

Challenges in Recovering Resources from Acid Mine Drainage

D. Kirk Nordstrom¹, Robert J. Howell², Kate M. Campbell¹, Charles N. Alpers³

¹U.S. Geological Survey, Boulder, CO, 80303 USA, dkn@usgs.gov, kcampbell@usgs.gov

²SRK Consulting, CF102HH, Cardiff, Wales, UK, rhowell@srk.co.uk

³U.S. Geological Survey, Sacramento, CA, 95819 USA, cnalpers@usgs.gov

Abstract Metal recovery from mine waters and effluents is not a new approach but one that has occurred largely opportunistically over the last four millennia. Due to the need for low-cost resources and increasingly stringent environmental conditions, mine waters are being considered in a fresh light with a designed, deliberate approach to resource recovery often as part of a larger water treatment evaluation. Mine water chemistry is highly dependent on many factors including geology, ore deposit composition and mineralogy, mining methods, climate, site hydrology, and others. Mine waters are typically Ca-Mg-SO₄±Al±Fe with a broad range in pH and metal content. The main issue in recovering components of these waters having potential economic value, such as base metals or rare earth elements, is the separation of these from more reactive metals such as Fe and Al.

Broad categories of methods for separating and extracting substances from acidic mine drainage are chemical and biological. Chemical methods include solution, physicochemical, and electrochemical technologies. Advances in membrane techniques such as reverse osmosis have been substantial and the technique is both physical and chemical. Biological methods may be further divided into microbiological and macrobiological, but only the former is considered here as a recovery method, as the latter is typically used as a passive form of water treatment.

Key words mine wastes, acid mine drainage, recoverable resources

Introduction

The demand for copper, during the Bronze age for tools and weapons and then later for fiscal instruments, was a driving force in the early exploitation of copper (Markoe, 2000; López, 2015). Such demand led to the application of copper cementation in the processing of mine waters in Spain and Sardinia as early as 3000 BC by Phoenicians. Copper cementation was adopted later by Roman miners and subsequently spread to become common in the recovery of copper from mine waters and acid leaching until the advent of solvent extraction (Audsley et al., 1961; Lewis and Jones, 1970; Jones and Bird, 1972; Markoe, 2000; Howell et al., 2013; Ávila, 2015; López, 2015).

The combination of high mining costs, increasingly stringent environmental obligations, and exhaustion of historically important metal sources has led to re-assessment of alternative sources of metals (Hsu and Harrison, 1994; Vegliò et al., 2003; Howell, 2004a; Gaikwad et al., 2010). During the last two decades, interest has increased for recovering marketable products from acid mine drainage (AMD), raffinates, and other forms of solid and liquid wastes from mining and mineral processing activities. Lottermoser (2010) cites more than a dozen examples of the reuse or recycling of mine wastes. Macaskie et al. (2009) mention the potential for environmental bionanotechnology for AMD in an article entitled "Today's wastes, tomorrow's materials for environmental protection." Michalková et al. (2013) dis-

cuss the production of ferrites and hematite from AMD. Tamaura et al. (1991) demonstrated the production of ferrites from AMD more than 25 years ago. A Japanese group demonstrated the feasibility of combining sulfid(iz)ation with neutralization for selective extraction of Cu, Zn, and Fe from AMD (Wang et al., 2013).

The two main components of AMD, Fe and Al, are observed to be removed naturally in downstream drainage during oxidation and increase in pH (Nordstrom, 2011). An engineering study demonstrated separation resulting in high purity of Fe and Al from coal mine drainage (Wei et al., 2005) including magnetic nanoparticles (Wei and Viadero, 2007). The main challenge is not so much finding or studying possible technologies, but rather adopting the best “stream” of technologies for a particular site given the composition of the water, the target recovery product(s), the cost and ease of transportation, and the distance to a potential buyer.

This paper is a preliminary review of the numerous types of chemical, electrochemical, and microbiological methods that have been, or could be, investigated to selectively extract potentially marketable products from AMD. The review describes some of the inherent advantages, limitations, and challenges associated with various resource recovery methods.

General types of separation methods

Methods for separating and extracting substances from AMD can be classified in two broad categories: chemical and biological. Chemical methods include solution, physicochemical, and electrochemical technologies. Advances in membrane techniques such as reverse osmosis have been substantial and the technique is both physical and chemical. Biological methods may be further divided into microbiological and macrobiological, but the macrobiological (mostly phytoremediation and wetlands) will not be considered here because these are predominantly passive remediation techniques, not generally used as recovery methods. Chemical methods, along with evaporation, represent some of the more attractive options for resource recovery from acid mine waters.

Chemical methods can be subdivided into

- Oxidative precipitation (primarily to precipitate hydrous ferric oxides)
- Metal reduction methods such as Cu cementation
- Solvent extraction (SX)
- Sulfide precipitation (SP)

Physicochemical methods include

- Reverse osmosis (RO)
- Evaporation
- Ion exchange (IX)

Electrochemical methods include

- Electrowinning/electroplating
- Electrocoagulation

- Hydrolysis and H₂ production
- Electrodialysis
- Electrokinetics

Microbiological methods include

- Sulfate reduction
- Fe reduction
- Metal reduction (in addition to Fe and Cu)
- H₂ production

Combinations of these methods, for example

- Electrochemical cells with semi-permeable membrane
- Bioelectrochemical systems such as microbial fuel cells or microbial electrolysis cells for metal reduction and H₂ production
- Electrowinning with solvent extraction or ion exchange
- Solvent extraction with ion exchange
- Sulfide precipitation with alkali neutralization

Potentially recoverable products

In addition to the obvious metal products that may be recovered such as Cu, Pb, Zn, and Cd, both the high concentrations of SO₄²⁻ and the resulting “clean or useable” water itself should be considered as potential products. Many of today’s mines are located in arid regions where water is in high demand and SO₄²⁻ can contaminate water supplies. If most of the metal contaminants and sulfate are removed, then the only remaining concern typically would be for elevated concentrations of salt components such as sodium, chloride, fluoride, or highly conservative constituents such as nitrate.

AMD chemistry

Decisions on evaluating these methods for practical applications require an understanding of the types of AMD that might be encountered. Although it would be impossible to adequately represent all types of mine water compositions, a few generalizations can be made. Water compositions for AMD can be associated with coal mines, non-radioactive metal mines (hydrothermal deposits of Cu, Pb, Zn, Cd, Au, Ag, As, Sb, Co, and Ni), and radioactive mines (deposits of U, V, Ra, and Th, which will not be considered here).

Coal mines do not typically contain dissolved concentrations of “potentially economic” metals such as Cu, Pb, Zn, Cd, Ag, and Au high enough to consider for extraction. When they produce acid drainage, concentrations of Fe and Al predominate with occasional contamination from As, Co, Mn, Ni, and Se (Cravotta, 2008).

Mine (metal) water chemistry is highly dependent on many factors including geology, ore deposit composition and mineralogy, mining methods, climate and many others. Mine waters are typically classified as Ca-Mg-SO₄±Al±Fe with a broad range in pH and metal content. In many cases, these waters contain metals that approach similar grades to those

of metallurgical operations (Plumlee, 1995). As an example, the chemistry of mine waters from several copper mines of different geological settings were compared to an acid leach circuit and concentrations of copper in the mine waters approached that of a pregnant leach solution.

Table 1: Typical composition of mine waters from common deposit types and SXEW process waters. Metal concentrations in mg/L, pH in SIU (Bowell et al., 2013)

Parameter	Volcanogenic Massive Sulfide	High Sulfidation Epithermal	Manto deposit	Porphyry	Copper SXEW (porphyry)
pH	<1–6	2–4	<2–6	2–8	<2
Cu	<0.1–6,800	<0.01–5,400	<0.01–790	<0.01–2,100	~6,000
Zn	<0.1–>10,000	<0.1–3,900	<0.01–4,300	<0.01–80	<500
Fe	10–>10,000	<1–28,000	<1–5,500	<0.01–1,700	~2,000
Pb	<1–165	<0.1–12	<1–210	<6	<100
Ag	<1–630	<1–90	<1–580	<2	~5

Acid drainage from hydrothermal deposits of “potentially economic” metals often contain high concentrations of these metals grossly correlating with lower pH, that is, the lower the pH, the higher the acidity and the higher the concentration of metals (Table 1). These AMD waters are among the most difficult to address for either remediation or resource recovery because acidities can be extremely high, with pH values as low as -3.6 (Nordstrom and Alpers, 1999). These high concentrations of Fe and Al can interfere with the efficient extraction of other metals due to formation of hydroxides having high attenuation capacity by almost any extraction process.

The pH of AMD is most commonly 2.2 – 3.5, because of the buffering system in aqueous solutions derived from pyrite oxidation (Nordstrom and Campbell, 2014). Lower pH values do occur in many areas but they are either not so common or not very many measurements have been taken to document them. Higher pH values than 4 are not usually a major water-quality problem because at this pH and higher most of the Fe has oxidized, precipitated as hydrous ferric oxides (such as schwertmannite, ferrihydrite, or goethite), and taken many contaminants out of solution by sorption or co-precipitation. At pH values of 4 – 5.5, Al precipitates and removes additional metals. Some metals that typically are not removed by sorption or co-precipitation below pH 7 include Zn, Cd, Co, and Ni.

Typically, metal concentrations for AMD from precious metal mines will occur in decreasing concentrations of Fe, Al > Zn, Cu > Cd > Pb. Hence, Fe and Al figure prominently in the resource recovery scheme. The maximum concentrations found in portal effluent water at Iron Mountain, CA (pH ~1) are as follows: Fe reaches 19,000 mg/L, Zn reaches 2,500 mg/L, Al reaches 800 mg/L, and Cu reaches 500 mg/L. At Iron Mountain an estimated \$5.85 million in Cu and \$14 million in Fe discharged from 1994–2002 and has been deposited as

sludge in the open pit, the disposal site for lime-neutralized AMD (D.K. Nordstrom, USGS, unpublished data). Furthermore, the mine is estimated to continue discharging concentrated AMD for approximately 3,000 years based on current weathering rates and the known reserves of pyrite and other sulfides remaining underground (Nordstrom and Alpers, 1999).

Methods of separating or controlling Fe concentrations

Because Fe can occur in the dissolved state in either a reduced ferrous iron form (Fe(II)), or an oxidized ferric iron form (Fe(III)), there is an opportunity to control the redox species to separate or control Fe concentrations. Fe(II) is highly soluble, whereas Fe(III) is highly insoluble above pH 3 and is less soluble than Fe(II) even at low pH values. If the dissolved Fe is kept reduced as Fe(II) it could be kept in solution until other metals are separated and then it could be oxidized by microbes, air, or hydrogen peroxide to precipitate it as Fe(III). Alternatively, if most of the metals and other contaminants are removed, the result would be a ferrous-sulfate solution that could be evaporated. Ammonium could be added to increase the stability of the final product, for which a market already exists.

Precipitation of dissolved Fe(III) at pH values of 2 – 4 will typically produce schwertmannite, microcrystalline goethite, and/or ferrihydrite. Lower pH values may produce jarosite group minerals, which are not a desirable product because of the potential for containing high concentrations of contaminants such as Pb and As (Dutrizac and Jambor, 2000). Schwertmannite and goethite will also sorb these and other contaminants. A better product because of its purity would be hematite. However, hematite requires higher temperatures (generally > 100°C).

Metal recovery

Electrowinning for Cu is generally not done on AMD because concentrations of nearly 1,000 mg/L are necessary. One historical method that has worked well for Cu removal is Cu cementation. This method has a long tradition, as discussed above. At Parys Mountain in North Wales the process was applied throughout the nineteenth and early twentieth century in the production of Cu from mine water (Audsley et al., 1961). In these cells, roasted goethite-rich boulders (pig-iron ore) were placed and then diverted copper-rich mine water flowed through the pits to precipitate copper by the reaction:



However, this reaction does increase the ratio Fe(II)/Fe(III) in solution until hydrolysis removes the hydroxide. At Iron Mountain, CA, Cu cementation was used for many decades and observations show that influent Cu concentrations of 100 – 300 mg/L were reduced by 80 to 95% (Alpers et al., 2003). This efficiency may have been a function of pH, which was typically around 1 (Nordstrom and Alpers, 1999).

Biological methods of metal leaching as well as metal recovery through sulfur reduction and formation of sulfides has been evaluated (Peters and Ku, 1985; Barrett et al., 1993; Hsu and Harrison, 1995; Nodwell and Kratochvil, 2012). Reduction of SO_4 by microbial bioreactors

removes metals by sulfide precipitation. Commercially, native sulfur is used as a feedstock for the process (Nodwell and Kratochvil, 2012).

In recent years, a number of companies such as Paques in the Netherlands and BioteQ in North America have developed mine water treatment plants that reduce metal loadings by reacting sulfide gas with the mine water to form metal sulfides. The basic principle behind this process is the production of hydrogen sulfide (H_2S) from elemental sulfur via the action of anaerobic bacteria. The H_2S is reacted with a solution containing target metals and the metals precipitate from solution as insoluble sulfides. Dependent upon the solution chemistry and the target metals, pH adjustment of the solution may be required. In the case of copper, CuS will form over a wide pH range so typically no pH adjustment is required for this, although modification maybe required to remove competing ions.

Sulfide precipitation plants have been installed in several places around the world including the BioteQ plants at the Caribou and Raglan mines in Canada, Mount Wellington in Colorado, and the Bisbee mine in Arizona (Lopez et al., 2009; Nodwell and Kratochvil, 2012). In these locations, the produced metal-sulfide precipitate can be processed by conventional smelting operations; metals that would otherwise be lost are recovered, and the operations typically generate positive cash flows. However, the economics are adversely affected by the presence of Fe(II) that will also precipitate as a metal sulfide and consume sulfide, increasing costs (both capital and operational). These costs may be offset if the Fe(II) is oxidized to Fe(III), as ferric hydroxide precipitates may prove to be a commodity that can be reused in cements and construction materials. In microbial systems, additional reagents (nutrients, C source) and an optimal temperature range, typically within 20 – 35°C for sulfur reducers (Johnson and Hallberg, 2007).

At the Bisbee project, southern Arizona, the BioteQ plant had a design capacity of 10,900 m³/day with a solution composition of: Cu = 350 mg/L; Fe(III) = 550 mg/L. The project capital costs were about US \$2.5 million and operating costs were US\$0.20/lb Cu recovered, plus US\$0.18/lb transport/smelting costs (based on 2008 information). Costs increased later in the project as Cu grades declined (E. Wieland, BioteQ, written commun., 2017). Metal recovery from mine waters represents a potential source of revenue to offset water-treatment costs and in some places may even represent an economic gain in its own right.

The clean separation of metals such as Cu, Zn, and Cd by sulfide precipitation is dependent upon careful control of pH as it is adjusted upwards. Once the pH has reached 4 to 5, Al (\pm Si) will precipitate as a fairly pure hydroxysulfate (such as basaluminite). Rare earth elements (REE), if present, will precipitate with Al. Therefore, REE should be extracted either through ion exchange or solvent extraction to separate from the Al (before or after the Al precipitation). A similar approach is applied in the processing of clay-rich ores (Jordens et al., 2013). The Fe and Al also have potential for producing sulfate chemicals that are common coagulants in water treatment such as the ettringite process (Reinsel, 1999; Bowell, 2004b). The more soluble metals like Zn, Cd, Ni, and Co could be concentrated and sepa-

rated through ion exchange or solvent extraction processes (Veglió et al., 2003; Gaikwad et al., 2010). Ion exchange is proven technology for removing the remaining Ca and SO₄. Other components like Li can similarly be recovered (Bowell et al., 2013).

Summary

The recovery of metals from mine waters and effluents is not new, but over time, as recovery has gone from opportunistic to designed, the application of process technology has improved, making this approach a potentially viable option at more mine sites. The closure and abandonment of mining areas is rarely caused by complete consumption of a resource but rather is typically associated with diminishing financial returns based on metal values, or social, political, and environmental restrictions that lead to an uneconomic scenario for a resource unit. With regard to legacy mine sites, such as Iron Mountain, California, the removal and concentration of metals is a logical step in improving environmental water quality and in producing saleable products that can assist in offsetting water treatment costs. Each mine site requires a site-specific evaluation of the hydrogeochemistry and hydrology to determine the potential for recovering metals and to identify suitable technologies.

A caveat exists to applying these methods: even if the “resource potential” can be proven and the technology is shown to recover economic amounts of metal, there may still be little incentive to “re-mine” many legacy mining districts. New mining ventures may be held responsible for all past mining legacy issues, as well as any new disturbance, so a site-specific analysis is prudent to assess potential legal action from property owners or bankruptcy trustees who could lay claim to any recovered value.

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