

An overview of the use of Ion Exchange to extract wealth from mine waters

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Abstract

This paper provides an overview of the potential for recovery of value from contaminated mine waters and waste streams. It discusses various metal ions commonly found in acid mine drainage and other mine waters (mainly Co, Ni, Zn, and U) and evaluates at what concentration they become attractive to investigate for recovery using ion-exchange technology. Waste streams are often treated to achieve compliance with environmental legislation before discharge, but recovery of valuable materials from acid discharge waters can result in economic benefits as well; in certain cases, the recovery of such metals can actually cover the cost of capital and operation and provide an additional revenue stream to the mine. The economics depend on the nature of the valuable metals, their concentrations, and volumes required for treatment.

Ion exchange is well established in mining and metallurgical processing as a primary purification technology, treating process streams in which the levels of valuable metals are relatively high. To recover these same metals from surface runoff, tailings, contaminated ground water or mine decant waters; they must be present at a certain level before it becomes worthwhile to fully investigate options for their recovery. We reviewed a number of valuable metals that are likely to be found in mine waters and, based on the capital and running costs, determined the capital payback period for varying contamination levels. Technical issues were discussed and their effect on the economics explored.

Using the model developed, it is possible to show early on in a feasibility assessment whether there is economic benefit to the processing of waste water of a given composition from a mining operation. The specific case studies that informed the model are discussed.

Key words: Mine water, ion exchange, metal recovery, modeling, economics

Introduction

Appropriateness of ion exchange

Ion exchange (IX) is a well-established technology in the hydrometallurgical field as both a competing and complementary technology to solvent extraction. The advantage of IX over other methods such as solvent extraction or even precipitation is that ion exchange can still be viable when feed concentrations have dipped below the economic threshold of the other technologies. It is interesting to note that in some cases the lower the total concentrations of metals in an aqueous stream, the more efficiently an IX resin can perform (Liberti, L. 1983).

The concentration at which a valuable metal is present in a feed water is the largest factor to consider with IX, but economy of scale, and global metal pricing must also be considered. Another aspect that must be taken into account when considering IX for any application is the competing ions in solution that may take up valuable capacity on the resin, such as iron, that will elute with the metal of value and lower the purity of the final product, and elements that may poison the resin, reducing the active sites available for exchange. These are all explored below with the aim of creating a basis for deliberation and initial economic viability for any potential value recovery from metal-containing mine or waste waters.

Composition of typical mine waters

Any given mine water can be broken down into the following constituents: value containing elements, hazardous elements, low value elements that will co-load, IX poisons, and elements of little concern with regards to the IX process. Generally we can consider first base metals (copper, cobalt, manganese,

iron and nickel), lanthanides, precious group metals (PGMs), and sometimes uranium and vanadium to fall into the category of elements with economic value.

Because the source of mine waters can be so varied, and the composition of them so reliant on where in the process this waste has been produced or collected from, it has been difficult to give a rule of thumb for all potential applications. Elements that are most commonly found in mine waters that will negatively affect the performance of the resin include Fe^{3+} , Hg^{2+} , Pb^{2+} and Th^{4+} . Especially when it comes to using an iminodiacetic resin (for base metal recovery), these elements if found at significant levels can be detrimental to a business case.

Organic load must also be taken into account, particularly when considering surface water for treatment. A pretreatment step is fairly simple to implement, but without it the resin may prematurely fail. For the most efficient ion exchanger plant, the IX media must be protected from suspended solids, organics, and oil and grease, which can coat the surface of the resin beads or create channeling and pressure drop issues. Generally, however, IX is robust and even when fouled, steps can be taken to restore the capacity.

Strong oxidizing agents are however more problematic, as they can de-crosslink the resin (an irreversible process), weakening it and causing it to lose capacity. Activated carbon pretreatment is sometimes effective in reducing the oxidation potential and damage to the resin.

This technology can be theoretically suitable to metal extraction from the majority of effluent streams, bleads, as well as mine and decant waters. Recovery of valuable materials from acid discharge waters can result in some economic benefits; in certain cases the recovery of these metals can actually cover the cost of operation and capital expenditure. The economics depend on concentration and flow rate and various impurities. These are discussed and an economic model is presented. Three case studies are discussed and used as a basis for these models.

Discussion

Metal Concentration

The first influencing factor on the economics to consider is the concentration at which a particular metal is present in a possible feed source. When the concentration of metals in a stream is very low, efficiency of removal by an IX resin is relatively high because at that point it is film diffusion rather than particle diffusion that limits the kinetics. Metal leakage is very low, and the operating capacity of the resin increases.

Based on modeling done (proprietary) for existing applications in the metallurgical field, a series of data was generated for base metal recovery by varying the feed conditions to a fixed bed ion exchange set up, graphed in Figure 1. The resin types and operating capacities were modified according to the targeted metal, and the co-contaminants were based on specific case studies.

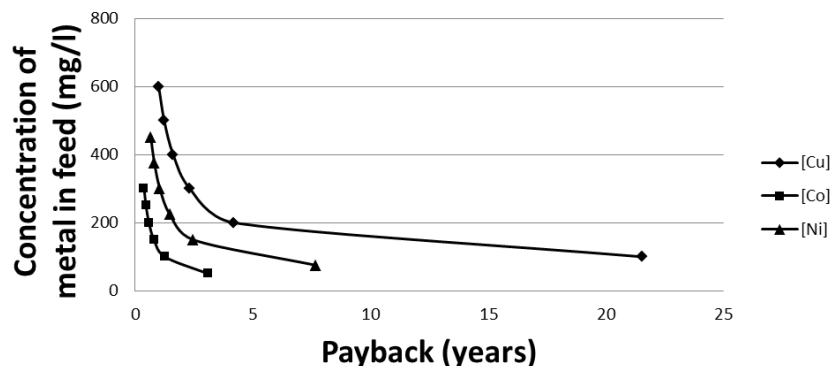


Figure 1 Base metals- Payback as a function of the level of various metals present in mine waters (at a flowrate of 10ML/day) based on metal prices of: Co=\$22/kg, Ni=8.7\$/kg and Cu=\$4.5/kg (February 2016)

It is important to note that where the concentrations are high, the rough guideline is that for levels above 1g/l, it may become more economical to investigate another technology, such as solvent extraction for recovery.

Two more examples are graphed below for Uranium and Vanadium (Fig 2 and 3). The chemical reagents, ion exchange resin, and calculated operating capacity have been modified for each example. The vanadium graph has been based on a case study with the aim of remediating vanadium leakage from a calcine dump. The vanadium is leached naturally by rain water and later by return of barren solution from the recovery plant.

Viability of this has been demonstrated at scale at Wapadskloof (4ML/day heap leach & IX vanadium recovery plant) operational from 2006 until 2010 (Grobler, C. 2015)

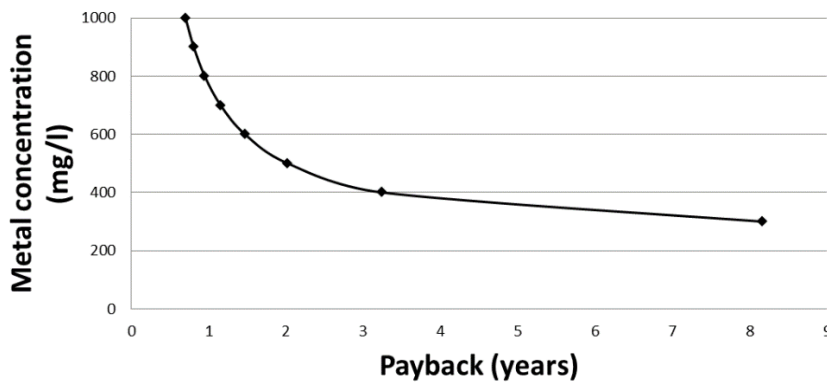


Figure 2 Vanadium- Payback as a function of the level of various metals present in mine waters (at a flowrate of 4ML/day) at Wapadskloof based on metal prices of: V=\$12/kg (April 2016)

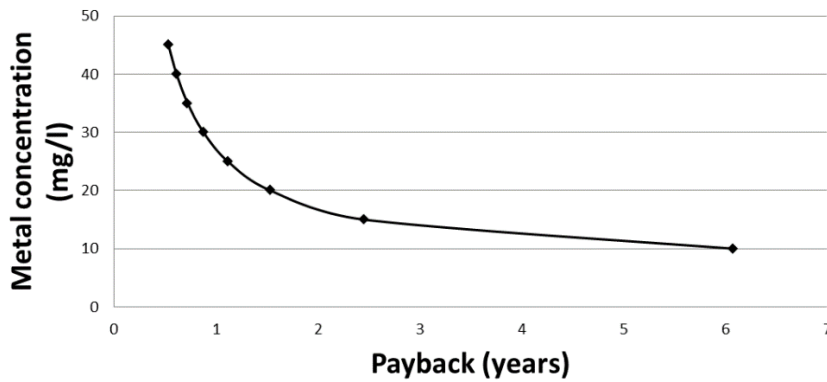


Figure 3 Uranium- Payback as a function of the level of various metals present in mine waters (at a flowrate of 10ML/day) based on metal prices of: U=\$60/kg (April 2016)

The model used for the payback on uranium has been based on a number of different applications rather than a specific case study. Site specific issues will affect the payback period but the graph serves to illustrate where the recovery may be economic.

Uranium and vanadium are both considered to be serious environmental contaminants and the economics can sometimes be offset by the reduction in environmental impact. Although often viewed as a complication, they can both be recovered with relative ease using IX.

Flowrate / economy of scale

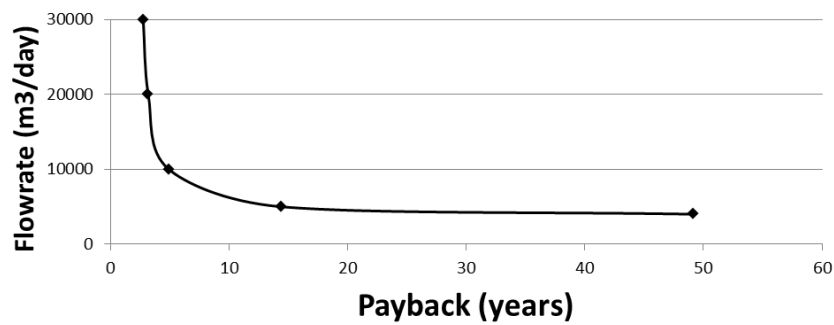


Figure 4 Example of payback period as a function of flowrate for Chibuluma Mines PLC

In Figure 4, a case study is represented (Hardwick, E. 2008). This particular example was modeled based on pilot work done at Chibuluma Mines PLC. The details of the case study, and some of the assumptions used for calculations are shown in Table 1, have been updated to 2016 figures. Assumptions on the costs of reagents are not detailed here. For operations smaller than 1MI per day it is recommended that another model is produced to calculate payback. There are some cost-saving measures such as the utilization of GRP vessels that should be taken into account with small flowrates that have not been worked into this particular model.

Table 1 Chibuluma Mines PLC, 2008. Full scale (10ML/day) calculations based on pilot scale testwork based on updated metal prices of: Co=\$22/kg, Ni=8.7\$/kg and Cu=\$4.5/kg (February 2016)

Metal Recovered (kg/Day)	
Co	264
Cu	3 215
Operating Costs as Percentage of Turnover	
	51%
Capital expenditure	\$4 425 000
Plant Payback (Years)	4.9

Competing ions/ poisons

Competing ions and poisons are very specific to the type of resin used. The resin choice is often made on how suitable it is for the recovery of a specific element, but it is possible for water to contain trace amounts of other metals that have an even higher affinity to the resin functional group, thus taking up active sites and reducing the capacity of the resin for the element of value.

Iron, especially in the ferric form, is commonly found in metallurgical streams. Most common IX resins have a high selectivity for trivalent iron. The iron may displace the desired element and poison the resin over time. Aminophosphonic resins may lose useful capacity over a period of months and therefore become uneconomic. It is possible to use a resin with a lower selectivity for iron upfront of these resins to protect them. Alternatively iron may be removed by precipitation by raising the pH above 3 and filtration.

Radioactive elements when present may make the recovered metal unsaleable. An example is thorium in the recovery of rare earths (Hubicki, Z.). Thorium may be removed by precipitation or selective elution. Uranium can be recovered separately on a strong base anion resin (Botha, M. 2009). Radium may be removed using a strong acid cation resin (Clifford, D. n.d.), whereas according to Chemviron Carbon “Radon can be removed from water by adsorption on activated carbon but after the adsorption, a radioactive decay process follows, in which radon is transformed into lead 210, a radioactive material.” (Ormslow, D. 2012).

Metal price fluctuation

The concentration at which a metal becomes economically viable for recovery is heavily dependent on the sales price of the product produced. Metal prices have varied greatly in the past, and their movements can be unpredictable. Below is a study done on the effects of LME shift on the economic tipping point of these types of applications, focusing on copper, cobalt and nickel as examples. It should also be borne in mind that the quoted LME prices are going to be higher than those obtained as a selling price. The form of the metal product (such as carbonate) is likely to affect the price. In cases where the recovered product can be returned to process, the full value may be obtained.

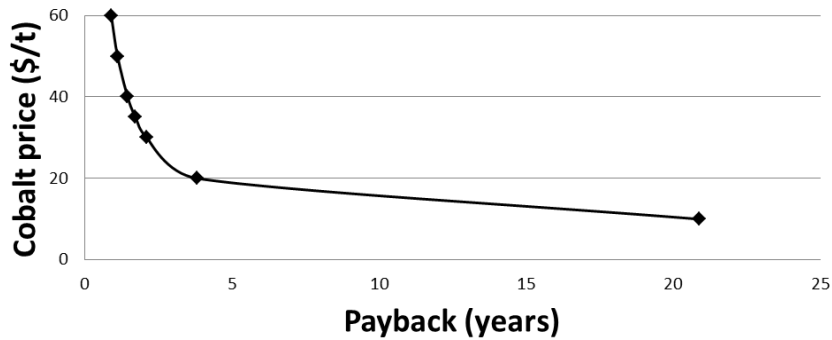


Figure 5 Example of payback period as a function of metal pricing (Co) where concentration of Cobalt in the feed is 50ppm, Flowrate 10Ml/day [Zambian cobalt refinery]

Figure 5 shows the effect of London metal exchange (LME) pricing on the economics of a prospective project, specifically for the case of cobalt. The assumption is that it is possible to extract 80% of the cobalt, with a conservative 20% allowance for downtime, and a product sale of typically 65-70% of LME.

Similar graphs can be created for other metals of interest, bearing in mind that the recovery percentage will be determined by the factors discussed, as well as the selectivity of the resin for the particular element, and operational factors.



Figure 6 Cobalt metal pricing fluctuation over 2005-2015
 Courtesy of infomine.com (Infomine Inc., 2016)



Figure 7 Vanadium metal pricing fluctuation over 2005-2015
 Courtesy of infomine.com (Infomine Inc., 2016)

Metal prices over the last 10 years show a strong downward trend (Fig 6 and 7); however even at their lowest point metal recovery can be economic at sufficient flow and concentration.

Conclusions

Very often waste streams from mines are considered as problems rather than opportunities. In some cases it is clear that such opportunities are worthy of further attention. In addition to the advantages to the environment there is also an economic return. When looking at trends, particularly over periods longer than 5 years, the metal prices are invariably downturned. Because of this depression in metal pricing, there have been operations that have become less economical, even for relatively high concentration streams. The recovery of metals in waste streams can improve the overall yield of a metallurgical processing plant, and return it to economic viability. Ion exchange can be economic where other technologies cannot be, and it is worth considering a stream for treatment even at reasonably low concentrations of desirable metal.

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