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A different kind of ore-identifying mine waters suitable for metal recovery

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Few geochemists have missed reading at least some of the plethora of environmental geochemistry data generated in the last few decades on mine water chemistry from operating and abandoned mines.

Mine water chemistry is highly dependent on many factors including geology (Figure 1), ore deposit composition and mineralogy, mining methods, climate and so on.

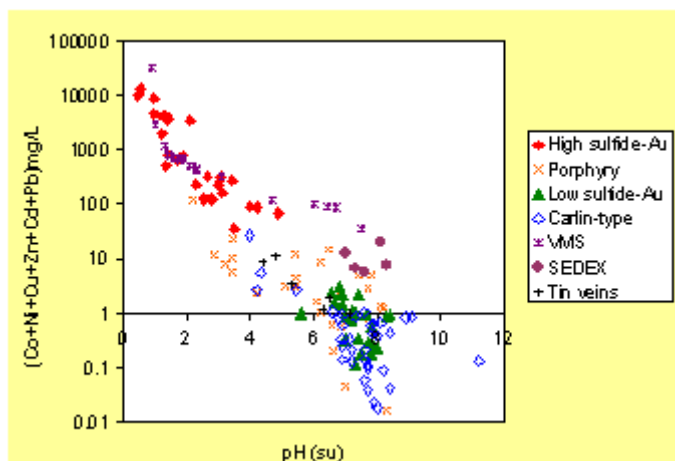
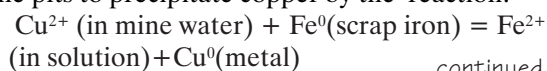


Figure 1: Ficklin plot of mine waters from different ore types showing contrasting base metal concentration dependent on ore deposit geology

Mine waters are typically $\text{Ca-Mg-SO}_4 \pm \text{Al} \pm \text{Fe} \pm \text{HCO}_3$ 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 (Table 1).

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). If sustainable could it be possible that these waters represent a different kind of ore?

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 (pig-iron ore) and then divert copper rich mine water through the pits to precipitate copper by the reaction:



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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)
pH	<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

Such processes were used throughout the following four millennia including places such as Parys Mountain in North Wales (Figure 2). Copper obtained in this fashion is fairly pure with the precipitate obtaining a purity of 90% and better.



Figure 2: Copper cementation pits from the nineteenth century, Parys Mountain, Anglesey, Wales.

As many ore bodies reach full maturity or are exhausted possibly the legacy of former mines could represent a new lease of life for these mining districts providing an “ore” source in perpetuity, truly “sustainable mining”!

But is that really value in such an exercise? An evaluation on mine waters in southern Spain identified that mine impacted waters hosted significant “ore-grade” concentrations of several metals with often quite noticeable discolouration of surface water (Figure 3).



Figure 3: Mine water discharge impacts, Rio Tinto, Southern Spain. Mine waters at this location typically contain 300-700 mg/L Cu; 800-2000 mg/L Zn; as well as measurable concentrations of other metals such as Pb, Cd, Ag, Be, Fe, Mn, Co and Ni.

The calculated value of gross metal product being released into the Rio Tinto river in southern Spain is estimated at being in excess of US\$12000 a day (based on November 2003 metal prices), primarily as copper and zinc but also a wide range of valuable trace components as well (such as Ag, Pb, Cd, Li, Be, Ga, Ge, Sn, Te, Tl, U and REE). However, the reality is there is a big difference between total metal value and that which can be economically recovered. So what options exist for metal recovery from mine waters? 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 operations such as Dos Amigos in Chile produce copper from a low tenor feed of 300 mg/L with 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

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Figure 4: Traditional zinc tankhouse where metal is recovered by electrolysis. KCM, Bulgaria.

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. The basic equipment layout for such an operation is shown in Figure 5.

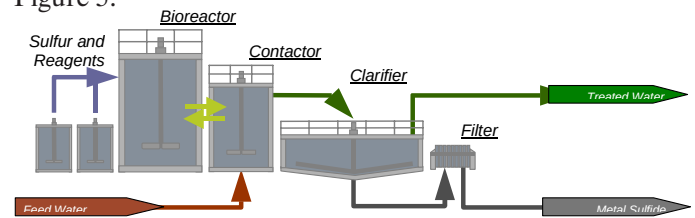


Figure 5 Typical plant layout for a sulfate reduction- metal precipitation plant.

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 (Figure 6). 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.



Figure 6: BioteQ plant, Bisbee mining district Arizona

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 10,900 m³/day with a solution composition of; Cu = 350mg/L; Fe³⁺ = 550mg/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.

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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.

However, in the current environment of high metal demand and exhaustion of historically important metal sources, different sources of metals will have to be found. The challenge for the exploration geochemistry community is to be able to identify such opportunities and be equipped to evaluate them.

