated ore was leached for 60–120 days in batches of 16 columns, at which point roughly 75% of the total copper was leached for oxide ores and 60% of the sulphide ores. The leaching aid candidate achieved a 5–20% increase in copper recovery over columns without leaching aids with an overall standard deviation of less than 1% for the data between columns. In addition to the column testing, the leaching aids were subjected to bacteriological compatibility testing to ensure no adverse effect to the existing microorganisms in the ore. Results of the testing showed little overall negative effect on the microorganisms. Surface-active surfactant type leaching aids tend to have a negative effect on solvent extraction and can have a negative effect on the electrowinning system. Leaching aid solvent extraction compatibility was accomplished by batch and continuous processes. The testing included extraction/stripping kinetics, selectivity, phase disengagement, loading and organic solubility testing. In conclusion, the increase of copper leach recovery and the low toxicity of these compounds to SX-EW will be discussed.

Keywords: Leaching Aid, Column Leaching, Oxides, Mixed Sulphides, SX Compatibility, Bio-compatibility
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1. Introduction

The initial details of the leaching aid work were presented at Copper 2016 (Bender). At the time, the results for the leaching aids were slightly better than the results for the control columns. Further work identified more optimal chemistry and dosage for the original oxide ore.

In addition, work was conducted on a mixed sulphide copper ore from a customer. The results of the later trials were dramatically improved from the initial results. We have also conducted trials simulating the use of seawater and high nitrate concentrations which might be found at some South American mines.

The solvent extraction compatibility is of great importance to customers (Kordosky). Leaching aids are not removed from the PLS before SX or EW processes. In general, these compounds are meant to lower surface tension in the aqueous which can cause an increase in coalescence and phase separation times. The increase in contact time between the PLS and the solvent extraction organic can lead to increased entrainment losses, poor transfer kinetics, hydrolytic degradation of the extractant, and/or nitration of the extractant if conditions are suitable. Poor transfer kinetics can be a result of the interfacial activity of the leaching aid. If the chemical compound is attracted to the organic-aqueous interface it can inhibit the transfer of copper and ultimately this can affect the net transfer of copper to the electrolyte.

Lab phase work has been completed at this stage. We have progressed to field scale testing at several customers. This ongoing work will be presented in future articles.
2. Experimental

2.1 Column Testing

A mostly oxide ore was collected from a potential copper plant site. In order to reduce the variables in the leaching tests, the ore was precisely classified by SGS in Tucson, AZ. The ore was a mostly copper oxide ore that had a P80 of 1.5" and a smallest fraction of -10 mesh. The distribution of the column charge can be found in Table 1. The copper concentration in the ore was 0.42% with 91.2% of the copper as acid soluble copper. Analysis of the ore was also verified by SGS in Tucson. Approximately 90 Kg of the agglomerated ore was leached for 60 days in batches of 16 columns, at which point roughly 75% of the total copper was leached (total copper on column was approximately 380 g). Agglomeration was accomplished by mixing the various fractions in a cement mixer with 1.75 Kg of water and 1.52 Kg of sulfuric acid. The acid was calculated as 25% of the total acid consumption by ore. The agglomerated material was then transferred to columns for the leaching trials. Figure 1 is a picture of the classified ore and the loaded column.

Mixed sulfide ore was collected from a customer site. The ore was processed in the same manner as the oxide ore. The leachable copper in a 90 Kg column charge was approximately 63 g. The procedure for leaching was essentially the same as for the oxide ore. Sixteen 2 M by 20 cm PVC columns were used to hold the 90 Kg of ore. A distribution felt was used to evenly dispense the lixiviant solution onto the ore. Four of the columns were constructed of clear PVC so that the system could be visibly inspected. Each column had its own high precision pump and lixiviant reservoir. Solution was collected from the bottom of the column into buckets which eventually were put into analytical balances so that the amount of solution could be easily tracked. The leach rate was 8 mL/min of 10 g/L sulfuric acid at 68ºC.

Samples were collected daily for the first 30 days of the 60 day leaching trials. For each column, a sample was analyzed for pH, free acid, copper concentration by AA, surface tension, and oxidation potential (ORP). The lixiviant samples were also analyzed sequentially to ensure that there was no contamination or change in concentration of chemical species. The solution feed rates were measured frequently and if any adjustments were needed, the appropriate changes were made.
2.2 Compatibility

Lab circuits were set up with individual surge tanks. Each surge tank was filled with 500ml of 10% v/v LIX984N that has been contacted once with O:A 1:1 QC electrolyte (160 g/L sulfuric acid and 35 g/L copper). Flow rates were 30 mL/min of organic and 30 mL/min of aqueous. Mixer speed was kept at 1750rpm. Circuit operation was performed at room temperature, which was approximately 21°C. The feed solution was a mine site PLS. The lab circuits were run with continuous mixing. Visual observation during and at the end of the run showed no increase in emulsion or crud. The starting organic and the three organics after continuous circuit testing were put through a standard kinetics test. Phase disengagement testing was performed as per the BASF technical service process. Leaching aid concentrations for the testing were tested in great excess in order to determine onset of critical micelle concentration.

2.3 Biological Testing

The biological testing was performed by Universal Bio Mining, a research group working on biological heap leaching. A quantitative growth curve study was performed to determine the effect of the chemical additives on two organism temperature groups, mesophiles and moderate thermophiles (28 and 42 degrees Celsius). These groups contained 3 sub-groups of metabolic function (heterotroph, iron oxidizers, sulfur oxidizers), primarily consisting of bacteria with several archaea. The growth curves were scheduled to be completed within 45 days or when the cultures are deemed stabilized. Growth media utilized was UBM’s base salt media UX2 with appropriate substrates and optimal initial pH values for each organism. Each BASF chemistry was tested in triplicate and at three (3) different concentrations; 0.5x target concentration, target concentration, and 2x target concentration. Samples on triplicate cultures were taken every 3 – 5 days depending on the growth rate of the organisms, and cell counts were performed.
3. Results and Discussion

3.1 Biological Testing

Compatibility testing with sulfur and iron oxidizing bacteria as well as heterotrophic bacteria was conducted to ensure that the leaching aid will not negatively affect the biological respiration necessary to convert secondary or mixed sulfide copper to copper sulfate in solution. Biological species relevant to various mining sites were inoculated with the leaching aids and given relevant feed solutions; Acidophilium acidophilum (AA) – heterotroph, Acidiphilium cryptum (ACRP) – heterotroph, Acidithiobacillus ferrivorans (AFER) – iron and sulfur oxidizer (tested on iron), Acidithiobacillus ferrooxidans (AFEX) – iron oxidizer, Acidithiobacillus thiooxidans (ATEX) – sulfur oxidizer, Leptospirillum ferrooxidans (LFEX) – iron oxidizer, Acidithiobacillus caldus (ACALD) – sulfur oxidizer, Leptospirillum ferrophilum (LFER) – iron oxidizer, Ferroplasma acidiphilum (FACID) – archa bacteria iron oxidizer, Ferroplasma acidarmanus (FARM) – archa tested on iron oxidation, and Sulfobacillus acidiphilum (SACID) – archa tested on iron oxidation (Figure 2).

For the two heterotrophs, organisms that derive their nutrition from organic chemical species, there was no negative effect for the AA and for the ACRP there was an initial loss of population but there was a recovery which included a scavenging of organic from the death of organisms. In the case of the sulfur oxidizing bacteria, there was little impact of the leaching aid on the cell populations. For the ACALD there was a slowing down of population growth at approximately 14 days; however, then the population growth resumed. Iron oxidizing species were either not affected at all or had some level of inhibition. AFEX and LFEX were the two iron oxidizing bacteria that showed the most growth inhibition. After 40 days LFEX population was a little more than an order of magnitude less than the control while the AFEX population was two orders of magnitude less than the control. The difference in the metabolic rates did not seem to have a correlation to the difference in growth between control and leaching aid inoculation. In addition, the concentration of the leaching aid did not seem to influence metabolic activity.

The initial shock to the biological populations was observed in the leaching of mixed sulfides. Leaching was negatively affected for approximately two weeks. Thereafter, the columns inoculated with leaching aid showed a substantial increase in leaching rate as expected.
Acidithiobacillus ferrooxidans (AFEX)

Acidithiobacillus caldus (ACALD)

Acidithiobacillus thiooxidans (ATEX)

Leptospirillum ferriphilum (LFER)

Leptospirillum ferrooxidans (LFEX)

Ferroplasma acidiphilum (FACID)
3.2 Chemical Compatibility

There has not been a significant effect on phase disengagement when using the leaching aid in the appropriate dosage, which is approximately 25 ppm. At doses up to 4 times the operating dosage, the aqueous continuous phase disengagement time (PDT) are within the error of the experimental method. At extremely high concentrations, 10 times dosage, there is an effect on the aqueous continuous phase disengagement, although it is still not a dramatic effect. Organic PDT were not affected at any concentration of leaching aid tested, up to 50 times the operating dosage. The results of the phase disengagement testing are illustrated in Figure 3. Since the volumes of lixiviant are so large in leaching systems, it is extremely difficult to add multiple quantities of the desired dosage. It should be relatively easy to keep from substantially overdosing the lixiviant.
Chemical compatibility was first tested using a batch test method in jacketed beakers as per BASF QC testing procedures. The testing was performed with up to 50 ppm leaching aid in solution, which would be twice the normal operating concentration. There was no negative effect on extraction kinetics, strip kinetics or phase disengagement time. Table 1 contains the details for the testing.

### Table 1. Solvent extraction compatibility for a batch test using leaching aids versus a batch test control

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Assay Barren Organic</th>
<th>E30</th>
<th>E300</th>
<th>S30</th>
<th>S300</th>
<th>Phase Separation O, A (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>Copper (g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>% equilibrium</td>
<td>1.42</td>
<td>4.72</td>
<td>4.75</td>
<td>1.64</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>98.30%</td>
<td></td>
<td>99.04%</td>
<td>75, 95</td>
</tr>
<tr>
<td>20 ppm leaching acid</td>
<td>Copper (g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>% equilibrium</td>
<td>1.43</td>
<td>4.69</td>
<td>4.73</td>
<td>1.64</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>98.75%</td>
<td></td>
<td>99.37%</td>
<td>80, 85</td>
</tr>
<tr>
<td>50 ppm leaching acid</td>
<td>Copper (g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>% equilibrium</td>
<td>1.42</td>
<td>4.69</td>
<td>4.72</td>
<td>1.65</td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>99.95%</td>
<td></td>
<td>99.04%</td>
<td>75, 95</td>
</tr>
</tbody>
</table>

A continuous circuit was operated in order to determine if there was an effect on the kinetics of extraction or stripping when operating with a low concentration of leaching aid. Results can be found in Table 2. While the test operated at slightly lower than the 25 ppm eventually determined to be the most optimal leaching aid concentration, the 15 ppm concentration of leaching aid had no effect on extraction kinetics, strip kinetics or phase disengagement time. Test conditions were using a 1Ex1Ex1S configuration, 10 v/v% LIX 984N, mine PLS and synthetic LE were used in the continuous circuit.

### Table 2. Solvent extraction compatibility for a continuous circuit operation using leaching aids versus a continuous circuit control

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Assay Barren Organic</th>
<th>E30</th>
<th>E300</th>
<th>S30</th>
<th>S300</th>
<th>Phase Separation O, A (s)</th>
</tr>
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<tbody>
<tr>
<td>Fresh Organic</td>
<td>Copper (g/L)</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>% equilibrium</td>
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<td>4.69</td>
<td>4.77</td>
<td>1.67</td>
<td>1.64</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>98.30%</td>
<td></td>
<td>99.04%</td>
<td>60, 85</td>
</tr>
<tr>
<td>8 Hrs (w/o leaching acid)</td>
<td>Copper (g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>% equilibrium</td>
<td>1.53</td>
<td>4.75</td>
<td>4.81</td>
<td>1.68</td>
<td>1.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>98.75%</td>
<td></td>
<td>99.37%</td>
<td>55, 90</td>
</tr>
<tr>
<td>40 Hrs (15 ppm leaching acid)</td>
<td>Copper (g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>% equilibrium</td>
<td>1.53</td>
<td>4.73</td>
<td>4.78</td>
<td>1.67</td>
<td>1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>98.95%</td>
<td></td>
<td>99.04%</td>
<td>40, 90</td>
</tr>
<tr>
<td>80 Hrs (15 ppm leaching acid)</td>
<td>Copper (g/L)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>% equilibrium</td>
<td>1.56</td>
<td>4.80</td>
<td>4.87</td>
<td>1.70</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>98.56%</td>
<td></td>
<td>99.69%</td>
<td>35, 90</td>
</tr>
</tbody>
</table>
3.3 Toxicity

The leaching aid has been assessed a polymer exemption by the Toxic Substances Control Act (TSCA) Chemical Substance Inventory. Therefore, it is exempt from the standard toxicity testing required by non-polymer substances. The terms of the polymer exemption allow for manufacture and use of polymers without submission of a premanufacture notice or an exemption notice. A polymer exemption eliminates unnecessary EPA review of eligible, low risk, polymers. This exemption relies on comprehensive recordkeeping to fulfill compliance purposes. In addition, it adopts the international OECD (Organization for Economic Cooperation and Development) definition of Polymer.

Figure 4. Two meter column testing setup and the process for agglomerating the ore
3.4 Column Leaching

The leaching trials were conducted on two types of ore, a mostly oxide ore and a mixed sulfide ore. The oxide ore was chosen to minimize the variables in the testing. To further reduce the error in the data, each set of column trials consisted of 16 columns containing approximately 90 Kg of ore as described previously. Four columns were set aside as blanks and have no leaching aid added. For the leaching aids, test conditions were run in quadruplicate. Figure 4 shows the quadruplicate column setup and the ore agglomeration. The percent standard deviation in the results was typically less than 1%.

Trial 5 and 6 were based on the addition of leaching aid to a lixiviant added to an oxide ore. There was approximately 381 g of total copper in each column at 91.2% leachable copper, or ~347.5 g/column. The column trials were run so that the lixiviant was in a closed loop circulation. In some cases, solvent extraction was included to remove copper; however, this did not change the results and complicated the operation of the leaching columns. In the case of the results in Figures 5–6, the lixiviant was recycled into the columns (Figure 4). An attempt was made to determine if leaching aid was consumed during the trial; however, no consumption was noticed in the 60–120 day trials.

Results in Figure 5 are for Trial number 5. The goal of this trial was to determine if application of the leaching aid, added after agglomeration, impacts leaching in a closed cycle trial. A wide range of dosages were used to determine if the leaching aid concentration was essential to the leaching rate. Solvent extraction was performed until copper in raffinate was an appropriate level. The copper leached using the leaching aid was approximately 72% of the leachable copper for all three sets of conditions while the copper leached from the blank was approximately 56%. The results of this leaching data were achieved in 30 days.

The oxide ore was also used to determine if high concentrations of chloride or nitrate, conditions applicable to seawater systems in some areas of South America, had any effect. The results of this trail had a higher standard deviation than for the other leaching trials. All four sets of columns contained the leaching aid. It was noted that at concentrations of chloride approximately twice that of seawater, the leaching was slightly less than the control, which contained leaching aid. At a chloride concentration, approximately that of seawater there seemed to be little deviation from the control. The addition of lower concentrations of chloride led to an increase in leaching effectiveness over just using the leaching aid.
CHAPTER 3

Figure 6. Graphs for the leaching of copper from ore containing 347.5 g leachable copper/column and the plot of the percent of copper leached in excess of the control.

Average of total copper recovered per dosage rate

Value of copper leached as a percentage of control

Figure 7. Graphs for the leaching of copper from an oxide ore with leaching aid and lixiviant containing various concentrations of chloride and nitrate.

Average of total copper recovered per dosage rate

Value of copper leached as a percentage of control
Results in Figure 6 are for Trial number 6. The goal of this trial was to determine if application of the leaching aid, added during agglomeration, impacts leaching in a closed cycle trial. To extract copper from PLS, all the solutions for each set of conditions were collected into one drum per quadruplicate testing after weighing each sample collection container individually. Solvent extraction was performed until copper in raffinate was an appropriate level. The copper leached using the leaching aid was approximately 73–80% of the leachable copper while the copper leached from the blank was approximately 69%. While the results of the leaching were similar to Trial 5 after 30 days, the trial was allowed to continue for a total of 60 days.

A sulfide ore trial was performed on customer ore, Figure 8. The customer has a mixed primary/secondary sulphide ore. For the same 90 Kg column charge, there was approximately 63 grams of acid leachable copper. The leach time was extended to 120 days due to the nature of the leaching process. All other leaching conditions were kept the same as previous trials. It was noted that there was an initial shock of the bacteria, as was seen in the biocompatibility data. This shock was short lived, 2 weeks, and then results similar to the oxide trials were seen.
The leaching aid resulted consistently in between a 5 to 20% increase in copper recovery over the columns without leaching aids with an overall low standard deviation for the data. The low standard deviation in the results was due to the meticulous control of acid concentration, lixiviant flow, and distribution of lixiviant. It was determined that the concentration of chloride/nitrate can influence the efficiency of the leaching aid, with a slightly negative effect at very high concentrations. In addition to the column testing, the leaching aids were subjected to chemical compatibility testing to ensure that there are no negative effects on downstream processes. Based on the results of the current column testing, BASF is moving forward with customer trials.

References

Bender, J., et al, Leaching Aids for Dump and Heap Leach; SX Compatibility, Bilocompatibility, and Recycle of Lixiviant, Copper 2016

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