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Ion exchange resins for the treatment of cyanidation tailings Part 3 – Resin deterioration under oxidative acid conditions

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Abstract

Oxidative acid eluents comprising of H_2O_2 and H_2SO_4 have been proven to be effective in eluting base metal cyanide complexes from strong base resins. This study found that the repeated cycling between alkaline cyanide conditions and oxidative acid conditions does not affect the strong base or the total base capacity of strong base resins. However, it was found that a significant reduction of net operating capacity of the ion exchange resin bed, along with a small reduction of the total base capacity of the resin, takes place when this eluent is repeatedly used to elute resins loaded with a mixture of metal cyanide complexes. The reduction of the total base capacity is thought to be due to the oxidation of the resin by the oxidant in the presence of Cu^{2+} ions. A precipitate of copper hexacyanoferrate was detected in resin loaded with a mixed copper and iron cyanide solution. While the formation of this precipitate did not appear to have an impact on the total base capacity of the resin, it affected the net operating capacity of resin beds. These two processes gave rise to an approximately 1–3% reduction of the net operating capacity of the ion exchange resin columns per loading/elution cycle.

Keywords: Cyanidation; Ion exchange; Gold ores

1. Introduction

Cyanidation of gold ores has been practised in most parts of the world for over a century. The cyanidation process, patented by the McArthur and Forrest brothers, was first used at Crown Mine in New Zealand in 1889 (Smith and Mudder, 1991). Due to the toxicity of cyanide, and several high profile accidents leading to its release into aquatic environments, environmental protection authorities around the world have imposed stringent limits on cyanide discharges from gold cyanidation operations. As a result, tailing detoxification and cyanide management have emerged as key unit operations in cyanidation practices. Direct oxidation of cyanide is by far the most popular cyanide detoxification technique used in the mining sector today. Ion exchange, biological treatment, precipitation of cyanide as iron cyanide, and recovery by acidification are also applied in limited or partial capacities for removing cyanide from tailings. Ion exchange processes have several advantages over other cyanide detoxification processes. Ion exchange processes are capable of operating efficiently over the entire range of cyanide concentrations seen in most tailings streams. Further, ion exchange process can produce environmentally acceptable tailings, typically containing less than 1 mg/L CN_{WAD}. Nevertheless, the key challenge in using ion exchange resins for the treatment of cyanidation tailings is the elution and regeneration of resin.

Some processes use dilute mineral acids, which are sufficient to remove free cyanide and most CN_{WAD} complexes from resin. Copper cyanide complexes do not decompose yielding Cu^{2+} cations in the presence of dilute acids. Hence,

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unlike most CN_{WAD} complexes, copper cyanide is not removed from the resin (Tran et al., 2000). Further, cyanide complexes of iron, cobalt, gold and silver do not dissociate in mild acidic conditions. These elements are not eluted by dilute mineral acids either. Several elution techniques that use concentrated cyanide solutions to elute resin have also been reported recently. The Augment Process addresses the elution of copper using a strong alkaline copper cyanide solution. The Vitrokele Technology™ process employs a concentrated alkaline cyanide solution to elute copper from the resin. However, complete removal of copper has not been possible (Tran et al., 2000; Fleming, 1998). Further, the effectiveness of using a concentrated cyanide eluent to solve a cyanide contamination problem is also questionable.

2. Background

The inability to efficiently remove copper cyanide complexes from resins has restricted the widespread application of ion exchange for cyanidation tailings treatment (Tran et al., 2000). This led to the development of a new oxidative acid elution technique capable of eluting copper completely from the resin. This technique brings a strong oxidant into direct contact with resin loaded with cyanide complexes, subjecting the resin to high redox potentials. Oxidant in the eluent reacts with metal cyanide complexes on the resin, decomposing all CN_{WAD} cyanide complexes (including copper) to their respective metal cations and HCN. A portion of cyanide loaded on resin is also oxidised. The development of this elution technique was discussed in the first part of this series of publications (Fernando et al., 2002).

This process was successfully tested at pilot scale by treating approximately 14,000 m^3 of cyanide contaminated tailings solution. Results of this pilot scale test were reported in the second part of this series (Fernando et al., 2005). When the resin was repeatedly loaded with mixed metal cyanide species and eluted with the oxidative acid eluent, a gradual deterioration of the ion exchange resin performance was noted, along with strong discolouration of resin. Such changes in the resin were partly attributed to the precipitation of a highly stable copper–iron cyanide complex on resin surface. Oxidation of resin by the oxidant was also seen as another possible contributor to the deterioration of resin.

This article, the last in a three-part series, reports a study on the performance and the regeneration efficiency of resin, when the oxidative acid eluent is used repeatedly to elute base metal cyanide complexes from resin. Attention is given to studying the effect of oxidative acid conditions on the total and strong base capacities of the resin and the resulting effect on net operating capacities of resin beds. Further, since strong cyanide complexes are not eluted by the oxidative acid eluent, the effect of the co-loading of cyanide species is also investigated.

3. Experimental

When the oxidative acid elution is repeatedly used to elute strong base anion exchange resin loaded with mixed cyanide complexes, the resin is not only exposed to a highly oxidising environment, but is cycled between high pH/low Eh loading conditions and low pH/high Eh elution conditions. To investigate the impact of these processes on ion exchange resin, the total base and strong base capacities of a commercially available strong base ion exchange resin were measured while the resin bed was subjected to 30 cyanide loading and oxidative acid elution cycles.

The interaction of metal cyanide complexes during the oxidative acid elution, resulting from the co-loading of these cyanide complexes to the resin, has the potential to adversely affect the resin performance, as it may lead to the precipitation of metal cyanide double salts on the resin. This was investigated by repeatedly loading and eluting ion exchange resin beds with loading solutions containing various levels of iron and copper cyanide complexes.

Finally, resin samples from above studies were characterised using X-ray fluorescence spectroscopy (XRFS) and powder X-ray diffraction (XRD) to identify any inorganic chemical species accumulated on the resin. Further, the microstructure of these resin samples was compared with that of fresh resin using scanning electron microscopy (SEM), to investigate if any significant structural changes have taken place.

3.1. The effect of oxidative acid elution conditions on resin performance

An ion exchange resin column containing 10 mL (wet settled volume, chloride form) of Purolite A500 resin was used for this study. The loading solution, the wash water, and the eluent were fed to the ion exchange column using a DIONEX Gradient Pump. Loading was conducted with an alkaline cyanide solution. As this part of the study was focused on the effect of repeated cycling between high pH/low Eh loading conditions and low pH/high Eh elution conditions, metal cyanide complexes were not introduced to the loading solution. In each cycle, the resin was loaded with 300 mL of solution containing 1250 mg/L free cyanide. The loading solution was prepared by dissolving the required amount of NaCN (MERC, Analytical Reagent) in deionised water. Loading solution pH was adjusted to 12.0 by adding the required amount of NaOH (UNIVAR, Analytical Reagent). Each loading step was 60 min in duration. The loading solution was fed to the column at 5 mL/min flow rate. After each loading step, the column was rinsed with 25 mL of deionised water at 5 mL/min flow rate.

After each loading and the subsequent rinse, the column was eluted with the oxidative acid eluent. For each elution, 200 mL of oxidative acid eluent was used. The eluent, which contained 50 g/L H_2SO_4 (UNIVAR, Analytical Reagent) and 5 g/L H_2O_2 (UNIVAR, Analytical Reagent)