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# Comparison of activated carbon and ion-exchange resins in recovering copper from cyanide leach solutions

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ABSTRACT

The use of activated carbon and ion-exchange resins for recovering copper cyanide from gold leach solutions is compared in detail. When using activated carbon, the overall cyanide-to-copper ratio should be reduced to ~2 to achieve the most effective adsorption. This can be accomplished by dissolving metallic copper into the leach solution. However when using ion-exchange resins to recover the copper, it is not necessary to reduce the overall cyanide-to-copper ratio as the $Cu(CN)_3^{2-}$ complex, which is most prevalent in leach solutions, can strongly adsorb onto the resin. Whilst the elution of copper from carbon is relatively simple, the elution of copper from the resins is challenging. Among a variety of elution systems investigated, a cyanide soak followed by NaCl elution appears to be the most elegant, with the advantage of no regeneration of the eluted resin being needed. Two closed loop elution flowsheets have been investigated to recover copper from ion-exchange resin, with each having a different impact on the removal of thiocyanate from the leach solution by the resin.

## 1. Introduction

Cyanidation is the dominant process used for recovering gold from its ores. In recovering gold from copper-containing gold ores by cyanidation, some copper minerals are also dissolved by cyanide to form copper cyanide complexes. This can have a detrimental effect on the process efficiency and economics due to high cyanide consumption, reduced gold leach rates and poor gold recovery (Coderre and Dixon, 1999; Deschenes and Prudhomme, 1997; Muir et al., 1989; Nguyen et al., 1997; Sceresini and Richardson, 1991; Sceresini and Staunton, 1991; Tran et al., 1997). Restrictions are also increasing on the discharge of cyanide and copper cyanide complexes to tailings dams due to environmental concerns; copper cyanides are slower than free cyanide to be destroyed naturally, although they are less toxic than the equivalent free cyanide (Donato et al., 2007). This has resulted in an increase in the implementation of destruction processes before discharge to tailings. However, these processes can be uneconomical for high soluble copper concentrations. Therefore, various processes have been investigated and a number developed to economically treat copper-containing gold ores by either reducing the cyanide consumption or recovering and recycling the cyanide. These processes have previously been summarised by the authors (Dai and Breuer, 2009).

Due to the remaining issues with the current copper recovery/recycle processes, there is an opportunity to develop a new process that allows for the ease of gold recovery from copper-containing gold ores in which the copper is subsequently recovered and cyanide recycled. A schematic flowsheet of the general concept is shown in Fig. 1.

To avoid treating the entire cyanidation tailings stream, concentration to a clarified solution using ion-exchange resins or activated carbon was considered vital to the development of a potentially successful process. To recover cyanide as well as copper cyanide, an additional step is required to complex the cyanide, e.g. by the dissolution of metallic copper. If using activated carbon it is important to dissolve sufficient copper to convert $Cu(CN)_4^{3-}$ and the majority of $Cu(CN)_3^{2-}$ to easily absorbed $Cu(CN)_2^{-}$. The copper required for this process has been potentially recycled from the copper recovery process (Dai and Breuer, 2009). One of the concerns with carbon adsorption is the potential loss of cyanide via the copper catalysed oxidation to cyanate, particularly in the presence of activated carbon (Muir et al., 1988). However, a preliminary investigation carried out by the authors indicated that cyanide in the form of the aqueous copper cyanide complexes is more difficult to oxidise than that in the form of free cyanide.

The use of ion-exchange resins to recover metal cyanide complexes has received considerable attention in recent times due to their strong affinity for metal cyanide complexes (Bachiller et al., 2004; Leao et al., 2001; Leao and Ciminelli, 2002; Lukey et al., 1999a,b, 2000a; Riveros, 1993; Silva et al., 2003; Whittle, 1992). A universal conclusion from the previous studies is that the adsorption can be easily and effectively accomplished, but the elution is more challenging with no simple and effective elution method available. The major focus of the previous work has been on developing an

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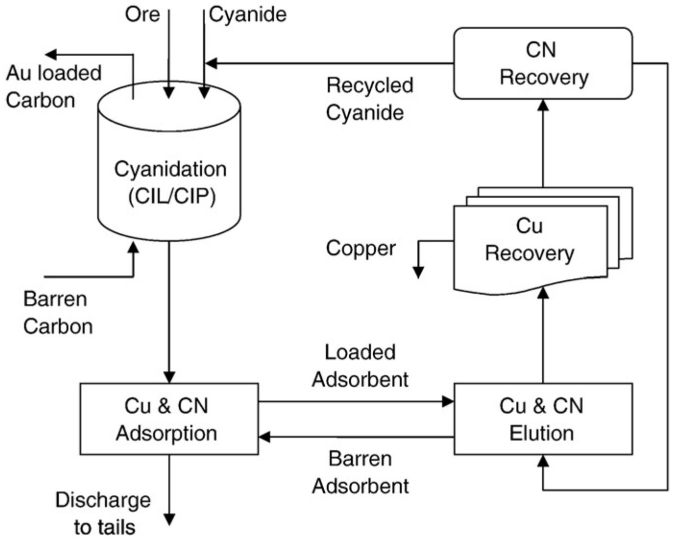

**Fig. 1.** Schematic of copper and cyanide recovery process concept for cyanidation discharge.

elution method which can selectively elute base metals before eluting the precious metals such as gold and silver. A typical stripping process that has been proposed previously is based on the selective removal of copper and iron by the use of NaCN followed by the elution of zinc and nickel by $H_2SO_4$ and then acidic thiourea to remove the gold and silver (Lukey et al., 2000a). Thiocyanate or zinc cyanide has been used as an alternative to elute the gold cyanide complex (Fleming and Cromberge, 1984; Lukey et al., 2000b). Leao et al. (1998) used 2 M $NaNO_3$ or NaCl to elute ferrous cyanide complex from the IONAC ASP-1P resin and achieved >75% efficiency in 10 bed volumes when the pH of eluant was adjusted to 10.5. Lukey et al. (2000a) used 2 M KCl + 8 mM free cyanide to elute copper and iron from a commercial resin Amberjet 4400 and achieved 63% efficiencies for both metals in 8 bed volumes. Due to a different focus of this previous work, there has been no systematic research conducted on the recovery of copper cyanides alone using resins.

This paper describes the development of a resin elution method to accommodate the need of copper cyanide recovery in the proposed flowsheet (Fig. 1), and compares strong base ion-exchange resins with activated carbon as a potential adsorbent in recovering copper cyanides within this proposed flowsheet.

## 2. Experimental methods

All experiments were carried out using fresh solutions prepared from analytical grade reagents and deionised water. Unless stated otherwise, experiments were conducted at pH 10.5 and ambient temperature. Copper cyanide loading solutions of various concentrations and cyanide-to-copper ratios were prepared by dissolving copper cyanide powder (CuCN) in a cyanide solution, with pH adjusted to 10.5 using sodium hydroxide.

For carbon adsorption, new carbon (Kuraray QA6/12HAH) was screened (+2.36 and −1.70 mm removed), washed and dried at 60 °C prior to use. Equilibrium measurements were made using 200 mL of a loading solution with 0.5 g carbon placed in a 250 mL plastic bottle and rolled for 24 h at 50 rpm. The use of a high solution volume to carbon mass ratio in conjunction with an air tight seal minimised the loss of cyanide via the carbon catalysed oxidation of cyanide by oxygen. Sample solutions were taken prior to and after the experiment for copper assay by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The loaded copper was eluted from carbon using a mixture of 20 vol.% acetonitrile, 50 mM NaCN and 0.25 M NaOH, a copper elution method developed by the authors which has an elution efficiency close to 100% (Dai et al., 2007). The loading at 24 h was treated as a pseudo-equilibrium loading and was calculated from the mass balance based on the copper stripping.

For the resin adsorption kinetics study, 200 mL of solution containing 8 mM copper at various cyanide-to-copper ratios was mixed with 3 mL (wet settled volume) of strong base anion-exchange resin, Purolite A500/2788 (chloride form; polystyrene crosslinked with divinylbenzene polymer structure; quaternary ammonium functional group; total capacity 1.15 M; 1 mL of wet settled resin when dried at 60 °C weighs 0.334 g), shaking in a water bath at 25 °C for 24 h. 3 mL solution samples were taken at 0, 10, 30 min, and 1, 2, 4, 6 and 24 h for copper assay. The copper loading was calculated based on the decrease in copper concentration after accounting for the copper removed in sampling, and is reported as moles per litre of wet settled resin (in chloride form), which for simplicity is designated as M. For the batch elution experiments, 15 mL (wet settled volume; chloride form) of Purolite A500/2788 resin was firstly loaded with copper from 1 L of a solution containing 4 mM copper (CN:Cu = 4) for 24 h using bottle roll at 20 rpm (the final copper loading was calculated to be 0.26 M). 1.5 mL of the loaded resin was then shaken with 50 mL of each of the eluants investigated in a water bath, with solution samples being taken at 1, 3, 5 and 24 h for copper assay. Because the eluants containing ammonium chloride, ammonium nitrate, acetate or benzoate were at a low pH, samples taken from these solutions were mixed with 1.5 M NaOH to prevent HCN emission. The batch elution efficiency was calculated based on the increase in copper concentration in the eluant in 24 h. For the thiocyanate and ammonium thiosulfate eluants, which had a very high elution efficiency, the barren resin was further treated with 0.5 M $NaClO_4$ + 0.05 M NaCN (two stages) to strip all the residual copper off the resin, and the stripping efficiency was calculated based on the total copper eluted. The eluant containing 3.5 M $MgCl_2$ was prepared by adding concentrated hydrochloric acid to a MgO slurry until saturation which was indicated by a sudden decrease in pH.

For column resin elution experiments, 8 mL (wet settled volume; chloride form) of Purolite A500/2788 resin was loaded with copper using a conical flask with overhead stirrer from 800 mL of a solution containing 3 mM copper cyanide, 3.5 mM free cyanide and 9 mM thiocyanate for 24 h (for the simulation of a closed loop resin recovery process, the resin was loaded from 15 mM rather than 9 mM thiocyanate to simulate the resin being returned with thiocyanate at steady state). The loaded resin was rinsed and then packed into an 8 mL column. The resin was then eluted using various elution conditions at a flow rate of 2 bed volumes per hour and ambient temperature. Solution samples were collected using a fraction collector and analysed for copper and thiocyanate using a High Performance Liquid Chromatography (HPLC). The barren resin was further treated using the same $NaClO_4$ method described above. This gave a good copper mass balance.

Sodium acetate was analysed by HPLC using an anion-exchange column and UV detection.

## 3. Results and discussion

### 3.1. Copper cyanide adsorption

#### 3.1.1. Comparison of adsorption kinetics

Fig. 2 shows a comparison of the kinetics of copper cyanide adsorption onto activated carbon and an ion-exchange resin. As can be seen from the resin adsorption data set, ln[Cu] vs. time gives a straight line for the first 4 h of adsorption. This indicates that the adsorption of copper cyanide onto strong base resins is a first order process described by Eq. (1). The rate constant, $k$, was determined from the slope of this plot to be 1.72 $h^{-1}$. It has been indicated in a previous study by the authors that the initial stage of carbon adsorption at low loadings is also a first order process due to the