Assessment of mine waters suitable for metal recovery

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Mine 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 Ca-Mg-SO₄ \pm Al \pm Fe \pm HCO₃ with a broad range in pH and metal content. In many cases these waters contain metals that exceed trigger limits that indicate a potential to impact human health or cause an impact to flora or fauna.

Evaluation on mine waters in southern Spain, Chile and North Wales has identified that mine impacted waters hosted significant "ore-grade" concentrations of several metals with often quite noticeable discolouration of surface water. The options that exist for metal recovery include

- Metal precipitation using biogenic produced hydrogen sulfide such as in the Paques or BioteQ systems;
- Copper cementation using copper reduction on iron metal;
- Direct electrowinning of from ARD;
- Ion exchange recovery directly from ARD
- Direct solvent extraction and electrowinning. Metals areextracted using conventional hydroxyoxime extractants, stripped using a spent electrolyte solution and then electrowon in conventional cells.
- Solvent impregnate recovery using the Umatilla process followed by stripping with spent electrolyte and electrowinning to produce copper metal.
- Hybrid of ion exchange solvent exchange that involves two stage recovery involving chelation using ion
 exchange resin and conventional solvent extraction and electrowinning to complete metal, principally
 copper recovery.

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Table 1: Typical Composition of some mine waters and process waters. Parameter concentrations in mg/L except pH (various sources)

Parameter	Volcanogenic Massive Sulfide	High Sulfidation Epithermal	Mantos deposit	Porphyry	Copper SXEW (porphyry)
pН	<1-6	2-4	<2-6	2-8	<2
Cu	<0.1-6800	<0.01-5400	<0.01-790	<0.01-2100	~6000
Zn	<0.1->10000	<0.1-3900	<0.01-4300	<0.01-80	<500
Fe	10->10000	<1-28000	<1-5500	<0.01-1700	~2000
Pb	<1-165	<0.1-12	<1-210	<6	<100
Ag	<1-630	<1-90	<1-580	<2	~5

In a few cases such waters may host metal concentrations, particularly base metal concentrations, to levels that are similar to mineral process solutions (Table 1). Such ideas are by no means new, Phoenician miners in the Iberian peninsula, almost 3000 years ago, would build pits and load these with roasted goethite-rich boulders (pigiron ore) and then divert copper rich mine water through the pits to precipitate copper by the reaction:

 Cu^{2+} (in mine water) + Fe^{0} (scrap iron) = Fe^{2+} (in solution)+ Cu^{0} (metal)

Such processes were used throughout the following four millennium including places such as Parys Mountain in North Wales. Copper obtained in this fashion is fairly pure with the precipitate obtaining a purity of 90% and better.

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Mine water treatment options typically employed to mitigate environmental clean up tend to precipitate or remove metals as one or two products from which it is generally not economic to refine to recover the value. But options do exist for selective removal of certain metals, particularly copper, zinc, silver and uranium based on existing metallurgical recovery processes. The most commonly applied of these are copper cementation (as described above), electrowinning and biological reduction of sulphate or sulphur to produce a metal sulfide concentrate.

Solvent Extraction coupled with Electrowinning is the standard technique for copper cathode production from heap leach operations. Typically feed solutions for such a plant contain from 0.5-6 g/L Cu although a low tenor feed of 300 mg/L can achieve an extraction efficiency of 70%. However the solvent extraction is not without

difficulties and significant clay content in the copper loaded or pregnant solutions can reduce the SX process efficiency. The recovery of zinc through acid pressure leaching and electrolysis is also fairly standard and applied widely throughout the world

A benefit for mine water recovery from this process is that SX has been applied to a very wide range of acidic solutions; typical feed solutions have a pH of 1-2.

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 so as to form metal sulfides. The basic principles behind this process are the production of hydrogen sulfide (H_2S) from elemental sulfur via the action of anaerobic bacteria.

Sulfur + Bacteria_(anaerobic conditions) → sulfide

The sulfide is reacted with a solution containing target metals and the metals are precipitated from solution as the insoluble sulfide. Dependant upon the solution chemistry and the target metals, pH adjustment of the solution may be required. In the case of copper, the metal sulfide will form at a wide pH range so typically no pH adjustment is required.

Such plants have been installed in several places around the world including the BioteQ plants at the Caribou and Raglan mines in Canada and the Bisbee mine in Arizona. In these locations the metal sulfide precipitate produced can be processed by conventional smelting operations and metals that would be otherwise lost are recovered and the operations have proved to have positive cash flows. The economics are adversely affected by the presence of ferric. Ferric will also precipitate as a metal sulfide and so will consume sulfide increasing costs (both capital and operational). Additional reagents such as ethanol or acetic acid as well as nutrients are required. The bacteria require to be kept within an optimal temperature range typically 20-35°C.

At the Bisbee project in southern Arizona the BioteQ plant has a design capacity of 10,900m3/day with a solution composition of; Cu = 350mg/L; $Fe^{3+} = 550$ mg/L. The project capital costs are of the order of US\$2.5 million and operating costs are US\$0.20/lb Cu plus US\$0.18/lb transport/smelting costs.

In addition ferric hydroxide precipitates or sludges may also prove to be a commodity that can be reused in cements and construction materials.

Metal recovery from mine waters such as at the Bisbee plant, represents a potential source of revenue to offset water treatment costs and in some places may even represent an economic project in its own right. A caveat exists however, that even if the "ore potential" can be proven, and that the technology will recover economic amounts of metal there may still be little incentive to "re-mine" many old mining districts. New mining ventures may be held responsible for all past mining legacy as well as any new disturbance and the mere mention of metal value from these old districts could result in legal action from property owners or bankruptcy trustees who will lay claim to any recovered value.

This presentation presents a review of testwork and options for mine water treatment with a focus on the potential to recover metals from drainage. The "ideal" feed for metal recovery (principally copper and zinc) is from acid drainage with low ferric iron content, reasonably consistent feed flows and with a low turbidity