Preprint 10-017

UNDERSTANDING ACID CONSUMPTION AND ITS RELATIONSHIP WITH COPPER RECOVERY

M. L. Free, Univ. of Utah, Salt Lake City, UT
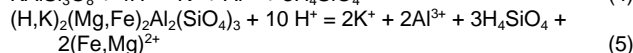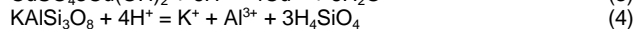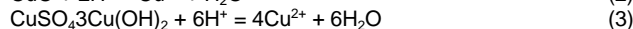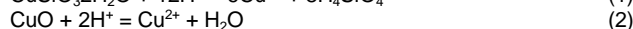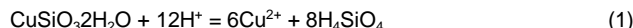
ABSTRACT

Acid consumption in copper heap leaching is determined by the minerals present in the ore. Gangue minerals such as biotite and chlorite consume acid together with copper-bearing minerals such as chrysocolla and malachite. Acid consumption is affected by the rate of acid application and the particle size. Some gangue minerals undergo alterations and cause precipitate formation during acid leaching. Other minerals form due to precipitation as dissolved ion concentrations from a variety of mineral sources combine to exceed saturation levels. Copper recovery is related to all of these events. This study presents information on acid consumption of various gangue minerals as well as data for copper recovery from an associated copper ore.
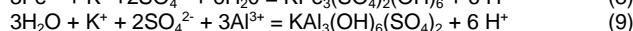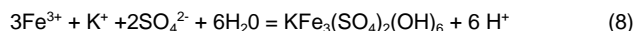
INTRODUCTION

Acid consumption during copper leaching of oxide ores is a very important issue. Acid consumption can determine whether or not a project is economically and technically feasible. The cost of supplying acid to a leaching operation is closely tied to the acid consumption, the price of acid, and the necessary transportation distance. Ores that consume large quantities of acid often present substantial technical challenges for copper recovery. Although some information about acid consumption is available in the literature for typical leaching papers (Gonzales and Torres 1995; Kelley and Zirate 1995) as well as more extensive overviews (Jansen and Taylor 2003; Baum 1999), detailed measurements are generally not available.

Consumption of acid by ore is dependent on mineralogy, solution pH, solution application rate, and particle size. These same factors affect the extraction of copper. Copper minerals in oxide deposits are often acid consuming minerals. Thus, copper extraction is related to acid consumption. Common acid consumption reactions associated with copper oxide ore leaching include (Jansen and Taylor 2003):

$$CuSiO_3 2H_2O + 12H^+ = 6Cu^{2+} + 8H_4SiO_4 \qquad (1)$$
$$CuO + 2H^+ = Cu^{2+} + H_2O \qquad (2)$$
$$CuSO_4 3Cu(OH)_2 + 6H^+ = 4Cu^{2+} + 6H_2O \qquad (3)$$
$$KAlSi_3O_8 + 4H^+ = K^+ + Al^{3+} + 3H_4SiO_4 \qquad (4)$$
$$(H,K)_2(Mg,Fe)_2Al_2(SiO_4)_3 + 10\,H^+ = 2K^+ + 2Al^{3+} + 3H_4SiO_4 + \\ 2(Fe,Mg)^{2+} \qquad (5)$$
$$Fe_2O_3 + 6H^+ = 2Fe^{3+} + 3H_2O \qquad (6)$$
$$FeO(OH) + 3H^+ = Fe^{3+} + H_2O \qquad (7)$$

Acid consumption releases species that cause by-products such as include jarosite and alunite to form as shown respectively in Equations 8 and 9:

$$3Fe^{3+} + K^+ + 2SO_4^{2-} + 6H_2 0 = KFe_3(SO_4)_2(OH)_6 + 6\,H^+ \qquad (8)$$
$$3H_2O + K^+ + 2SO_4^{2-} + 3Al^{3+} = KAl_3(OH)_6(SO_4)_2 + 6\,H^+ \qquad (9)$$

These species produce precipitates that can restrict acid consumption as well as release acid, thereby altering the acid balance.

Each mineral reaction has an associated equilibrium that can be determined by thermodynamics. Each reaction will have a specific pH at which equilibrium is achieved under each solution environment. However, as leaching takes place the concentration of various species in the system changes, thereby affecting the pH at which equilibrium is attained. Most of the reactions shown are very sensitive to acid concentration as indicated by the relatively large stoichiometric coefficients in the reaction equations. Thus, acid concentration is a key factor in determining acid consumption, although it should also be understood that the pH inside a leaching operation varies according to flow rate, history, and location.

Acid leaching of oxide ores can result in at least three general scenarios for acid consuming minerals as depicted in Figure 1. Some acid consuming minerals dissolve. Some acid consuming minerals dissolve and rapidly form a precipitate at the surface that restricts further leaching. Other acid consuming minerals gradually transform into secondary minerals during the leaching process, resulting in a secondary mineral layer. The same events can occur inside of pores within the mineral particle, which can result in pore blockage that restricts or eliminates some accessibility of mineral grains within the matrix, which can reduce recovery. However, as particle size decreases the effect of pores and associated potential blockage decreases because more of the minerals are liberated. Very fine particles cannot form thick precipitate or secondary mineral layers that passivate the surface. Thus, very fine particles of passive film forming acid consuming minerals are more likely to consume additional acid during normal leaching times than larger particles. Thus, size plays an important role in observed acid consumption.
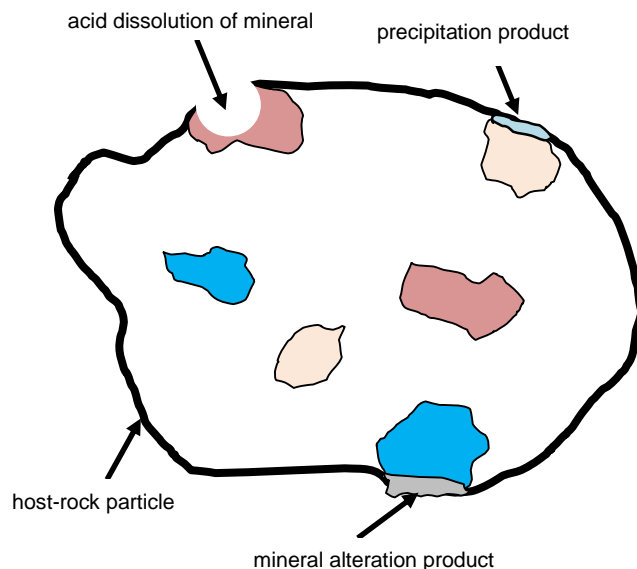
Figure 1. Schematic diagram of ore leaching with three different types of acid consuming minerals after some exposure to acidic leaching solution; one type of mineral that forms a mineral alteration product, one type that is associated with a precipitate coating, and one type that dissolves as indicated.

In this study the acid consumption behavior of several acid consuming minerals and associated ore were evaluated to determine the relationship amongst pH, acid consumption, and copper recovery.

One of the primary goals of this study was to identify pH levels that correspond to primary acid consumption and copper extraction events.

EXPERIMENTAL PROCEDURES

In order to investigate the behavior of minerals during leaching, a number of leaching tests were conducted. Mineral samples were pulverized, then attrition milled for 6 one-hour cycles to achieve 50 % minus 3 microns. A Spex mill was used with 10 grams of mineral charge with 50 vol% grinding media (5mm and 3mm steel balls) in a 150 cm3 container. The leaching tests were performed using 1 gram of pulverized mineral particles in 20 ml of water. The particles were suspended by stirring with a magnetic stirring bar. Sulfuric acid (1.14 M made from reagent grade stock) was added at a rate of 40 microliters per minute using a syringe pump. The pH was monitored using a pH electrode throughout the course of leaching. Copper extraction was measured using a copper ion selective electrode. Data from the pH probe and copper ion selective electrode were recorded digitally throughout the tests as needed. The minerals investigated were andesine, augite, montmorillonite [(Na, Ca)(Al, Mg)6(Si4O10)3(OH)6 - nH2O], sanidine, enstatite, chlorite [((Fe, Mg, Al)6(Si, Al)4O10(OH)8)], biotite [(K (Fe, Mg)3 AlSi3 O10 (F, OH)2,)], and sodalite [(Na4Al3(SiO4)3Cl)] purchased from Wards Natural Science. A small number of experiments were performed using 30 grams of pulverized material per liter with acid addition to control pH as specified set points until 30 minutes of acid consumption stabilization was achieved.

Vacuum impregnation of dye (1 M dichloro-indophenol, sodium salt) in leached ore particles was used to identify pores and leached areas by light microscopy. Impregnated samples were dried then mounted in epoxy and polished using 180 grit, 600 grit, 1200 grit, 1 um alumina, and 0.05 um alumina media (purchased from Buehler) and mineral oil. Vacuum impregnation of leached ore particles with a solution saturated with lead nitrate was used to help identify cracks and pores. Impregnated material was dried following impregnation under vacuum, then cracked and prepared for scanning electron microscopy.
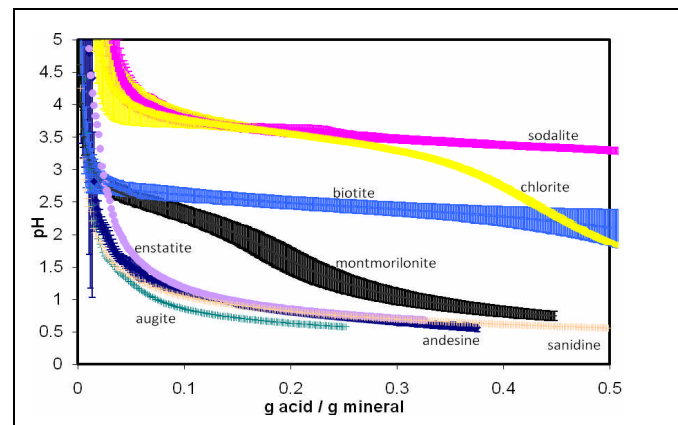
RESULTS AND DISCUSSION

Results from constant rate acid addition (0.04 ml/min in 20 ml) experiments with pure minerals (1 g/20ml) are presented in Figure 2. The data for sodalite, chlorite, biotite, and montmorillonite in Figure 2 represent the average values and associated standard deviation ranges from 2-4 test runs for each mineral. These results show that there are specific pH levels where acid consumption is dominant. These results also provide a practical reference for the quantity of acid needed to achieve specific pH levels in such experiments. Figure 2 shows that augite, andesine, enstatite, and sanidine have no specific pH at which acid consumption occurs, and their associated pH versus acid curves follow very closely with those of pure water, which has no specific pH at which acid consumption occurs rapidly. Compensation for the effect of water will be evaluated later. Figure 2 shows that sodalite consumes acid at pH levels between 4 and 3.4, chlorite consumes acid rapidly between pH 3.8 and 3.4, biotite consumes acid readily between pH 2.8 and 2.5, montmorillonite consumes acid most significantly between pH 2.7 and 2.0. Knowing the acid consumption behavior of pure minerals can be used to predict acid consumption in blends of minerals when the relative proportions of acid consuming minerals are known.

Figure 3 shows data from a pure mineral blend used to simulate a hypothetical ore with high acid consumption together with predicted consumption data. The predicted acid consumption trend is based on weighting pure mineral acid consumption data according the proportions of the pure minerals in the pure mineral blend. The predicted acid consumption trend fits the measured acid consumption trend reasonably well.

However, it should be clear that the acid consumption measured in all of the tests with data in Figures 2 and 3 is based on pulverized pure mineral particles that are more likely to consume acid than the same minerals found in ore particles. In addition, these tests are performed in suspensions with a 20:1 water to solid ratio, which is much higher than industrial practice. Furthermore, much of the reported acid consumption is associated with reducing the pH of the water. Thus, these tests provide useful insights, but the associated data cannot be applied directly to industrial practice.

Figure 2. pH and acid consumption data from constant rate acid addition (0.04 ml/min in 20 ml) experiments with pure minerals (1 g mineral/20 ml water). The data for sodalite, chlorite, biotite, and montmorillonite in Figure 2 represent the average values and associated standard deviation ranges from 2-4 test runs for each mineral.
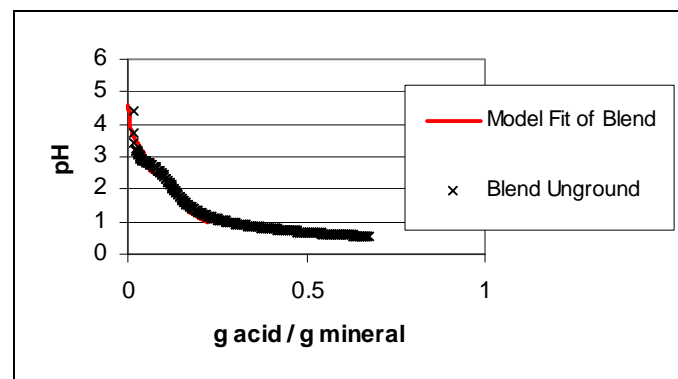

Figure 3. Comparison of measured and predicted pH and acid consumption for a proprietary blend of pure minerals, some of which are acid consuming.

Additional longer term testing was performed using pure minerals to determine acid consumption at different stabilized (1/2 hour of stabilized acid consumption) pH levels with compensation for acid consumption due to the water present in the vessel. Associated plots are presented in Figures 4-6. Figure 4 shows that chlorite consumes a considerable amount of acid at a pH of approximately 4.5 as well as additional acid between a pH of 1.5 and 1.0. Figure 5 shows that montmorillonite consumes a significant amount of acid between pH levels of 3.5 and 2.5. Biotite consumes acid between pH levels of about 6 and 3. Although these tests were each performed over a period of several days using pH controllers and acid pumps to maintain stability at individual pH set point values, the effect of reaction kinetics and passivation/precipitation were not evaluated directly. However, despite some uncertainty with these measurements, the technique is useful in identifying pH levels needed to cause significant leaching of acid consuming minerals.

The primary concern for copper producers is copper production and associated recovery. The recovery of copper produced from oxide ore leaching is related to the pH of the solution applied. Figure 7 shows the relationship between pH and copper recovery for a

pulverized copper ore sample. For the data set shown in Figure 7, the copper recovery is low until the pH drops below 3.5.
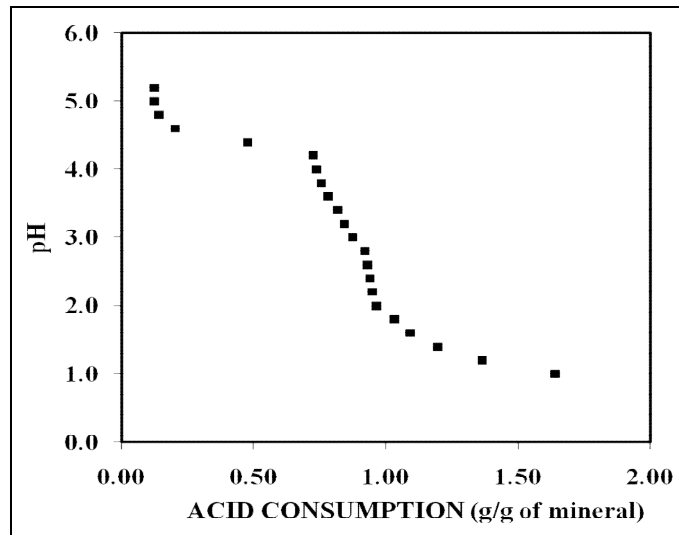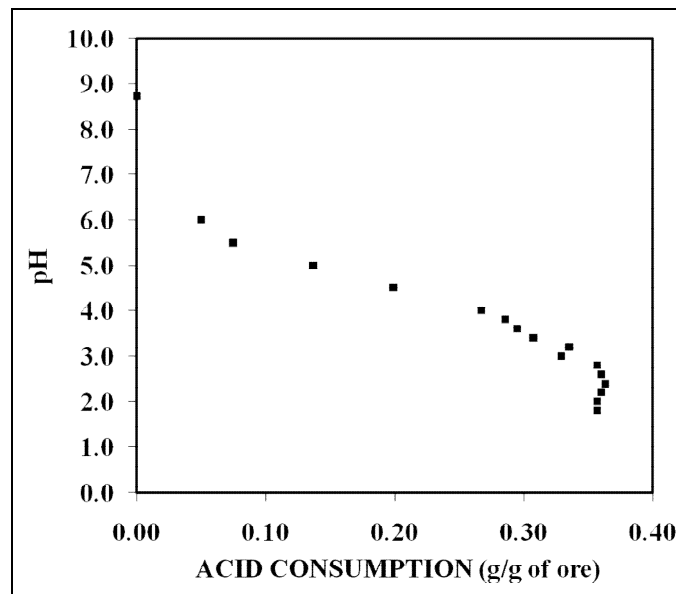

Figure 4. Acid consumption at various pH levels from finely ground chlorite mineral sample. (Consumption of acid needed to reduce the water pH has already been subtracted.)
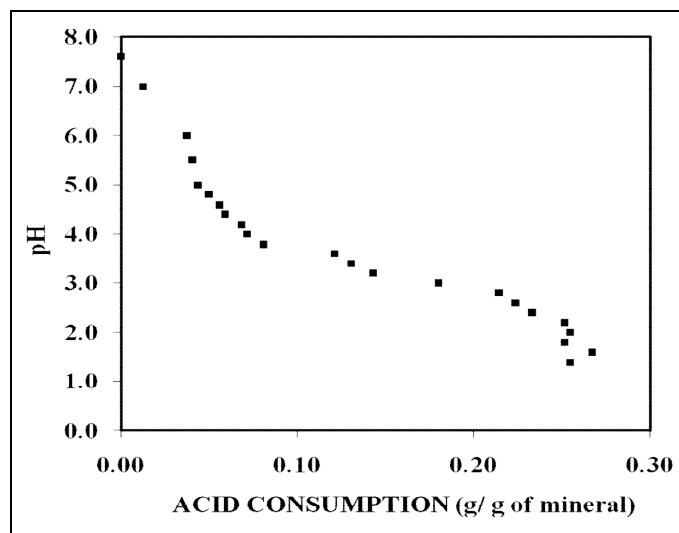

Figure 5. Acid consumption at various pH levels from finely ground montmorillonite mineral sample. (Consumption of acid needed to reduce the water pH has already been subtracted.)

As copper is leached from ore particles, voids remain in the host rock matrix. It is anticipated that some of the associated rock pores and voids could have precipitates or mineral alteration products that restrict access to some valuable mineral particles in the host rock matrix. In order to evaluate this possibility, leached ore particles were infiltrated with either a dye for light microscopy evaluation or lead nitrate for subsequent scanning electron microscope analysis. The results from these experiments are presented in Figures 8 and 9. The image in Figure 8 shows an extensive network of pores remaining after leaching. No specific constricted pores are noted in the image. Figure 9 shows residual lead nitrate as light areas on a dark background that result from fracturing a leached or particle after lead nitrate infiltration and subsequent drying. Figure 9 suggests that a pore network existed prior to fracture. No direct evidence of leaching associated precipitation is visible, although energy dispersive spectroscopy (EDS) indicated that some calcium was present. It was not determined whether the calcium was associated with a precipitate or with natural minerals in the ore sample.

Figure 6. Acid consumption at various pH levels from finely ground biotite mineral sample. (Consumption of acid needed to reduce the water pH has already been subtracted.)
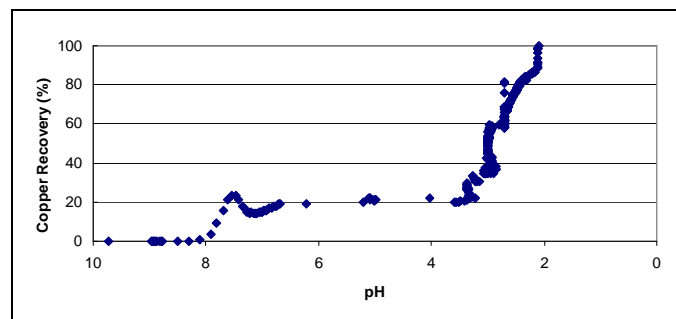
Figure 7. Comparison of copper recovery and solution pH for constant acid addition tests. Copper recovery determined based on a mass balance and copper ion selective electrode copper data during the test.
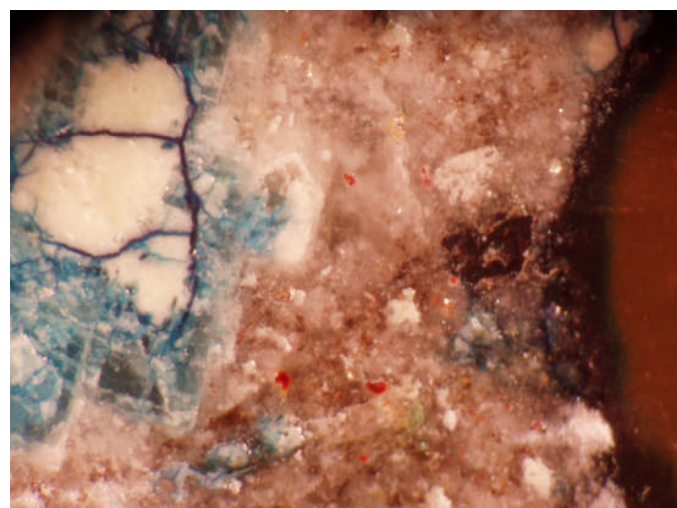

Figure 8. Microscope view of leached copper ore particle cross-section after vacuum impregnation with a blue dye. The horizontal length of the image is approximately 5 mm.

In an effort to determine if precipitation events associated with acid leaching are occurring, ore samples before and after leaching

were pulverized and examined by X-Ray Diffraction. Results from this evaluation are presented in Figure 10. Figure 10 shows the presence of sulfate minerals such as calcium sulfate and some magnesium sulfate that were not present in the ore prior to leaching. These results indicate that exposure of the copper ore to sulfuric acid leaching resulted in some precipitation.

Figure 9. Scanning electron microscope backscattered electron image of a fractured leached ore particle surface after impregnation with lead nitrate to highlight pore areas in white.
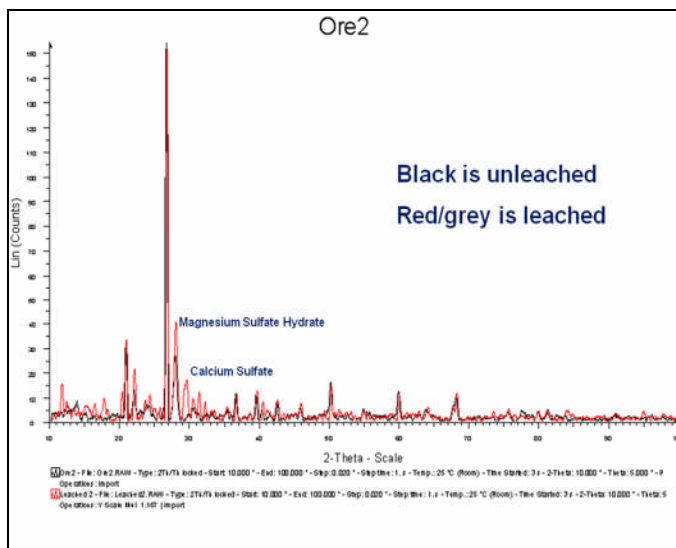
Figure 10. X-Ray Diffraction data for unleached (black) and leached (red in color or grey in black and white) ore particles illustrating sulfate precipitates in leached ore relative to unleached ore.

CONCLUSIONS

Results from this study show the effect of specific acid consuming minerals on acid consumption as a function of solution pH. The information in this paper also describes different techniques that can be used to quantify acid consumption of minerals and mineral blends. Results in this paper also show the relationship between solution pH and copper recovery for one ore sample. This study provides useful information about the relationship between pH, acid consumption, and copper recovery associated with sulfuric acid leaching of copper from oxide ore.

ACKNOWLEDGEMENTS

REFERENCES

Baum, W. 1999. The use of a mineralogical data base for production forecasting and troubleshooting in copper leach

operations, Copper 99, Volume IV, 394. Littleton, CO: SME.

Gonzales, I. and Torres, N. 1995. Southern peru Copper Corporation – Toquepala/Cuajone leach project, Copper

99, Volume IV, 807. Montreal, CA: CIM.

Kelley, R. J. and Zirate, G. 1995. Heap leaching of copper oxide ores – scale-up between laboratory and pilot-plant

results, Copper 99, Volume IV, 743. Montreal, CA: CIM.

Jansen, M. and Taylor, A. 2003. Overview of gangue mineralogy issues in oxide copper heap leaching,

http://www.altamet.com.au/Technical%20Papers%20and%20Articles/ALTA%20Copper/Overview%20of%20Gangue%20Mineralogy.pdf, Accessed October 16, 2009.