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INFLUENCE OF PH AND REDOX CONDITIONS ON COPPER LEACHING

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ABSTRACT
Leaching behavior of metals from a mineral processing waste at varying pH and redox conditions was studied. Effect of combinations of pH and Eh on leaching of copper is described. Leaching of copper was found to be dependent on both pH and Eh. Higher concentrations of Cu were seen leaching at lower pH values than at higher. At lower pH values variation in copper leaching with changing redox conditions was minimal. Changing redox through aeration promoted leaching at pH values of 11 and 7 probably, due to interactions of Cu with carbonate and bicarbonate ions. Values in the range of 71-76 percent of copper, originally present in the waste, were recovered in the leachant at a pH of 3. Majority of leaching was found to occur within a short period of time indicating high initial rates of leaching/dissolution of copper in the waste. These experiments highlight the importance of use of different pH-Eh conditions in studying the leaching behavior of different metals.

INTRODUCTION
The Toxicity Characteristic Leaching Procedure (TCLP) was developed to predict leaching potential of hazardous waste and its impact on surface and groundwater. The test was developed to study leachate concentrations of hazardous materials, under a mismanagement scenario, when they are co disposed with municipal waste. The test uses leaching of waste at either of two acidic pH values *i.e.*, 2.8 and 5.0. While low pH

leachant can extract many metals, some metals soluble at higher pH values are either underestimated or totally unaccounted for. The method also has limitations for application to different waste matrices. Since certain oxyanion concentrations are underestimated by the use of TCLP, leaching studies were conducted to determine the effect of different processes and leachants on the leaching potential of mineral and organic wastes. The final goal of study is to propose alternate methods applicable for a variety of waste matrices.

It is widely recognized that solubility and leaching of metals is a function of pH, redox and complexation. Leaching behavior of municipal waste, stabilized waste and construction material has been studied by many researchers (Van der Sloot *et al*., 1996). While pH is controlled in many leaching studies (Fallman and Aurel, 1996, Sanchez et al 2003), effect of combinations of pH and Eh on leaching potential has not received a great deal of attention. The current study was conducted to study the effect of combinations of pH and Eh on the leaching behavior of a mineral processing waste.

MATERIALS AND METHODS

Waste used in the study originated from a copper mine in Yerington, NV and contained high concentrations of several metals including copper and arsenic. Redox conditions were controlled by bubbling nitrogen, air, or oxygen, and pH adjustments were achieved by auto addition of NaOH and HNO_3. Additions of the acid and base were controlled by the pH sensing and controlling unit. MilliQ water was used as the leachant. A liquid/solid ratio of 20 (50g in a liter) was used for all leaching studies. The reactor was run for 48 hrs with samples being taken at various time intervals. The samples were preserved for metal analyses. Analyses of metals were carried out using an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Appropriate SW-846 methods were used for the different metals.

RESULTS AND DISCUSSION

Figures 1, 2 and 3 show the leaching of copper in the reactor at three different pH levels combined with varying oxidizing/reducing conditions. Data shows that leaching of copper is a function of both pH and Eh. A maximum of 76 percent of copper present in the waste was leached within 48 hrs at pH 3. Lower pH values favored the recovery of copper. Concentrations of copper recovered were controlled more by pH than by the redox conditions prevailing within the system at this pH. While oxyanions are not recovered at low pH using the TCLP procedure, metals such as copper can be effectively extracted. At higher pH values, especially at pH 11 changing the redox through aeration showed an increase in the amount of copper leached. This might be due to complexation of Cu with carbonate and bicarbonate ions. Differing interactions of copper with carbonation and carbonate ions on copper leaching from municipal solid waste incinerator bottom ash (Meima *et al*., 2002; Gau and Jeng 1998). While carbonation through aeration was found to decrease leaching of Cu due to a decrease in pH and adsorption to neoformed aluminum compounds (Meima *et al*., 2002), Cu extraction was enhanced with additions of carbonate and bicarbonate ions (Gau and Jeng, 1998). High initial leaching of copper at higher pH values followed by a steep drop

is probably due to dissolution of Cu during pH equilibration early in the run followed by, reabsorption or complexation reactions following a rise in the pH.

CONCLUSIONS

Leaching of copper was influenced by both pH and Eh within the system studied. Approximately 71- 76 percent of available copper was extracted at a pH of 3. Eh effect was more noticeable at higher pH values. Aeration increased copper leaching at pH 11 probably due to interactions of copper with carbonate ions. The TCLP procedure will function well in extracting copper in wastes since leaching of copper is a function of low pH. Leaching from a mine waste however, will be a function of both pH and Eh and interactions such as complexation, dissolution and reabsorption.

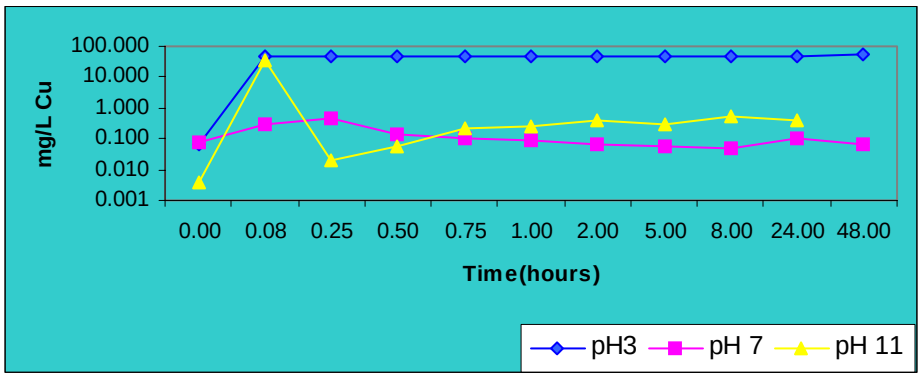

Figure 1. Leaching of copper under reduced (nitrogen bubbling) conditions.

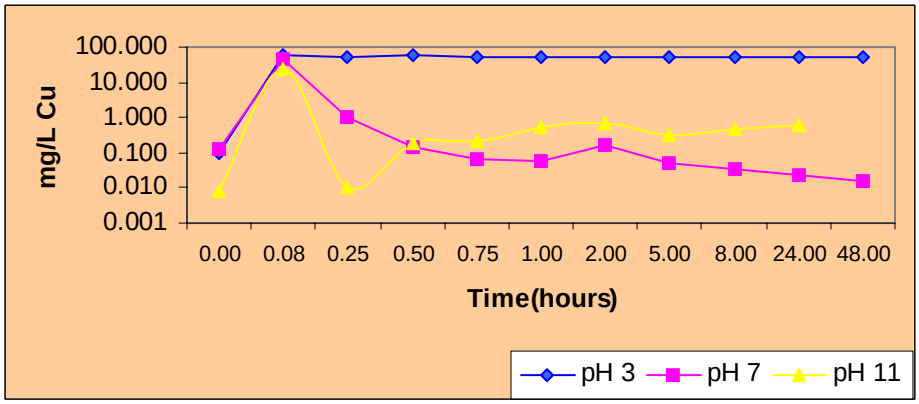

Figure 2. Leaching of copper under oxygenated (air/aerated) conditions.

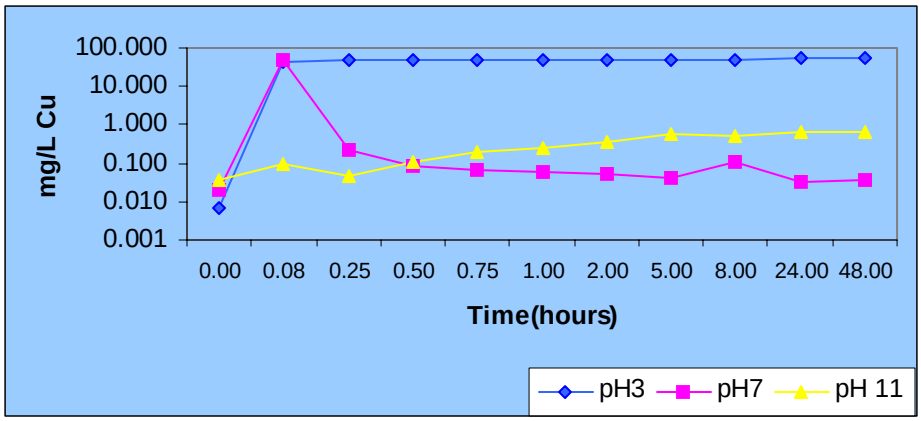

Figure 3. Leaching of copper under oxygenating (oxygen bubbling) conditions.

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