

Effect of agglomeration binders on the copper solvent extraction process

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Abstract

Binders have been suggested as an aid for agglomeration to improve copper recovery in heap leaching operations. However, it has not been established if the use of binders would negatively affect the solvent extraction process, which is used to purify the pregnant leach solution from the heaps and remove any contaminants. Such negative effects would lead to an increase in processing costs or a decreased in copper production. The controlled studies reported here have shown that some binders (a polyacrylamide and a waste treatment additive) did not interfere with the solvent extraction process. Other binders (a polyvinyl acetate emulsion and tall oil pitch) negatively impacted copper solvent extraction and, therefore, should not be used in copper heap leaching plants.

Key words: Agglomeration, Binders, Copper, Heap leaching, Solvent extraction

Introduction

In a copper heap leaching circuit, heaps of ore are leached using sulfuric acid solution, also referred to as raffinate. As the raffinate percolates through the heap, it dissolves the copper in the ore and is referred to as pregnant leach solution (PLS). The PLS contains copper in solution, but it needs to be concentrated and purified to make the metal salable. The solvent extraction/electrowinning stage (SX/EW), shown in Fig. 1, is the process used to extract the copper from the pregnant leach solution (PLS). When the PLS is collected at the base of the heap, it usually contains 1 to 5 kg $\text{Cu}^{+2}/\text{m}^3$. Solvent extraction can be used to prepare the PLS for the electrowinning circuit by separating Cu^{+2} from other ions, increasing its concentration from 40 to 50 kg $\text{Cu}^{+2}/\text{m}^3$.

Leach heaps are often plagued by permeability problems that lower the copper recovery. Fine particles are able to migrate downwards in the heap, clogging the spaces between the larger ore particles. This results in the formation of impermeable layers in the ore bed, causing the solution to percolate through the heap unevenly. One way to increase copper recovery from a heap is to use a binder in agglomeration to improve heap permeability. In previous studies (Lewandowski and Kawatra, 2008) a number of effective binders were identified that were effective in the acidic leach solutions needed for copper heap leaching. They immobilized fines and prevented the “channeling” and “ponding” effects that could otherwise

slow the leaching rate and reduce copper recovery. These binders could, therefore, be useful in agglomerating ore in leaching heaps. However, if a binder is used in agglomeration of the ore, there is always the possibility that some of the binder may be washed out of the heap with the PLS. If any of the binder washes out of the leach heap, it is necessary to make sure that this agglomeration additive would not negatively interfere with the solvent extraction process. It was of particular interest to determine whether the specific binders that had been found to be effective agglomerating agents interfered with solvent extraction. Studies were, therefore, carried out to determine whether binders dissolved in the PLS would interfere with solvent extraction. It is also possible that the binders could be transferred by the solvent extraction into the electrowinning process, and could potentially affect the growth of copper on the cathodes. However, any effects on cathode growth are beyond the scope of this paper and have not yet been examined.

Theory

Solvent extraction (Fig. 2) is carried out in two steps. First, the copper-containing PLS from the heap is mixed with a hydroxyphenyl oxime organic extractant dissolved in petroleum distillate, producing an organic phase that is approximately 10% (by volume) extractant. Mixing the organic with the PLS forms an emulsion, with high surface area between the PLS and organic phase. This

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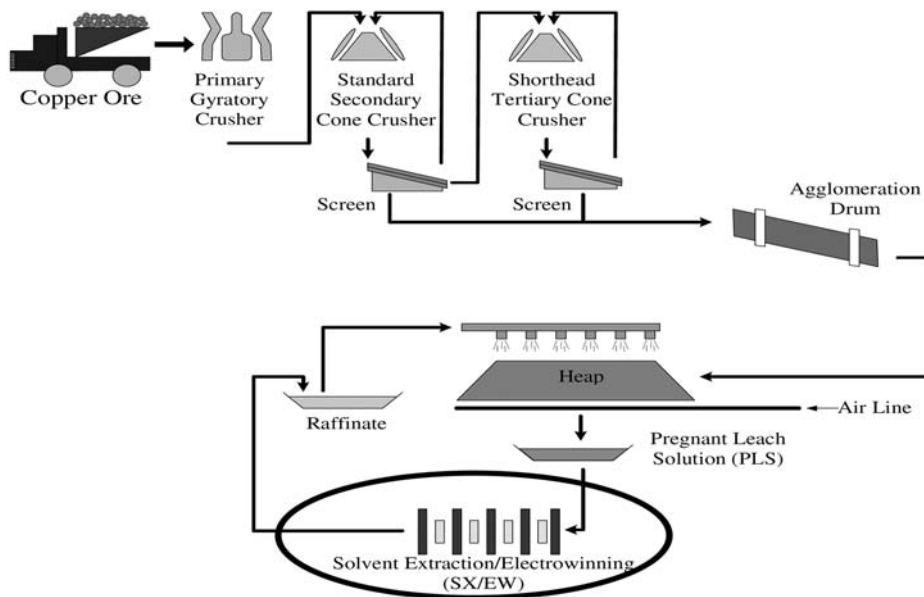
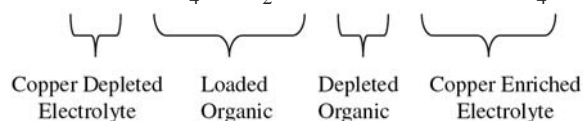
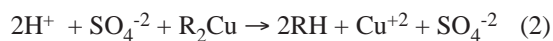
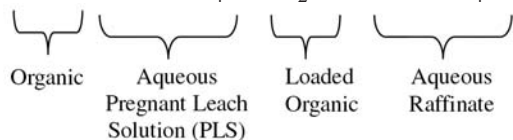
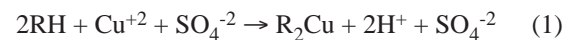


Figure 1 — Solvent extraction/electrowinning circuit in a copper heap leaching process (adapted from GE Infrastructure, 2004).

promotes rapid transfer of copper from the PLS to the organic phase. This allows the Cu^{+2} from the PLS to be transferred to the organic extractant according to the reaction shown in Eq. (1) (Biswas and Davenport, 1994) and depicted in Fig. 3. After the PLS is mixed with the organic extractant, the mixed solution is allowed to segregate, with the emulsion breaking to form a bottom layer (copper depleted aqueous raffinate solution, which is recycled back to the leach heap), and a top layer (copper-loaded organic extractant). This loaded organic is passed to another mixer where it is mixed with a sulfuric acid electrolyte ($\sim 170 \text{ kg H}_2\text{SO}_4/\text{m}^3$). In the second mixer, a reverse reaction takes place, as shown in Eq. (2) and depicted in Fig. 4. The copper is stripped from the organic and concentrates into the sulfuric acid electrolyte (Biswas and Davenport, 1994). The concentrated electrolyte can then be transferred to an electrowinning circuit where it can be plated onto cathodes, which are then sent to melting and fabrication.



A common problem in solvent extraction is crud formation, a stable aqueous/organic emulsion that is caused by solids and vegetation in the PLS that prevents separation from occurring between the aqueous and organic layers and increasing the time it takes for the phases to separate. Biswas and Davenport (1994) stated that crud formation could also occur due to surfactants that may be used in leaching. If crud formation can occur with surfactants, there is a possibility that it could occur with the

use of other products, such as agglomeration binders.

When being passed through the first stage of solvent extraction, if the binder coats the organic droplets, as shown in Fig. 5, the copper would not be transferred due to the binder barrier. If this occurred, the organic particles would also take longer to separate from the leach solution and combine back together, due to the binder layer around their surfaces (Cheng et al., 2000).

Given that agglomeration binders are typically long-chain polymers, there was significant potential that they could promote crud formation. A study was, therefore, carried out to determine whether these specific binders interfered with solvent extraction, causing low copper-transfer rates and high settling times. It was also possible that binders could be transferred into the organic phase and then exchanged back into the purified copper electrolyte for electrowinning. It is possible that such transfer of agglomeration binders into the electrolyte could affect the deposition of metallic copper on the cathodes. However, the potential for crud formation is a more immediate problem, as excessive crud levels would halt the solvent extraction process and prevent the copper from being transferred into the electrolyte at all. The question of how binders might affect electrowinning is beyond the scope of this paper, and would need to be addressed in a future study.

Experimental procedure

In previous studies (Lewandowski and Kawatra, 2008) a number of effective binders for agglomerating copper ore were identified. To determine the effect of these binders on the SX process, a laboratory test procedure was developed that simulated the two stages of the solvent extraction process using a separatory funnel, sulfuric acid, simulated pregnant leach solution (PLS) mixed with a binder and an organic extractant.

Materials. Simulated PLS was required to create consistency between tests. Biswas and Davenport (1994) stated that PLS usually contains approximately 1 to 5 $\text{kg Cu}^{+2}/\text{m}^3$ of solution. This was consistent with copper concentrations in the PLS from

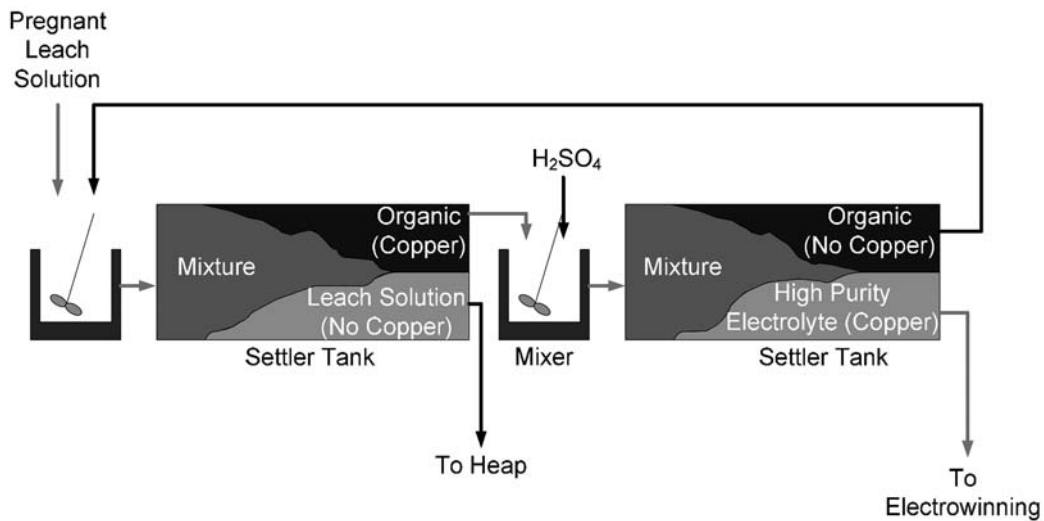


Figure 2 — Solvent extraction process.

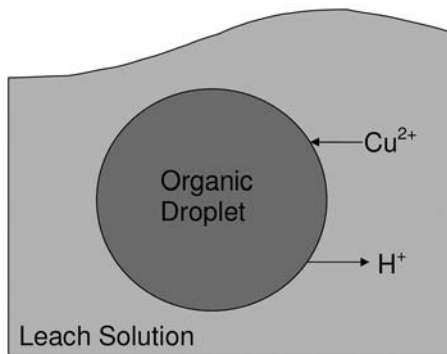


Figure 3 — Transfer of copper from the leach solution into the organic droplets.

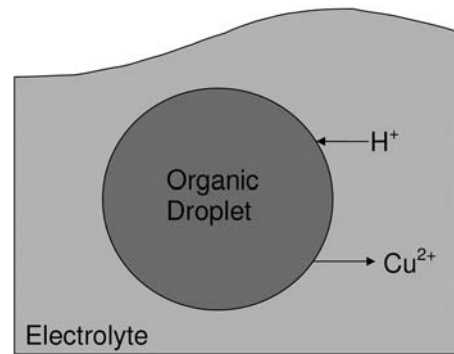


Figure 4 — Transfer of copper from the organic droplets into the sulfuric acid electrolyte.

previous leach studies (Lewandowski and Kawatra, 2008). A simulated PLS solution was created out of raffinate (dilute sulfuric acid leach solution) and reagent-grade copper sulfate (CuSO_4) to contain $2.5 \text{ kg Cu}^{2+}/\text{m}^3$ of solution. Raffinate received from a southwestern heap leaching facility was used to simulate plant conditions as closely as possible.

The binders selected were those that showed promise for improving copper recovery in column testing (Lewandowski and Kawatra, 2008). These binders are identified as polyacrylamide-1, polyvinyl acetate emulsion-1, waste treatment additive and tall oil pitch.

Organic used in this study was received from the same southwestern heap leaching facilities' solvent extraction circuit as the raffinate solution.

Procedures. The simulated PLS was prepared by adding 9.31 g of CuSO_4 per liter of raffinate (sulfuric acid leach solution), which had an original concentration on average of 0.13 g Cu/L, for a total concentration of 2.5 g Cu/L. A separate sulfuric acid solution was also prepared to a concentration of 170 g H_2SO_4 per liter of distilled H_2O (Biswas and Davenport, 1994).

Copper concentrations of the solutions throughout this study were determined using standard atomic absorption (AA) analysis procedures. The PLS was diluted by a factor of 1:100

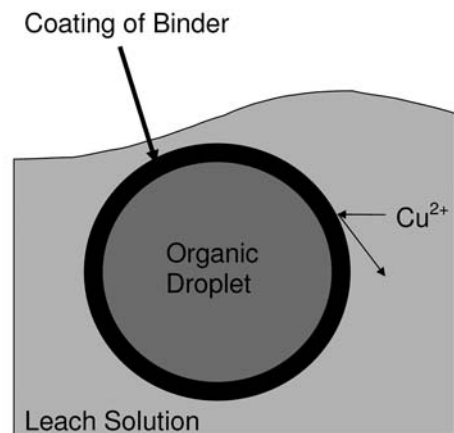


Figure 5 — Potential interference of a binder with copper transfer and settling rates.

before being analyzed by AA, and the sulfuric acid samples were diluted by a factor of 1:1000 before being analyzed.

In each test, 0.031 g of the selected binder was added to 500 mL of simulated PLS. This concentration would result if

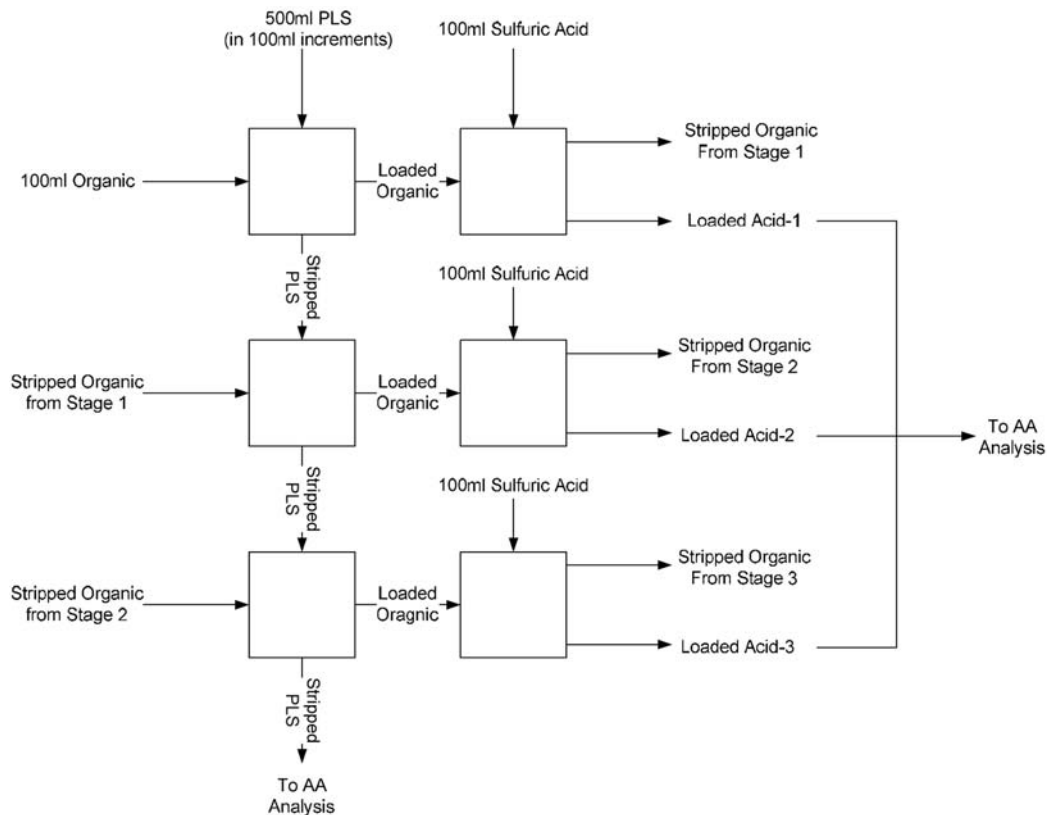


Figure 6 — Process flow diagram for the laboratory solvent extraction mixing process.

4.54 g of binder per ton of ore were washed out from the heap into the collected PLS. The binder and simulated PLS were mixed and allowed to stand for 24 hours before being used in the solvent extraction testing.

To prepare the organic, a sulfuric acid wash was performed to remove any copper that may have been contained in the organic phase. One hundred milliliters of organic was mixed with 100 mL of 170 g/L H_2SO_4 in a separatory funnel for 2 minutes by lightly shaking the funnel on its side forward and backwards approximately 60 times per minute. On settling, the two layers separated, and the bottom sulfuric acid layer was drained from the funnel. After the sulfuric acid was drained, an additional 100 mL of fresh sulfuric acid was added to the separatory funnel. The organic and acid were mixed again for 2 minutes and allowed to stand before the loaded sulfuric acid was drained from the bottom of the funnel. At this point it was determined that the organic was clear of any remaining copper.

After necessary preparations were made, the laboratory solvent extraction process was conducted. The solution flows are somewhat complicated. Therefore, a flow diagram is shown in Fig. (6) for clarity. First, 100 mL of simulated PLS/binder mixture was added to the 100 mL of cleaned organic in a 500 mL separatory funnel. The PLS and organic were then mixed for 1 minute using the same mixing procedure used for the organic. As soon as the separatory funnel was set upright in a ring stand, a stopwatch was started to measure the pregnant leach solution separation time. After separation occurred, the copper depleted PLS was removed. Another 100 mL of copper-rich simulated PLS was added to the organic and mixed for 1 minute before being removed from the funnel. This process was repeated until all 500 mL of the simulated PLS/binder mixture was passed through the organic.

After passing 500 mL of simulated PLS through the organic, the now loaded organic was stripped with sulfuric acid. One hundred milliliters of 170-g/L sulfuric acid was added to the separatory funnel containing the 100 mL of the loaded organic. The solution in the funnel was mixed for 1 minute. Again, the time it took for the H_2SO_4 to separate from the organic was recorded. The copper-rich H_2SO_4 was drained from the funnel and set aside.

The simulated PLS, which had been passed through the organic once, was then passed through the stripped organic again using the same procedure. The organic was then stripped again using 100 mL of H_2SO_4 . This procedure was completed one more time, for a total of three passes.

Finally, samples of the PLS after the copper was removed and the H_2SO_4 used to strip copper from the organic were tested for copper concentrations using atomic absorption (AA). This allowed for an analysis of the copper and iron contained in the samples.

Results

Once the copper concentrations of the simulated feed PLS and the PLS after processing were determined, the amount of copper transferred from the PLS to the organic could be determined, as shown in Fig. 7.

The simulated PLS with no added binder was used as the baseline test. The remaining tests were completed with a mixture of a selected binder combined with the simulated PLS. The copper removals when using the polyacrylamide-1 as well as the tall oil pitch and waste treatment additive were almost identical to the removal when using no binder. The polyvinyl acetate emulsion-1 mixture inhibited the transfer of copper by about 30%.

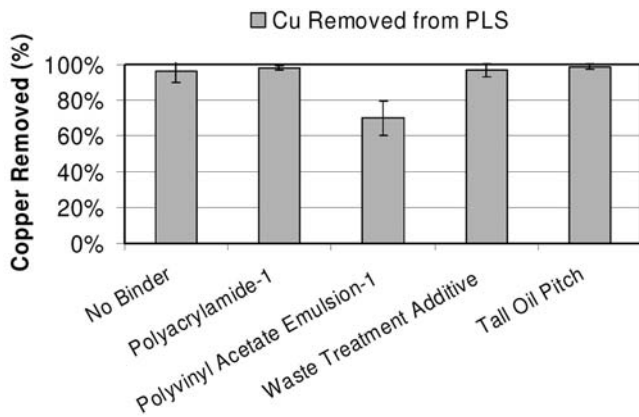


Figure 7 — Concentration of copper that was transferred from the simulated PLS feed to the organic. Error bars are two standard deviations and are based on three experimental results. The polyacrylamide-1 and the tall oil pitch had very small error bars.

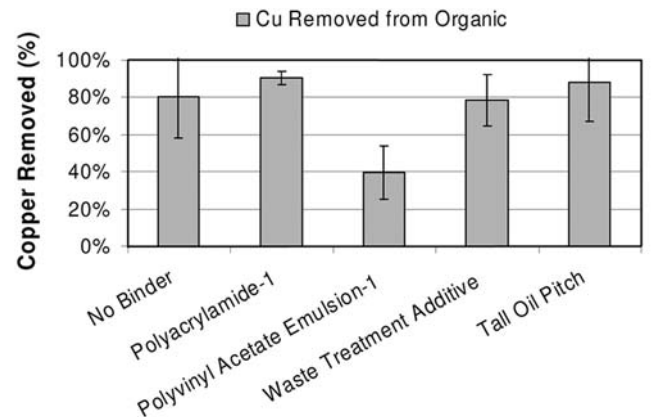


Figure 8 — Concentration of copper that was transferred from the organic to the H_2SO_4 electrolyte solution. Error bars are two standard deviations and are based off of three experimental results.

The copper-loaded organic was then mixed with a high concentration sulfuric acid solution, allowing the copper to be passed from the organic into the H_2SO_4 solution. The degree of copper transfer from the organic to the sulfuric acid is shown in Fig. 8. This percentage of copper transfer compares the amount of copper that was in the sulfuric acid to the amount of copper that was available in the copper-loaded organic phase.

The polyacrylamide-1 was similar to the baseline extraction when comparing the amount of copper removed from the organic into the H_2SO_4 solution. The tall oil pitch and waste treatment additive were also not statistically different from the no-binder case. However, the polyvinyl acetate emulsion-1 inhibited the copper extraction from the organic to the sulfuric acid by approximately 60%.

After the simulated PLS was mixed with the organic for 1 minute, the phase disengagement times were measured. It was important to know that the use of the binders was not going to affect the time it took for the solutions to separate. Increased phase disengagement time would mean that a plant would need more equipment or larger settling trays to accommodate more liquid for longer periods of time. The settling time for the various binder mixtures is shown in Fig. 9.

The polyvinyl acetate emulsion-1, which inhibited both the transfer of copper from the simulated PLS into the organic and the transfer of copper from the organic into the sulfuric acid solution, also had an increased phase disengagement time, which varied considerably. There were times where it took more than 600 seconds (10 minutes) to settle. Anything greater than 10 minutes was stopped before settling was complete. This is the minimum size of error bar based on the possibility that the average settling time may actually be greater than was reported in Fig. 9. The polyacrylamide-1 and waste treatment additive did not alter the settling time. The use of tall oil pitch slightly increased the settling time, over the simulated PLS (no binder).

It is critical for rapid electrowinning of high-purity copper, that impurities, particularly iron, are not carried from the PLS to the sulfuric acid electrolyte (Biswas and Davenport, 1994). Iron transfer was negligible between the PLS and the organic, for all experiments, as shown in Fig. 10.

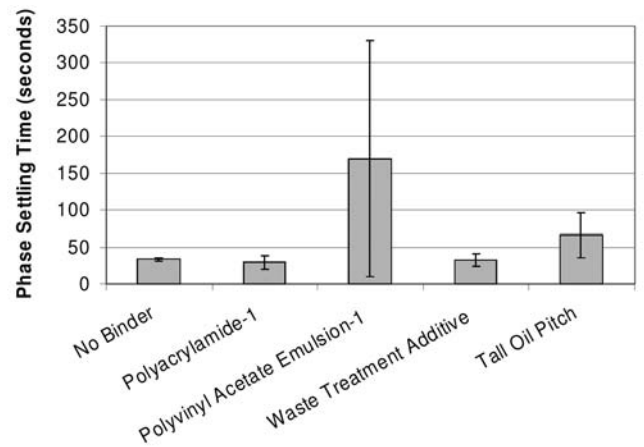


Figure 9 — Settling time for various binder mixtures. Error bars are two standard deviations and are based on three experimental results.

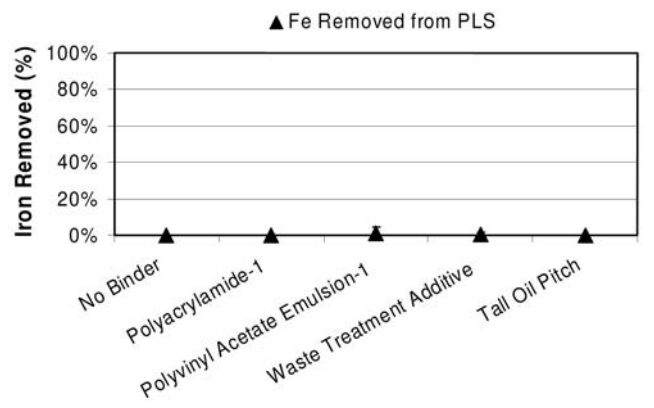


Figure 10 — Iron removal from the simulated PLS. Error bars are two standard deviations and are based on three experimental results. For all practical purposes, essentially no iron was transferred from the PLS to the organic for any of these experiments.

Discussion

The polyacrylamide-1 and waste treatment additive showed no interference with copper transfer or phase settling times compared to having no binder in the PLS. This indicates that these binders are not interacting with the organic. The tall oil pitch also did not interfere with copper transfer. However, the settling time for the tall oil pitch was slightly higher than the other binders, indicating that it may have been beginning to partially coat the organic droplets and interfere with droplet coalescence. The polyvinyl acetate emulsion-1 was a clear example of how a binder may negatively interfere with copper transfer and settling time, as it greatly increased the phase settling times by making it harder for the organic droplets to recombine back together. If this were a binder that was used in the field it would lead to lower copper recovery from solution and longer separation times.

Conclusions

When using a binder in agglomeration in copper heap leaching, there is a possibility that some of the binder may leach out with the pregnant leach solution. This study was completed to verify that if any binder leaches out of the heap, that it would not negatively interfere with the solvent extraction circuit. Any interference in solvent extraction would in turn negatively affect the electrowinning circuit, and in the end decrease the production of copper.

After performing laboratory-scale solvent extraction tests,

it was determined that the polyacrylamide-1 and the waste treatment additive did not have negative effects on the solvent extraction process. The use of tall oil pitch increased the phase separation settling time slightly over using no binder. The use of polyvinyl acetate emulsion-1 inhibited copper transfer the greatest, while also greatly increasing the phase disengagement time between the organic and PLS.

It was hypothesized that increased phase disengagement times were due to the binder coating the surfaces of the organic particles and interfering with their abilities to combine back together. A coating on the surfaces of the organic droplets would prevent copper from being transferred between the PLS and organic as well as between the organic and sulfuric acid electrolyte.

Before any binder is used in agglomeration, it should be tested using a solvent extraction and electrowinning procedures to verify that it will not negatively affect copper production. If the binder were to interfere, as the polyvinyl acetate emulsion-1 did, then decreased copper transfer could be expected.

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