INVESTIGATING THE IMPACT OF HIGH TEMPERATURE AGITATION LEACHING IN THE RATE OF OXIME DEGRADATION

By

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ABSTRACT

Agitation tank leaching is a widely used method in the African Copper Belt to facilitate the rapid dissolution of copper from mid to high grade copper ores. As ore grade has begun to decline and the relative abundance of secondary sulfide mineralization is increasing, plants have implemented or are considering treating calcined ore from a roaster to increase or supplement copper production. This process would cause an increase in the temperature of the pregnant leach solution (PLS) produced. The extraction step occurs in relatively mild acid conditions of 1-10g/L sulfuric acid, which is significantly lower than the 150-200g/L sulfuric acid level that copper solvent extraction (SX) reagents are contacted with in the stripping stage of most processes. However, the higher temperature range of 40-60°C is thought to be linked to an observable increase in the acid-catalyzed hydrolysis rate of the oxime reagents commonly used to selectively extract the copper from the PLS after agitation leaching.

This study shows the results of an experiment conducted to investigate the rate of hydrolysis observed from sustained contact with the PLS produced from these leaching conditions and temperatures. The results will be contrasted for the most common types of extractants currently used in the market and discuss the potential implications of those results.

Keywords: hydrolysis, agitation leaching, degradation

INTRODUCTION

African operations, particularly those in the African Copper Belt, are known for high ore grades and because of this the leaching of these ore bodies is typically done in agitation tanks.[1] Due to the mild temperatures and exothermic acidic leaching conditions, agitation tank leaching systems usually operate with temperatures between 35°C to 45°C, in which almost all the copper is leached in a matter of hours. Ultimately, resulting in a higher-temperature pregnant leach solution (PLS) going into the solvent extraction (SX) operation. Although the effect of higher temperatures in the SX circuit have positive effects on kinetics and copper transfer, the effect on diluent evaporation and degradation of the extractant are quite noticeable and negative. High temperatures lead to a faster loss by degradation of the extractant and as consequence the buildup of degradation products that negatively affect the physical operation of a plant by increasing entrainments.

As ore bodies around the world transition from easily leachable minerals to more refractory minerals, the processing route is likely to become more aggressive. Several operations in the Copperbelt are considering incorporating roasting or pressure leaching of sulfides into the overall flowsheet. The net effect of this will be an increase in the temperature of the PLS going to SX. Outside of the Copperbelt, several leaching technologies for primary sulfides are being proposed for heap and dump leach operations that will incorporate novel bacteria operating at higher temperatures[1]. Again, this will likely result in significantly higher PLS temperatures which will have to be accommodated in the SX plant.

In an SX operation, stripping stages typically have a much higher acid concentration and are run at higher temperatures than the extract stages. As expected, degradation of the oxime is higher in the strip stages than in extract. Questions have been posed by operators and technology developers as to how high a temperature can be tolerated in an SX plant with the commercially available extractants. Previous studies have investigated the effect of high temperature under stripping conditions and in this paper the effect of a higher temperature PLS was studied. Also, since there would be a need for extractants that can be more resistant to these aggressive conditions, BASF has developed a novel copper extractant that has greater stability at higher temperatures in addition to other beneficial properties like greater Cu/Fe selectivity and being nitration resistant.[2,3,4.] The degradation of this novel extractant and its blends with conventional oximes was also examined in this study.

OXIME DEGRADATION

Acid-catalyzed hydrolysis is usually the most common type of oxime degradation in SX plants. This degradation is favored because of the high concentration of acid in the circuit where the oximes are hydrolyzed to their respective aldehyde or ketone. The accumulation of these degradation products increases the viscosity of the organic phase, which in turns causes operational turmoil in terms of slower disengagement times and higher entertainment, ultimately increasing reagent consumption for the SX operation. The main factors that affect the rate of hydrolysis are impurities, polarity of the organic, amount of oxime on the interface, acid concentration and temperature.[2] The mechanism of the hydrolysis of oximes is illustrated in Figure 1.

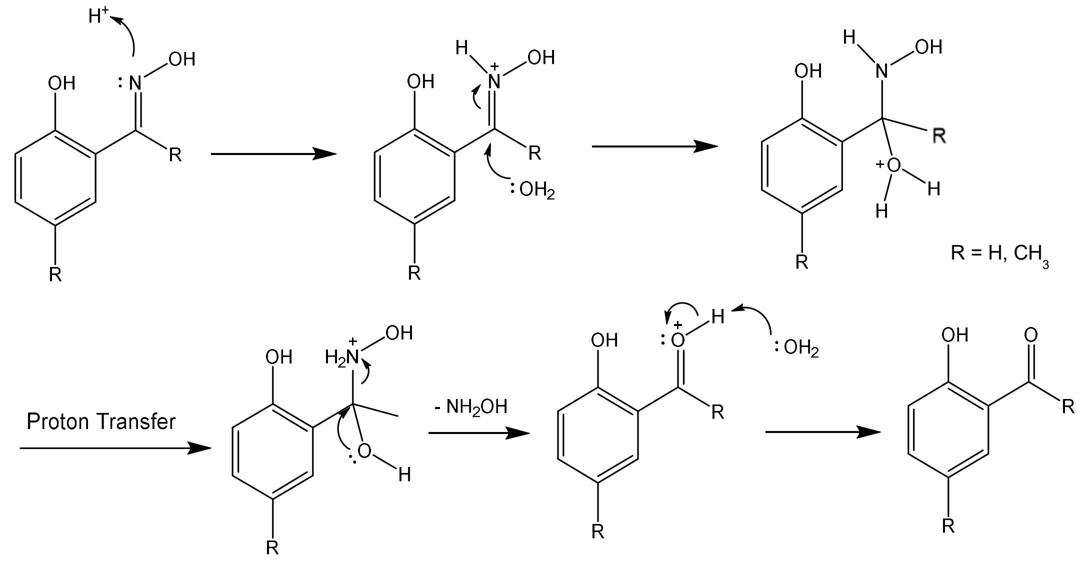

Figure 1. Acid-Catalyzed Hydrolysis of Oximes.

EXPERIMENTAL

Preparation of Aqueous Solution

A synthetic PLS containing 5g/L Cu^{2+}, 8g/L Fe^{3+}, 2g/L Fe^{2+}, and 5g/L H_2SO_4 was prepared by dissolving the required amounts of $CuSO_4 \cdot 5\ H_2O$, $Fe_2(SO_4)_3$, $FeSO_4$, and 97-98% H_2SO_4 in deionized water. The aqueous solution was prepared from reagent grade chemicals.

Preparation of Organic Solutions

Organic solutions targeting a max load of 8.4g/L Cu of LIX 860N-I, LIX 84-I, LIX 984N, LIX 10HS, LIX 2620HS, and LIX 0820HS, and a TXIB-modified aldoxime (found to be contaminated with a small amount of ketoxime) were prepared in SX-12. LIX 10HS is BASF's new-generation solvent extraction reagent, while the other two LIX HS reagents are blends of LIX 10HS and conventional oximes. These solutions were equilibrated with a standard strip solution containing 35g/L Cu^{2+} and 160g/L H_2SO_4. Then filtered through Whatman 1PS filter paper.

Procedure and Equipment

Degradation testing was performed by continuously stirring the organic extractant with the synthetic PLS. The test vessels used were three-necked 1L jacketed round bottom flasks, each connected in series to a recirculating water bath with a constant target temperature. An overhead mixer was connected via an airtight stopper to the flask and the stirring speed was maintained at 500 ± 25 RPM. Samples of the emulsion were taken so as to keep the aqueous to organic ratio constant at a 1:1 O/A. The organic and aqueous phases were separated and the organic fraction was max loaded with a standard extraction aqueous phase containing 6g/L Cu, 3g/L Fe and a pH of 2. The organic was also stripped with a 250g/L sulfuric acid solution. The max loaded sample was analyzed for Cu by Atomic Absorption Spectroscopy (AAS) and the stripped sample was analyzed for degradation and for oxime ratio by High Performance Liquid Chromatography (HPLC). Figure 2 shows the degradation testing setup.

Figure 2. Degradation Testing Setup.

TEST RESULTS

Degradation Tests

Degradation of oximes via acid-catalyzed hydrolysis is constantly happening within an operation. The concentration of the degraded oximes typically increases if the degradation rate is faster than the loss of organic via entrainment or removal. In this testing, organic was never removed other than the sample taken to quantify degradation. Therefore, buildup of the degraded products took place inside the test vessel. As plant processes are more dynamic and complex, the degradation rate seen in this study cannot be associated to a specific operation. Nonetheless, these laboratory simulations compared the relative rates of degradation between the different formulations tested and it can be reasoned that the relative trends could be seen in a plant.

Figure 3 shows the degree of hydrolysis of the reagents tested when contacted with the synthetic PLS at 50°C for 221 days. The most prone to degradation was the TXIB-modified aldoxime, followed by pure aldoxime, then blends containing aldoxime, then ketoxime and finally LIX 10HS. As expected, the aldoxime had a higher degradation rate than ketoxime. This is expected as the steric hindrance between the two functional groups is higher in the ketoxime because of the methyl group, making the ketoxime more resistant to the nucleophilic attack of water that leads to its degradation[2,6]. Blends that also contained a higher percent of aldoxime seemed to have a higher degradation rate than pure ketoxime and pure LIX 10HS. As the amount of aldoxime in the blend decreased, the more resistance the blend was to hydrolysis. Likewise, substituting a higher percent of the conventional oximes with LIX 10HS formulated blends that were more resistant to degradation, and with pure LIX 10HS being the most hydrolytically stable out of all the reagents tested.

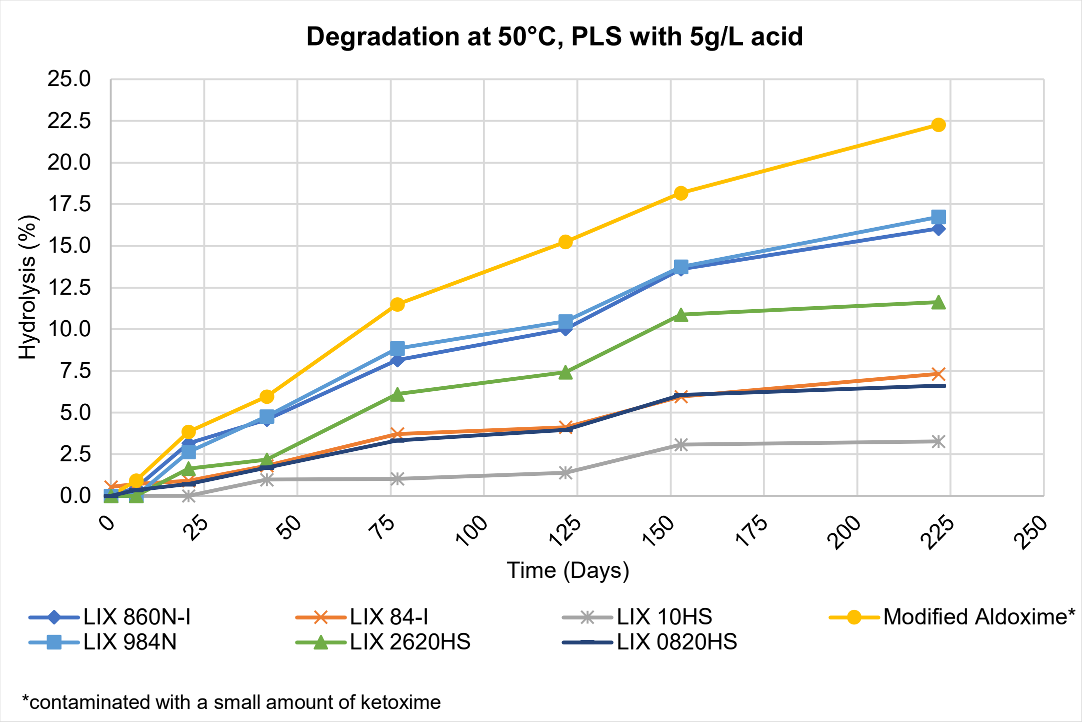

Figure 3. Hydrolysis Percent of Reagents Tested at 50ºC.

The copper max load of the organic solutions correlates with the degradation data and can be used as another means to track degradation. The strength of the copper extractant decreases when the oxime functionality degrades as degradation products do not load copper. Hence, there is less oxime to extract copper from the PLS and a decrease in max load would be expected as shown in Figure 4. The max load trend shows an inverse relationship with the degradation data in the graph above.

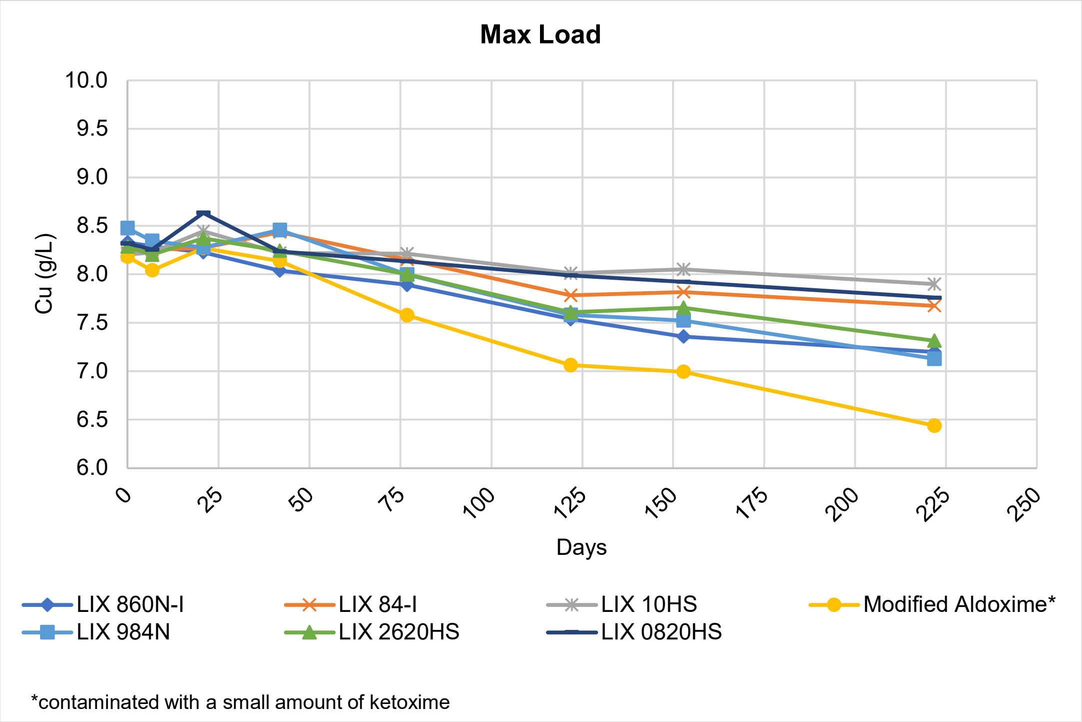

Figure 4. Max Load of reagents tested.

Degradation testing was also performed at an even higher temperature of 60ºC. As already discussed, increasing the temperature accelerates the degradation of oximes. Therefore, in this study the effect of a 10ºC increase in temperature was tested. These tests are still running at the time of paper submission, but preliminary data shows the same trend of degradation with the TXIB-modified aldoxime degrading the fastest, followed by pure aldoxime, then blends containing aldoxime, then ketoxime and finally LIX 10HS.

Figure 5 shows the degree of hydrolysis of the reagents tested when contacted with the synthetic PLS at 60°C for 57 days. By just increasing 10ºC, the rate of acceleration is roughly twice as fast for the oximes tested. For example, at 60ºC the degree of hydrolysis for the modified aldoxime at 57 days was calculated at 16%, while at 50ºC temperatures at 57 days was calculated at ~8%. This shows that if an operation increases the temperature even by 10ºC, a drastic negative effect on the health of the organic will most likely occur. All the negative effects of entrainment and evaporation, as well as the increase in reagent consumption would occur now at a more rapid pace.

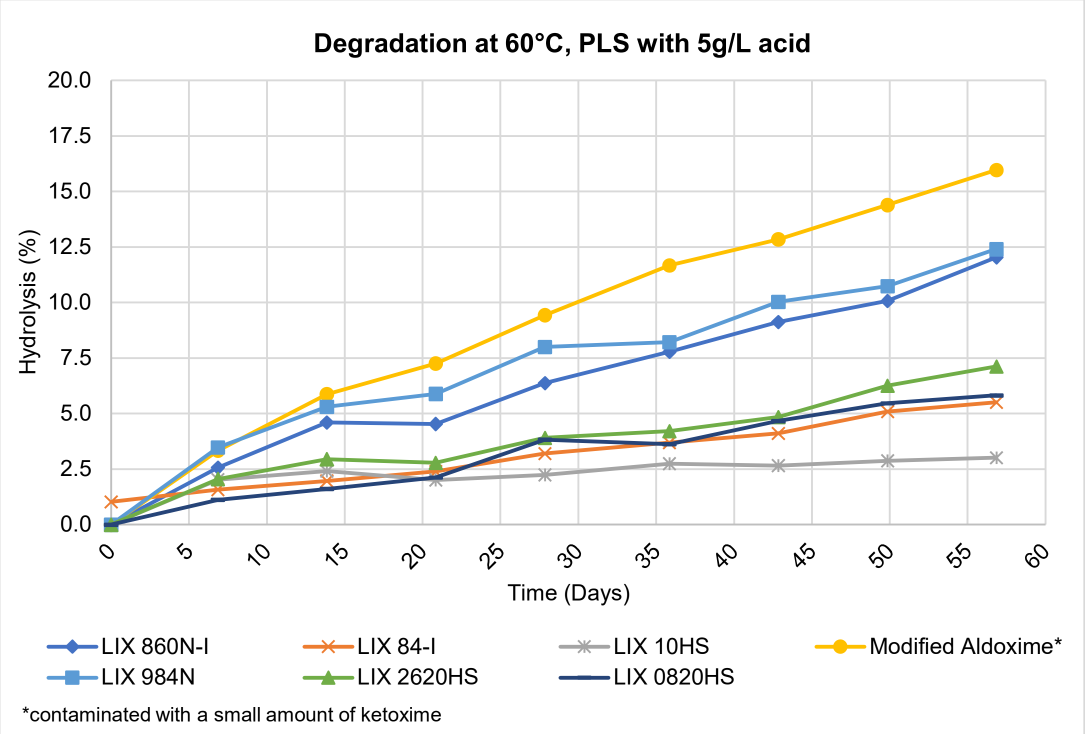

Figure 5. Hydrolysis Percent of Reagents Tested at 60ºC.

Previous accelerated degradation testing has been done using a synthetic stripping stage electrolyte with a 180g/L acid concentration at 45ºC.[2] It is known that degradation of oximes occurs faster in the stripping stages compared to extract stages due to the harsher conditions in stripping. Figure 6 illustrates the rate of hydrolysis for the modified aldoxime, pure conventional oximes and BASF high temperature extractants. As seen, the trend is similar to the ones found in the experiment for this paper, with the aldoximes degrading the fastest, followed by ketoxime and lastly the novel BASF high temperature reagents for solvent extraction.

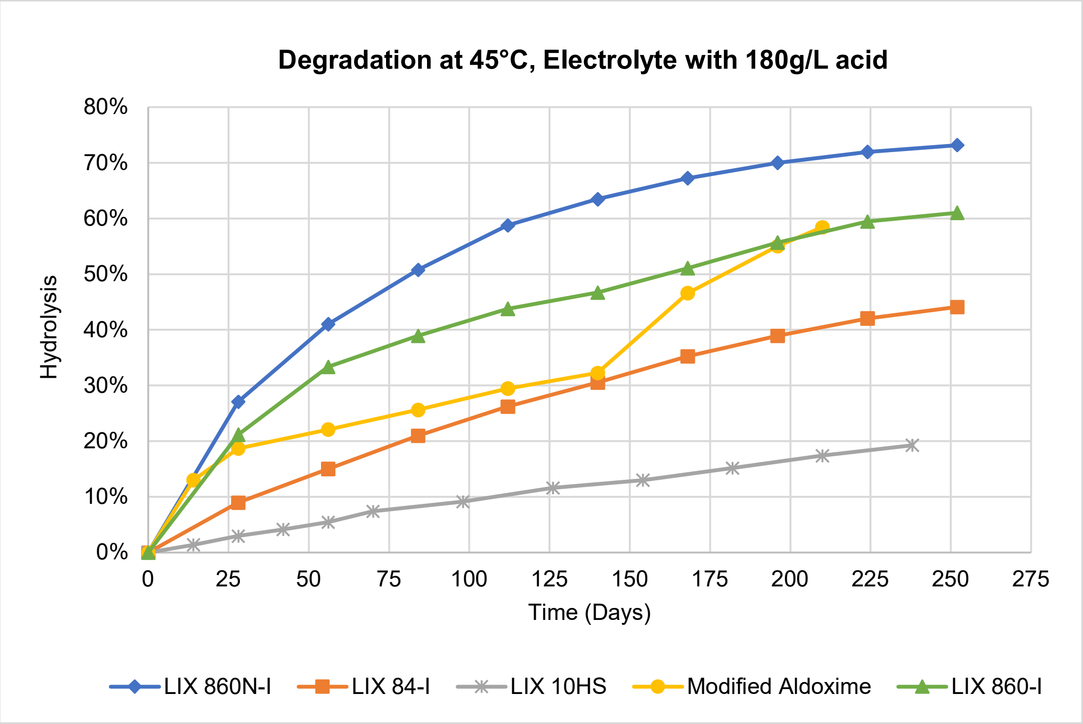

Figure 6. Degradation of different extractants at 45ºC when contacted with a 180g/L H_2SO_4 synthetic electrolyte.[1]

CONCLUSIONS

Degradation by acid-catalyzed hydrolysis is inherent to a copper solvent extraction operation and the degree as to which it is controlled can have negative effects on the plant. As the industry considers more aggressive leaching and processing techniques that will result in higher temperatures in both extract and strip, the impact of accelerated degradation needs to also be considered. This is difficult to quantify in a static laboratory setting since an operating SX plant is a dynamic process and an equilibrium is always reached between the rate of degradation, the concentration of degraded products in the organic phase and organic make-up/losses. However, the test work results have shown that at 50ºC degradation rates are high and are amplified significantly further with a 10ºC increase to 60ºC. BASF's novel extraction reagent LIX 10HS (and blends) have proven to provide higher resistance to degradation, even at higher temperatures, than the conventional ketoxime and aldoxime reagents.

Although not part of this study, the effect of higher temperature on the diluent component of the organic phase would also have to be considered and investigated.

ACKNOWLEDGMENTS

The authors would like to thank many of the colleagues in the BASF Tucson laboratory for their contributions in this project of collecting and analyzing samples, helping in the project setup and with intellectual support.

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