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Electrochemical Recovery of Metals in Mining Influenced Water: State of the Art

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Abstract The need for treatment of dilute metal contaminated water as a residual from mining and mineral processing facilities is ubiquitous. Electrochemical technologies have the potential to provide selective and measurable recovery of base metals from dilute mining influenced water. However, the technology is currently not widely used in the treatment of mining influenced water (MIW). The principles and a review of the application of cementation and electrowinning to mining influenced water for metal recovery is presented. Copper recovery under acidic conditions was the only economically recovered metal from dilute mining influenced water.
Keywords metal recovery, electrochemical, cementation, electrolysis, electrowinning

Introduction

Mining influenced water (MIW) may negatively affect the environment because of its acidity as well as metals concentrations. Since its introduction in 1859, the standard treatment process for metal removal from mining influenced water is lime or limestone precipitation (Schönaich-Carolath in Tarnowitz 1860, Wolkersdorfer 2008). In lime precipitation, all the metals are removed together as oxyhydroxides or co-precipitate. Consequently, the sludge formed is a mixture of metals that is not amenable to economic metal recovery, as economic metal recovery requires the creation of metal purity and forms need by the secondary source processing facilities.

Electrochemical deposition of metals is widely used in metallurgical processing and treatment of high metal waste streams (e.g. electroplating waste) to recover a high purity metallic form (Wendt et al. 2012). The process takes advantage of the electropotential differences between a metal targeted for deposition on a cathode and the anodic material used. Target metals with electropotential of sufficient difference allows for selective metal recovery. Electrochemical deposition can be accomplished by taking advantage of natural electropotential differences between cathodic and anodic materials (cementation) or by applying a current to the anodic material (electrowinning; fig. 1). Technology selection depends on what other metals are present in the water and the electropotential relative to the target metal.

Cementation is essentially the replacement of one metal by another on a solid material. This process relies on the natural thermodynamic potential difference between the two metals. In this process, the cemented metal (e.g. copper) changes from the ionic state to the zero valent metallic state, whilst the cementing metal (e.g. iron) changes from a zero valent metallic state to the ionic form. Ultimately, the cementation process proceeds when the cementing metal has a more negative electrochemical potential than the cemented metal. Thus, copper cementation with iron results in the deposition of copper and a concomitant release of iron into solution. As the build up of the copper reduces the rate of deposition, a periodic replacement of the iron metal is required to maintain effective removal rates.

Electrowinning is the deposition of a metal from solution due to an applied electrical potential. The dissolved metals migrate toward the cathode, are reduced and deposit on the cathode. In general, the anode composition (effectively inert) is selected to limit its oxidation and thus promote the oxidation of water at the anode. Electropotential for the hydrolysis of water to oxygen and hydrogen ion is a function of pH. Thus, the pH of the solution is an important factor in the rate and efficiency of metal deposition as well as the specific characteristics of the target metal, the cathode and the anode.

Electrochemical recovery processes have been applied primarily to high metal concentration solutions (>> 1000 mg/L) at low pH (< 1) in waste streams where competitive metals tend to be at much lower concentrations than the target metal (e.g. electroplating waste). Plumlee (1999) summarized the base metals (Cd, Co, Cu, Ni, Pb and Zn) concentration of mine drainage from a broad range of specific mineral deposits as a function of pH. In the pH range of 1 to 7, the summed concentration of base metals ranged from 10 mg/L to a few 1000 mg/L. Information available on electrochemical processes is not for the typical conditions present for a large range of MIW containing base metals of potential value. The objective of this paper is to assess why electrochemical processes remain underemployed for dilute MIW treatment and to identify potential options to facilitate utilization of electrochemical processes for metal recovery from MIW.

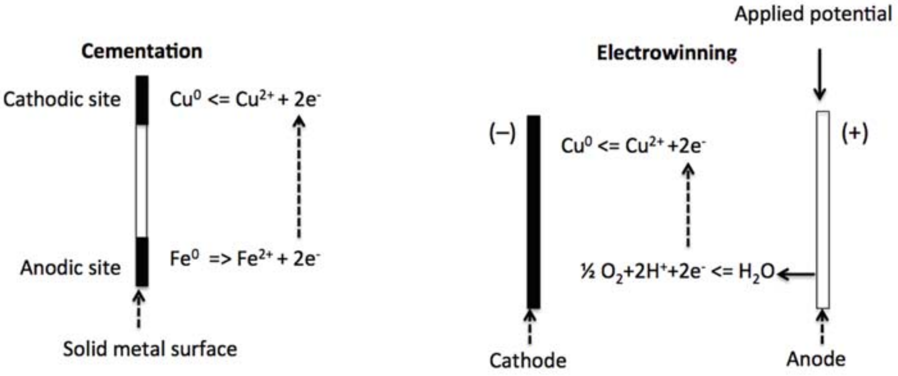

Fig. 1 *Schematic of electron transfer that occurs in cementation and electrowinning.*

The available literature on the use of electrochemical methods for recovery of metal value from MIW was limited in searchable databases of journal articles and conference proceedings. Copper was the only metal consistently targeted for recovery in dilute MIW treatment. Most of the studies are laboratory based, with only a few examining actual MIW. At the time of writing this paper, one case study on the application of cementation to the economic recovery of copper from pit lake water was found. Similarly, only one case study was found on the application of electrowinning to the recovery of copper from pit lake water.

The cementation case study was the treatment of MIW from the Berkeley Mine Pit, Butte, Montana. Major base metals in a grab sample from the Berkeley Pit MIW were Cu ≈ 200 mg/L and Zn ≈ 500 mg/L, Cd, Ni and Pb were < 2 mg/L, in addition the iron was ≈ 300 mg/L and the pH was 2.9 (Hatfield et al. 1996, Huang and Liu 1995). Montana Resource, a mining company located in Butte Montana, is currently operating a copper recovery system using the Berkeley Pit water. Recovery operations were started in 1998, suspended in 2000, and restarted in 2004. Based on available information, the company plans to operate the copper recovery system for about 20 years in total (Gammons and Tucci 2012). In the Berkeley Pit, the method consists of pumping water from deep in the Pit and passing the MIW through scrap steel cans. In this step, the copper cements onto the steel cans and a concomitant amount of iron is released into solution. Ultimately, the recovered product contains 70% to 80% copper that is processed further to create high purity metallic copper. The iron-enriched water contains about 30 mg/L of residual copper and flows by gravity to the water surface of the Berkeley Pit. It should be mentioned, that the situation at the Berkeley Pit is unique as treatment of the MIW to remove other metal contaminants of concern is not required for

Montana Resource at this time. Treatment of a portion of the Berkeley pit water will be required in the future to limit the surface water level to an agreed upon maximum value.

The electrowinning case study found was on the comparison of electrodes for treatment of the water from the closed copper mine Cerovo RTB Bor, Serbia (Gorgievski et al. 2009). In the Cerovo Open Pit, the major base metals from the MIW were Cu ≈ 1000–1500 mg/L and Zn > 20 mg/L, Cd, Ni and Pb were < 1 mg/L, iron less than 10 mg/L and the pH was 3.5. The high concentration of iron in many MIWs is a deterrent to the application of electrowinning for metal recovery. Copper removal was examined as a function of type of cathode, applied current and reaction time and the deposited copper purity was higher than 95% with minor amount of iron. The lowest levels of residual copper in solution (100 to 300 mg/L) were observed for the copper cathodes after 200 to 350 minutes of reaction time. They also observed that the porous copper cathodes were better than the carbon felt cathode used in terms of current efficiency and specific energy consumed. The electrowinning process was never implemented for remediation of the Cerovo MIW. At the time the electrowinning study was done, the Cerovo mine had been closed since 2002 and remediation plans were being evaluated. In 2012 the Cerovo mine reopened for operations and plans to upgrade the processing facilities and expand the pit are underway.

Feasibility considerations that limit the use of electrochemical metal recovery for dilute MIW include market, technical, economic and administrative (Smith et al. 2013). In both of the case studies examined, the recovered product receivers each had responsibilities for the mine water cleanup and were former operators of the respective mine sites. The responsibility for the mine water quality incentivized the former operators to identify and develop a process flow scheme that produced an economically viable product. The former mine operators were not required to treat all the MIW to regulated discharge levels, which significantly improved the economics. In addition, the operators owned facilities that could take the recovered product and purify to a saleable form. Potential regulatory and liability issues were mitigated by the relationship that the two former mine operators had with the MIW source.

Based on the currently available technology, the use of electrochemical methods for dilute MIW treatment schemes will require pre- and or post-treatment processes. Higher metal concentrations (>1 g/L) than typically observed in dilute MIW should improve the recovery efficiency and economics of electrochemical methods. Thus, processes that produce a concentrated stream in conjunction with a more dilute stream are an option. The concentrated stream would be only a portion of the original water flow. Thus, a higher concentration of metals would improve the electrochemical process effectiveness and the lower volume of water would require a smaller reactor volume. Two methods that have been tested on MIW to produce concentrated metal streams are membranes and ion exchange.

Membrane processes used for metal removal from MIW include reverse-osmosis and nanofiltration (Rieger et al. 2009). Both processes will produce a concentrated side stream containing the majority of the metal ions as shown in fig. 2 for nanofiltration. However, nanofitration can produce higher fluxes at a lower pressure and thus has lower capital and operating costs. Nanofiltration of acidic MIW (pH 2.6) was able to produce a concentrate stream of 30% of the influent flow and three times the initial concentration. Thus, copper at an initial concentration of 590 mg/L was increased to 1920 mg/L in the concentrate. The permeate flow was 70% of the influent flow and the residual copper was 15 mg/L (Mullet et al. 2014). The copper concentration of almost 2 g/L could be targeted by cementation or electrowinning for recovery.

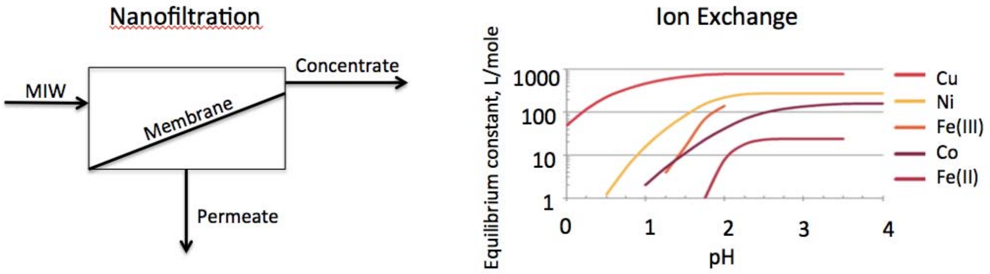

Fig. 2 *Nanofiltration flow diagram and relative equilibrium constants for copper selective ion exchange resin as a function of pH. Ion exchange graph is from Dow M-4195 product information.*

The ion exchange process recovers metal ions from a dilute stream and produces a concentrated stream when the resin is regenerated (Wilmoth et al. 1977). Resin manufacturers are continually improving the selectively of ion exchange resins for specific metals. A resin with a high selectivity for copper is shown in fig. 2. This ion exchange resin was used to selectively extract copper from a solution that contained 85 mg/L Cu, 100 mg/L Ni, 47.5 mg/L Co, 40 mg/L Pb, 6.0 g/L Fe, 47.5 g/L Mn at a pH of 0 (Diniz et al. 2005). After 46 bed volumes, 99.9% of the copper was removed. The copper occupied half the sites even though copper was only 0.1 mole percent of metals in the influent water. In addition, copper could be selectively eluted if a first elution step with sulfuric acid was used to remove the majority of other metals. A second elution with ammonia hydroxide produced a concentrate with 99.2 % copper and the other 0.2 % contained Ni, Co and Pb on a molar basis. Effluent copper from the ion exchange column was less than 1 mg/L.

Conclusions

Copper is the most viable target for electrochemical metal recovery from MIW because of the high purity of metallic Cu formed by both cementation and electrowinning. Copper recovery from dilute MIW by cementation with iron can produce a produce amenable to economic smelting. Copper recovery by cementation can be achieved without an input of electropotential. The concomitant release of anodic iron into the solution will increase iron load to subsequent MIW treatment. Electrowinning requires an input of electropotential but is able to direct electrons to the oxidation of water components, thus, eliminating the concomitant release of anodic metal. Electrochemical methods offer advantage production of an economically recoverable product with no chemical requirements and relatively simple operation and maintenance.

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