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THE ELUTION OF METAL CYANOCOMPLEXES FROM POLYACRYLIC - AND POLYSTYRENE - BASED ION EXCHANGE RESINS USING NITRATE AND THIOCYANATE ELUANTS

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Abstract - Ion exchange resins can potentially be applied in cyanide recycling to address growing environmental concerns over the use of cyanide during gold extraction. In the present work the elution of copper-, iron-, and zinc-cyanocomplexes from polyacrylic- and polystyrene-based resins was studied. It was found that iron and copper cyanides are easily eluted from polyacrylic- and polystyrene-based ion exchange resins using either SCN^- or NO_3^-. However, elution of the zinc cyanide complex from polystyrene-based resins was poor when using nitrate solution as eluant. Besides, an increase in elution temperature from 25 °C to 50 °C improved the elution of iron and zinc cyanides from polystyrene-based resins using a nitrate eluant; however temperature did not have any significant effect on other metal cyanocomplexes or for elution using thiocyanate. It was therefore proposed that the optimal combination of resin-eluant was site-specific, and depends on the features of the effluent, processing temperature, eluant concentration, and ion exchange resin under consideration.

Keywords: Cyanide recycling: Ion exchange resins; Thiocyanate; Nitrate; Gold extraction; Elution.

INTRODUCTION

Accidental spillage of cyanide-containing effluents is a serious threat to water streams and especially to aquatic life. Recent reports of cyanide leakages in estuaries justify the application of better practices for cyanide management in the gold industry (Ciminelli, 2002). In the last twelve years, six major accidents in which cyanide-containing tailings were released into the environment have been reported. Probably the most publicized of these accidents occurred in Romania in the year 2000. In this instance, approximately 100,000 m^3 of tailings containing cyanide, metals, and other toxins reached the Danube River, whereby approximately 2 million inhabitants had contact with the poisoned water (DeVries, 2001).

As a result of such widely publicized accidents, countries including Greece and Turkey as well as the State of Montana in the USA have banned the use of cyanide by the mining industry. This has led various research groups worldwide to investigate alternative lixiviants to cyanide for gold extraction. The most promising lixiviant identified so far as a replacement

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*To whom correspondence should be addressed for cyanide in gold extraction is thiosulfate. It is considered non toxic and inexpensive and previous work has shown that the gold leaching rate is higher than that of cyanide. Despite these advantages, cyanide will continue to be very attractive for the reasons summarized below (Ritchie et al., 2001):

(i) High gold recoveries are achieved;

(ii) Cyanide readily forms a complex with gold in a wide range of pH and Eh, thereby making the process very robust.

(iii) The use of cyanide for gold extraction is a well-established process; therefore the costs of extracting gold should be lower than those with new and industrially unproven lixiviants.

Considering that cyanide is still being applied extensively in the gold industry, the International Cyanide Management Code has imposed an average cyanide concentration limit of 50 mg/L weak acid dissociable (WAD) for open-pond water (Ciminelli, 2002) in the plant. As average plant concentration is usually higher than this limit, some form of cyanide remediation is becoming a very compelling interest for the industry.

Currently, cyanide destruction processes have been applied to lower the cyanide concentration in process streams. Essentially, these destruction processes convert cyanide into a less toxic compound, such as cyanate. Alkaline chlorination, hydrogen peroxide, Caro's acids, and INCO SO_2/air are chemical cyanide destruction methods based on this approach (Young, 2001b). Alternatively, biological treatment (Clark et al., 2001), addition of ferrous sulfate and natural attenuation (Young, 2001a) also reduce the WAD cyanide in tailings. These destruction processes are readily available, are routinely used, and have been shown to be very effective. However, their main disadvantage is that the cyanide ligand is destroyed in the process, which leads to a significant increase in processing costs.

Cyanide recycling is also an alternative, especially in those plants treating high-cyanide-consuming ores such as those of gold-copper and gold-silver. Cyanide can be recovered from either pulps or clarified solutions. In both situations ion exchange resins can be used as a step to concentrate the cyanocomplexes present in the effluents (Leão et al., 1998; Fleming, 2001), facilitating recycling. Unlike activated carbon, ion exchange resins load not only gold cyanide, but also all metallic cyanocomplexes. Furthermore, resins are not poisoned by organic matter and do not adsorb calcium magnesium or silica, as does activated carbon. As they are insoluble in aqueous phase, resins are ideal to load base metal cyanocomplexes at low concentrations. Resin in pulp (RIP) technology has already been applied in the gold industry (albeit predominantly in the former Sovient Union), and cyanide recovery can be achieved using strong base resins since they have a high affinity for base metal cyanocomplexes. After elution the loaded cyanide can be recovered by a route similar to that used in the AVR process (Leão and Ciminelli, 2000; Lukey et al., 2000a; Fleming, 2001).

The sorption or loading of base metal cyanocomplexes onto ion exchange resins has already been studied. It has been shown that a variety of resins can load cyanocomplexes produced by cyanidation of different gold ores (Leão et al., 2000). The factors that affect sorption behavior are well characterized and include resin matrix and functional group, solution composition (e.g. salinity), presence of impurities, and so forth.

Elution studies of cyanocomplexes from ion exchange resins have shown that is much more difficult than sorption. Acid elution is only effective with resins loaded only with zinc cyanide. In the presence of copper and iron cyanides, there is a precipitation of either CuCN or base metal ferrocyanides during the acidification process. Some researchers have studied the mild oxidative acidic elution of CuCN-loaded resin produced during acid elution. The idea is to oxidize Cu(I) to Cu(II), thereby producing $CuSO_4$ and HCN as products (Fernando et al., 2002). However, it has been shown that the resin can be poisoned if it contains a considerable concentration of iron cyanocomplexes.

An alternative to acidification is to use an alkaline solution as an eluant. The precipitation of metallic ferrocyanides is kinetically hindered and CuCN is not formed. Both zinc cyanide and saline solutions have been applied. While zinc cyanide elution has been extensively studied (Lukey et al., 2000b) and applied in the Golden Jubilee operation (Fleming, 1988), saline solutions have also been shown to be an effective alternative (Bachiller et al., 2004).

It has also been established that higher elution efficiencies can be achieved using alkaline chloride solutions (Lukey et al., 2000d), especially in the case of copper and iron. The thiocyanate elution of polystyrene-based resins has also been studied (Lukey et al., 2000b). However, the effectiveness of thiocyanate as an eluant for metal cyanocomplexes loaded on polyacrylic resins has not yet been addressed. Likewise, nitrate solution has also been suggested as a potential eluant, although its application has so far not been extensively studied.

In the present work, the elution of cyanocomplexes from polystyrene- and polyacrylic-based resins using thiocyanate and nitrate eluants at 25 °C and 50 °C was investigated. This work provides further insight into the mechanism of elution from resins for various metal cyanocomplexes and results in a greater understanding of how factors including effluent composition, processing temperature, and ion exchange resin characteristics affect the performance of the cyanide recovery process.

EXPERIMENTAL PROCEDURES

Two different ion exchange resins were investigated in the current work, namely (1) Dowex 1X8 (polystyrene, gel, exchange capacity: 1.2 meq-g/mL) and (2) Bayer AP-247 (polyacrylic, macroporous, exchange capacity: 1.0 meq-g/mL). These resins are strong basic anion exchange resins and contain try-methyl ammonium as the functional group. Prior to the elution studies, these resins were loaded with metal cyanocomplexes using an orbital shaker at 200 min^{-1} (*New Brunswick*).

Synthetic metal cyanide solutions were prepared by mixing copper (I) cyanide (CuCN, 99%, *Aldrich)*, potassium ferrocyanide trihydrate ($K_4Fe(CN)_6.3H_2O$, 98.5-102%, *Isofar*) and zinc sulfate heptahydrate ($ZnSO_4.7H_2O$, 99%, *Synth*) in distilled water at pH=10.5±0.5. A sufficient quantity of sodium cyanide (95%, *Synth*) was added to the solution to ensure a CN/Cu molar ratio of 3.5, a CN/Zn molar ratio of 4.0, and at least 400 mg/L free CN^-. Based on appropriate E_h-pH and speciation diagrams (Xue et al., 1984), it was assumed that the following complexes were predominant in the solution at the pH of loading: $[Zn(CN)_4]^{2-}$, $[Cu(CN)_3]^{2-}$, $[Cu(CN)_4]^3$, and $[Fe(CN)_6]^{4-}$.

The loading solution contained 300 mgFe/L, 200 mgCu/L, and 180 mgZn/L. After 24h loading a pseudo-equilibrium of the system was reached; thereafter the resin was separated from solution by filtration and the copper, zinc, and iron content in the aqueous phase was determined by atomic absorption spectrometry. The loading of each metal on the resin was obtained by mass balance. For the Dowex 1X8 resin, the average metal loading was 11.2 mg Fe/mL-resin, 10.8 mg Cu/mL-resin, and 7.8 mg Zn/mL-resin. For the Bayer AP-247 resin, the average metal loading was 11.0 mg Fe/mL-resin, 8.8 mg Cu/mL-resin, and 7.3 mg Zn/mL-resin.

Elution experiments were carried out in a water-jacketed glass column at both 25 °C and 50 °C. The column was filled with 10 mL of the loaded resin. After reaching the proper temperature, the eluant (either thiocyanate or nitrate solution) was passed upwards through the bed at a constant flowrate of 4.8 BV/hr provided by a peristaltic pump (Millan). This is a slightly lower rate than that applied by Lukey et al. (2000d). This flowrate enabled adequate sampling of the eluate in order to determine the elution profile of the resin while not fluidizing the resin bed. Twenty (20) bed volumes (BV) were passed through the column in each experiment. Air bubbles were removed using a thin glass rod. Eluate samples were taken at each 3-5 BV fraction. The flowrate was monitored periodically and no change was observed during the course of the elution experiment. All piping and connections were made with polyethylene tubing.

Metal concentrations in solution were determined by flame atomic absorption spectrometry (*Perkin Elmer AAnalyst 100*). Copper, nickel, and iron standards were prepared in cyanide solutions. The analysis was performed in the same week as the experiment to prevent any sample degradation.

RESULTS

The following discussion is of results of the elution of two types of commercial resins (Dowex 1X8 and Bayer AP247) using two types of eluants (thiocyanate and nitrate solutions) at two different temperatures (25 °C and 50 °C). Furthermore, the elution results for each loaded resin were compared for two different concentrations of the eluants (i.e., 1 mol/L and 2 mol/L).

Thiocyanate Elution

The elution profile for Bayer AP-247 resin using 1 mol/L NaSCN (at both 25 °C and 50 °C) is presented in Figure 1. The results show that at 25 °C greater than 90% copper cyanide and iron cyanide elution was achieved after 5 BV. Higher eluant volumes did not improve the recovery of either cyanocomplex. It can be seen that zinc cyanide elution was considerably hindered, reaching approximately 55% at 5 BV and 80% after 20 BV. It is also shown in Figure 1 that an increase in elution temperature from 25 °C to 50 °C resulted in an increase in the percentage of zinc cyanide eluted from the resin. For example, at 5 BV and 20 BV, more than 60% and 90% of the zinc cyanide was eluted from the resin respectively. It was important to note that there was no significant change in elution characteristics of either the copper cyanide or the iron cyanide complexes.

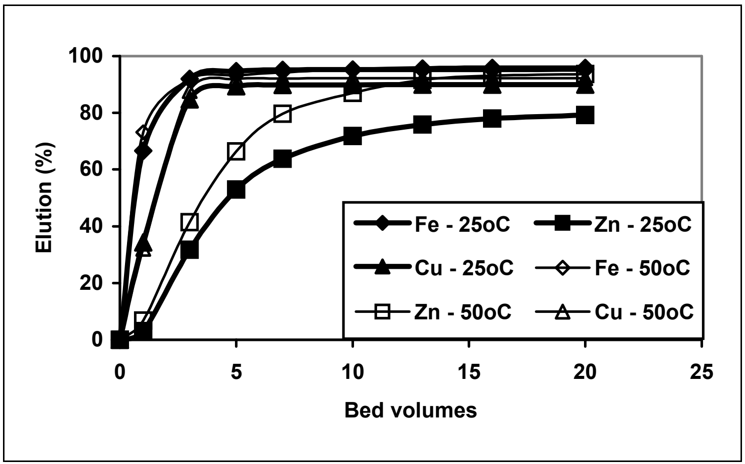

Figure 1: Elution of Bayer AP-247 ion exchange resin using 1mol/L NaSCN at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L; pH = 11.0–11.5.

The effect of thiocyanate concentration in the eluant on the elution of metal cyanocomplexes is presented in Figure 2. It is shown that using 2 mol/L thiocyanate at 25 °C both copper and iron cyanide elutions are slightly greater than that shown in the results obtained for 1 mol/L thiocyanate (Figure 1). However, the increase in thiocyanate concentration from 1 mol/L to 2 mol/L had the most prominent effect on the elution of zinc cyanide. By comparing Figures 1 and 2, it can be seen that the elution of zinc cyanide increased from approximately 55% to 75% after the first 5 BV. At 20 BV, the elution of zinc cyanide was approximately 81%, i.e., similar to that observed for 1 mol/L thiocyanate (Figure 1). This result suggests that an increase in thiocyanate concentration in the eluant facilitated the elution of the zinc cyanide complex, but the final percentage eluted was similar (at 20 BV).

It can also be seen in Figure 2 that temperature of the thiocyanate eluant had no significant effect on the elution of either copper or iron cyanide complexes. However, it can be observed that zinc extraction increased from 81% (25 °C) to 88% at 50 °C, which demonstrates that temperature improved zinc elution although its effect was not as great as the effect observed for 1 mol/L thiocyanate.

Comparing Figure 3 with Figures 1 and 2, it can be seen that the recovery of metal cyanocomplexes using thiocyanate eluants (1 mol/L or 2 mol/L) was initially slower from polystyrene-based resins than from polyacrylic-based resins. The elution results obtained for Dowex 1X8 (Figure 3) show that approximately 80% Cu, 40% Zn, and 65% Fe were eluted in the first 5 BV at 25 °C. Moreover, at 20 BV the elution of each metal complex reached approximately the same value of 90%. Similar to the trend observed in Figures 1 and 2, as the eluant temperature was increased to 50 °C, an improvement in the percentage of metal eluted was observed, particularly for the zinc cyanide complex.

By increasing the thiocyanate concentration in the eluant from 1 mol/L to 2 mol/L, it can be seen in Figure 4 that a significant improvement in total percentage eluted for each metal was achieved. For example, in these experiments approximately 99% Cu, 93% Zn, and 93% Fe were eluted at 20 BV (25 °C). A slightly higher percentage elution was achieved at a temperature of 50 °C. These results suggest that a temperature of 25 °C is suitable for elution of metal cyanocomplexes using 2 mol/L NaSCN.

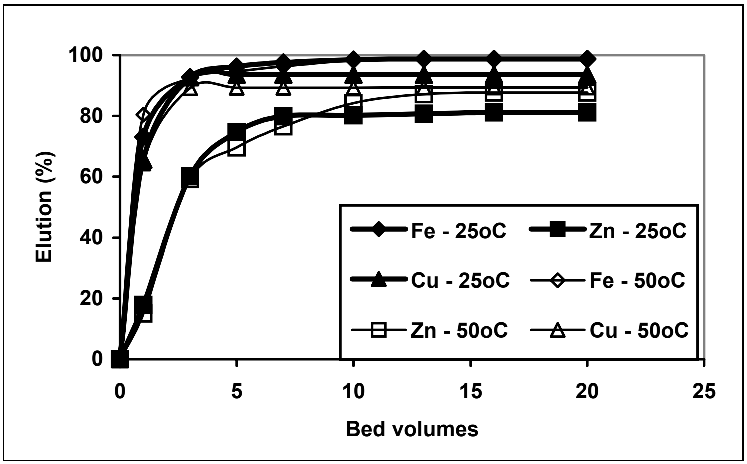

Figure 2: Elution of Bayer AP-247 ion exchange resin using 2mol/L NaSCN at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L in solution; pH = 11.0–11.5.

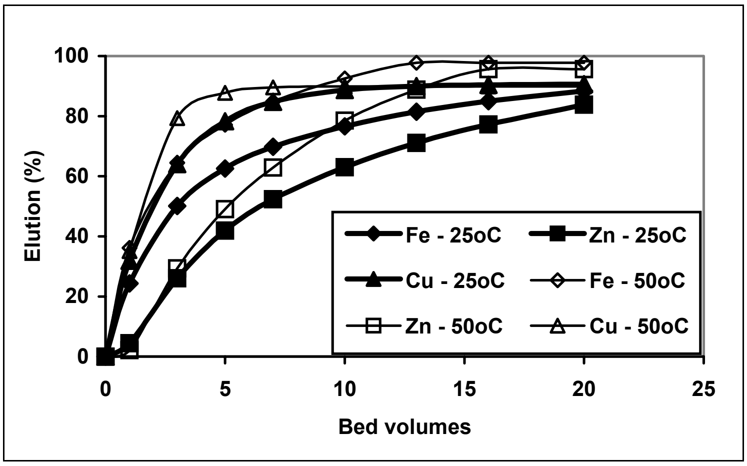

Figure 3: Elution of Dowex 1X8 ion exchange resin using 1mol/L NaSCN at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L in solution; pH = 11.0–11.5.

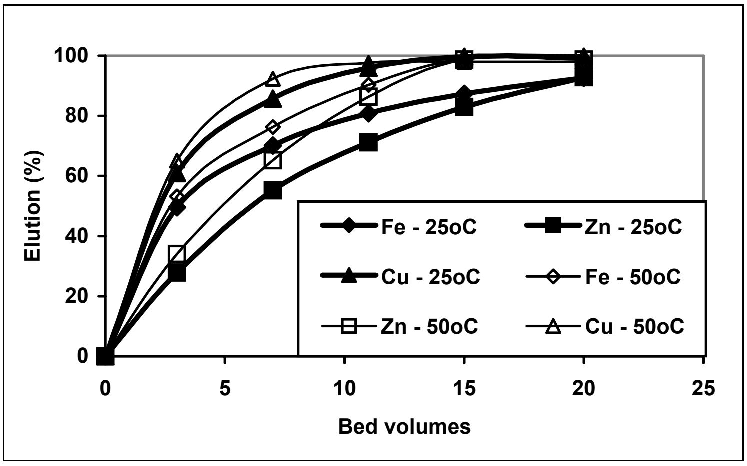

Figure 4: Elution of Dowex 1X8 ion exchange resin using 2mol/L NaSCN at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L; pH = 11.0–11.5.

Bachiller *et al.* (2004) eluted copper (~98%) from synthetic as well as industrial solutions with 1.25 mol/L NaSCN under batch conditions. Lukey et al. (2000a) studied the elution of cyanocomplexes from polystyrene-based resins using 2 mol/L NH_4SCN solutions (at pH 7.0) and showed that complete copper elution could be achieved at 16 BV, although low iron and zinc extractions were achieved, 39% and 35% respectively. Fleming and Cromberge (1984) also observed high copper (100%), lower iron (85%), and lower zinc (47%) elution with 2 mol/L NH_4SCN at pH 7.0. Similarly to the work of Leão and Ciminelli (2001), Lukey et al. (2000a) and Fleming and Cromberge (1984) suggested that the precipitation of Prussian blue-like compounds accounts for the low iron and zinc elution, i.e., the precipitation of either $Zn_2[Fe(CN)_6]$ or $Fe_4[Fe(CN)_6]_3$ was suggested (Leão and Ciminelli, 2000; Lukey et al., 2000c).

It is important to note that different metal concentrations sorbed on each resin and that the use of resins with different functional groups may have affected the percentage elution of metal cyanocomplexes in each case. However, as has been shown in the present work, the application of alkaline solutions greatly improved iron and zinc elution from resins using thiocyanate. It is proposed that this occurred because the precipitation of Prussian blue compounds is kinetically hindered at a high pH. The high recoveries of iron and zinc cyanides observed by Lukey et al. (2000b) using a 2 mol/L KSCN eluant support this proposition, as a pH of 12.0 was applied in that study.

Nitrate Elution

The use of nitrate solution as an eluant for metal cyanocomplexes has only recently received attention (Riveros et al., 1993). Leão et al. (1998) studied its application in the elution of copper-, iron-, and nickel-cyanide loaded resins and achieved good results in batch experiments.

Figure 5 contains the results obtained in the current work for the elution of the Bayer AP-247 ion exchange resin using 1 mol/L sodium nitrate solution. In contrast to the results obtained for the thiocyanate eluant (Figure 1), it can be seen that iron-, copper-, and zinc cyanide complexes were eluted from the resin to significantly different extents. Whereas the percentage elution of iron cyanide was approximately 80% at 5 BV and 95% at 20 BV, the percentage elution of copper cyanide was only 40% and 80% at 5 BV and 20 BV respectively. Furthermore, the elution of zinc cyanide was relatively poor, reaching only 20% at 20 BV. For the elution experiments conducted at 50 °C, it can be seen that there was only a minor improvement in the recovery of all metal cyanocomplexes.

For the elution experiments performed using 2 mol/L NO_3^- at 25 °C (Figure 6), it can be seen that the percentage elution of copper cyanide and zinc cyanide was significantly higher than when using 1 mol/L eluant. For example, copper elution increased from approximately 40% (1 mol/L NO_3^-) to 80% (2 mol/L NO_3^-) at 5 BV and from 80% (1 mol/L NO_3^- to 95% (2 mol/L NO_3^-) at 20 BV. Similar results had previously been reported in the literature for batch elution experiments using the polyacrylic resin Purolite A860S. For the experiments conducted at 50 °C (Figure 6), it can be observed that temperature had a noteworthy effect only on zinc cyanide elution at high nitrate concentrations. These results therefore establish that nitrate eluants are more effective than chloride solutions for the elution of metal cyanocomplexes from polyacrylic-based resins (Lukey et al., 2000d; Leão et al., 2001).

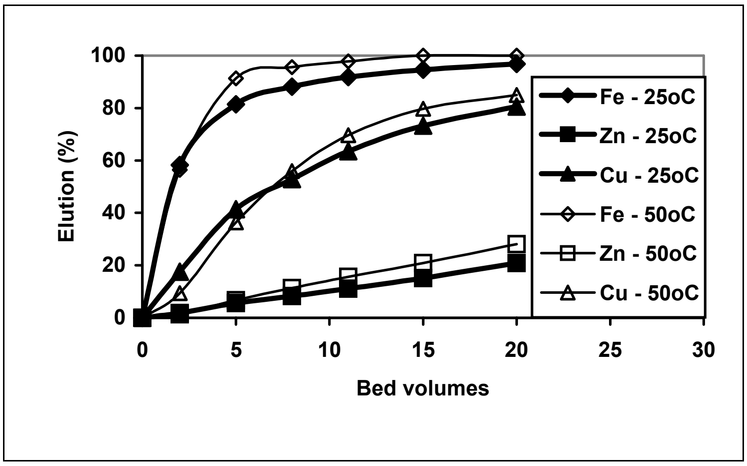

Figure 5: Elution of Bayer AP-247 ion exchange resin using 1mol/L $NaNO_3$ at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L in solution; pH = 11.0–11.5.

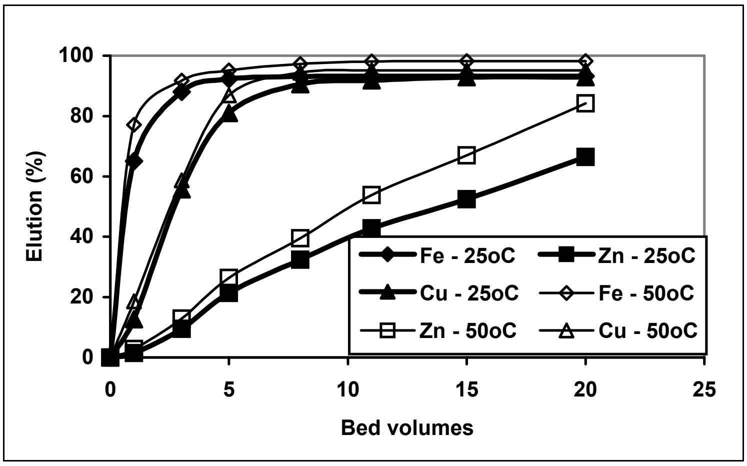

Figure 6: Elution of Bayer AP-247 ion exchange resin using 2mol/L $NaNO_3$ at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L in solution; pH = 11.0–11.5.

In Figures 7 and 8, results on percentage elution obtained for the Dowex 1X8 resin using 1 mol/L and 2 mol/L $NaNO_3$ solution respectively are presented. The most notable result that can be observed is that the percentage elution of zinc cyanide was poor, irrespective of elution temperature or concentration of NO_3^- in the eluant. In contrast, the recovery of copper and iron cyanide was greater than 85% at 20 BV using 2 mol/L NO_3^- (Figure 8). An increase in elution temperature to 50 °C resulted in a significant improvement in the recovery of iron cyanide (Figures 7 and 8). For example, in Figure 7, it can be seen that iron recovery increased from approximately 42% (at 25 °C) to 78% (at 50 °C) in the first 5 BV and effectively reached 100% at 20 BV (at 50 °C).

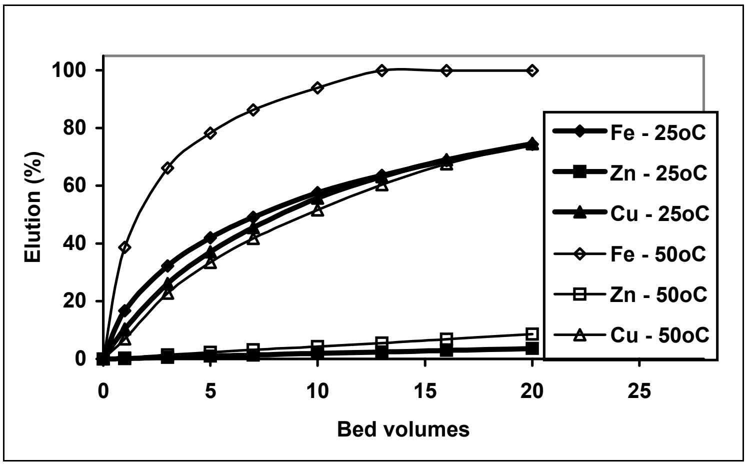

Figure 7: Elution of Dowex 1X8 ion exchange resin using 1mol/L $NaNO_3$ at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L in solution; pH = 11.0–11.5.

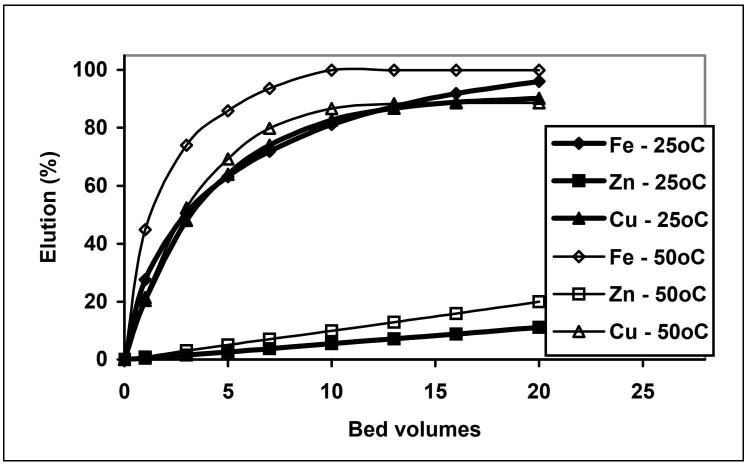

Figure 8: Elution of Dowex 1X8 ion exchange resin using 2mol $NaNO_3$ at 25°C and 50°C. $[CN^-]_{free}$: 300 - 400mg/L in solution; pH = 11.0–11.5.

Overall, the results presented in Figures 7 and 8 indicate that the application of a high $NaNO_3$ concentration and elevated temperature has a strong beneficial impact on the recovery of metal cyanide complexes from ion exchange resins. Leão and Ciminelli (2000) also studied the elution of cyanocomplexes using 2 mol/L $NaNO_3$ solutions at 25 °C in batches. In this instance, the macroporous resin Amberlite IRA900 (Rohm & Haas) containing trimethylammonium functional groups was used (this is similar to the Dowex resin used in the current work). Leão and Ciminelli (2000) found that iron and copper cyanide recovery was 96%, similar to the recovery obtained in the present work. Bachiller et al. (2004), achieved a slightly lower copper cyanide elution of 80% with a Bayer MP500 resin. Bachiller et al. (2004) also studied a sodium chloride eluant and found that the copper cyanide recovery was lower (84%) than that obtained with sodium nitrate at 50 °C. Lukey et al. (2000d) also tested sodium chloride (2 mol/L) solution as eluant for the gel-type resin Amberjet 4400 at 22 °C. A 83% Cu, 87% Fe, and 7% Zn cyanide recovery was observed. Therefore, by comparing the results of the current work with those published previously in the literature it can be concluded that nitrate is a better eluant than chloride for the recovery of iron and copper cyanocomplexes from polystyrene resins. Nevertheless, zinc extraction is low in both systems.

In Table 1 a summary of elution results obtained for both the Bayer AP-247 and Dowex 1X8 resins using NaSCN and $NaNO_3$ eluants at 25 °C and 50 °C is presented. It can be seen that for the polyacrylic resin, the overall iron cyanide elution was not affected by either the eluant type or the temperature, i.e., the recovery of iron cyanide from the resin was always greater than 90% irrespective of temperature. Furthermore, thiocyanate was more effective than nitrate for copper elution at 1 mol/L; however there was no difference in performance at higher eluant concentrations. Conversely, a higher zinc cyanide elution was achieved using thiocyanate rather than nitrate. In particular, the recovery of zinc cyanide using sodium nitrate as the eluant was poor.

Table 1: Elution of base metal cyanocomplexes from Dowex 1 X 8 and Bayer AP247 resins with NaSCN and $NaNO_3$ solutions at 25°C and 50°C.

Resin	Eluant	Eluant conc. (mol/L)	% Elution					
			25°C			50°C		
			Fe	Cu	Zn	Fe	Cu	Zn
Dowex 1X8	NaSCN	1	88	91	84	98	96	90
		2	93	99	93	99	98	99
	$NaNO_3$	1	74	75	4	99	75	9
		2	96	90	11	100	89	20
Bayer AP247	NaSCN	1	95	90	80	96	92	93
		2	98	94	81	98	89	88
	$NaNO_3$	1	97	81	21	99	85	28
		2	93	93	66	98	95	84

Overall loadings:
Dowex 1 X 8 resin: 11.2mgFe/mL-resin, 10.8mgCu/mL-resin, and 7.8mgZn/mL-resin.
Bayer AP 247resin: 11.0mgFe/mL-resin, 8.8mgCu/mL-resin, and 7.3mgZn/mL-resin.
Overall yields were been determined after 20 BV had passed through the resin bed.

For the polystyrene resin (Dowex 1X8), it was found that temperature was an important parameter for the elution of iron and zinc cyanide complexes. For instance, iron cyanide recovery was greater than 98% at 50 °C, while only 75% was observed at 25 °C (Figure 7). It was noteworthy that temperature did not significantly affect copper cyanide recovery from Dowex 1X8. Sodium nitrate was not recommended for zinc cyanide elution from the Dowex resin, since the metal elution with nitrate was the poorest observed in the present study: 20% was the maximum elution efficiency achieved.

The different patterns observed during elution of resins Dowex 1X8 and Bayer AP247 can be rationalized considering, among other factors, their structures and physical properties.

Ion exchange in systems with several counter ions is a complex phenomenon. The fluxes of both counter ions in solution as well as in the resin must incorporate the relative mobilities and affinities of the different species. Nernst-Planck equations must therefore be solved for all cyanocomplexes adsorbed in the resin (Helferrich, 1962). This results in a fairly complex mathematical description that needs to be solved numerically. The kinetic description of either thiosulfate or nitrate elution of cyanocomplex-loaded resins has not received enough attention to enable an accurate modeling of the elution experiments carried out in the present work. Notwithstanding, a qualitative discussion will be presented.

Previous work had shown that both resins have a higher affinity for zinc than for copper and iron cyanocomplexes (Riani et al., 2002). Considering the cyanide concentration in the present work, iron was present as $Fe(CN)_6^{-4}$; zinc, as $Zn(CN)_4^{-2}$; and copper, as $Cu(CN)_3^{-2}$ and $Cu(CN)_4^{-3}$. $Fe(CN)_6^{-4}$ is octahedral, $Zn(CN)_4^{-2}$ and $Cu(CN)_4^{-3}$ are tetrahedral, and $Cu(CN)_3^{-2}$ has a distorted tetrahedral structure in aqueous solutions (Sharpe, 1976). As already pointed out (Riveros, 1993; Leão and Ciminelli, 2000) the different affinities can be ascribed to the features of both the resins and the complexes: (i) nature of the exchange group, (ii) resin matrix, and (iii) resin-complex hydrophilic/hydrophobic interactions. The first one was not discussed in the present work as both resins have the same type of exchange group.

Dowex 1X8 is a polystyrene resin while Bayer AP 247 has a polyacrylic matrix. The polysterene structure is hydrophobic and as a result has an affinity for cyanocomplexes with a more hydrophobic character, such as the monovalent gold and silver cyanocomplexes. Conversely, the presence of carbonyl groups (C=O) in the structure of the polyacrylic resin Bayer HP247 makes it less hydrophobic than the to polystyrene ones (Riveros, 1993), which explain its larger affinity for the more hydrophilic complexes, such as $Fe(CN)_6^{-4}$ and $Cu(CN)_4^{-3}$. This explains the higher copper and iron loadings observed for Bayer AP 247 resin than for Dowex 1X8 (data not shown) as well as the higher zinc elution yield observed for the former.

The most important aspect is perhaps the concentration and distribution of exchange groups inside the resin beads. These commercial ion exchange resins have exchange capacities of 1.0 meq/mL-resin (polyacrylic) and 1.2 meq/mL-resin (polystyrene). Both resins showed a higher affinity for zinc cyanides than for the other complexes studied in the present work. Polystyrene resins showed large affinities for the divalent zinc and nickel cyanocomplexes, although they did not have the same shape (zinc cyanide is tetrahedral whereas nickel cyanide is square planar). It is therefore suggested that valence plays a more important role than complexes shape in adsorption on commercial ion exchange resins. Especially with polyacrylic resins, iron was the first to be eluted, followed by copper and finally zinc. Iron needed four exchange groups in the resin with an appropriate shape for loading and steric hindrance was the strongest for this complex. Similar behavior was observed for copper. The presence of copper in part as $Cu(CN)_4^{-3}$ may account for the affinity being lower than that observed for zinc cyanide. Overall, zinc cyanide as the complex with the highest affinity for both resins was taken up faster during loading. Conversely, it was released at the lowest rate during elution, especially in the case of nitrate solutions, which had a lower elution rate than thiocyanate.

One possible mechanism whereby elution can be carried out is the complexing of the adsorbed metal with molecules of the ligand. This approach was used to elute resin loaded with copper cyanide (Leão et al., 1998). A similar effect would be expected for thiocyanate elution, as thiocyanate was able to complex copper and iron (III). Nevertheless, the stability constants for cyanocomplexes of copper, iron, and zinc were larger than those observed for base metal-thiocyanate complexes, as shown in Table 2. This possibility is therefore unlikely. As a result it may be suggested that the elution mechanism for both eluants was ion exchange, where either thiocyanate or nitrate replaces the cyanocomplexes loaded on the resin (as shown in equations 1 and 2 for zinc cyanide).

$$2NO_3^- + \vdash Zn(CN)_4^{-2} \leftrightarrows 2 \vdash NO_3^- + Zn(CN)_4^{-2} \qquad (1)$$

$$2SCN^- + \vdash Zn(CN)_4^{-2} \leftrightarrows 2 \vdash SCN^- + Zn(CN)_4^{-2} \qquad (2)$$

where $\vdash$ represents the resin matrix.

Table 2: Stability constants for the metal – cyanide and metal- thiocyanate systems (Martel and Smith, 2003).

Complex	Stability constant Log(β)	Complex	Stability constant Log(β)
$[Fe(CN)_6^{-4}]$	35.4 (I = 0)	$[FeSCN]^+$	1.31 (I = 0)
$[Cu(CN)_3^{-2}]$	29.2 (I = 0)	$[Cu(SCN)_3]^{-2}$	11.6 (I = 5)
$[Cu(CN)_4^{-3}]$	30.8 (I =.0)	$[ZnSCN]^+$	1.33 (I = 0)
$[Zn(CN)_4]$	19.2 (I = 0)	$[Zn(SCN)_2]^0$	1.91 (I = 0)
		$[Zn(SCN)_3]^-$	2.00 (I = 0)
		$[Zn(SCN)_4]^{-2}$	1.63 (I = 0)

Achievement of a better elution with SCN^- than with nitrate was also observed for the resin Amberjet 4200 (O'Malley and Nicol, 2002) loaded with gold thiosulfate complexes. The effect of different concentrations (2.5 mol/L NH_4SCN and 2 mol/L $NaNO_3$ solutions) was assessed and it was demonstrated that the thiocyanate elution was faster and provided a higher metal concentration in the eluate than the nitrate solution. These results suggest that the nature and stereochemistry of the complex loaded on the resin are irrelevant during elution instead a specific interaction or affinity between SCN^- and NO_3^- and the exchange group is responsible for the elution features of the whole system. Thiocyanate is a highly polarized specie by virtue of the triple bond between C and N, and therefore it had a greater capacity than nitrate to elute metal cyanocomplexes from the resins studied.

This was corroborated by the effect of increased nitrate concentration − elution was improved by the higher nitrate concentration, while this effect was not as important as it was for thiocyanate.

CONCLUSIONS

The results presented in this study show that thiocyanate and nitrate solutions can be used to elute polyacrylic- and polystyrene-based strong base ion exchange resins loaded with copper, zinc, and iron cyanocomplexes. It was observed that iron and copper cyanides eluted more readily than did the zinc cyanide complex. Moreover, an increase in temperature from 25 °C to 50 °C had a small effect on both iron and copper cyanide elution, while the effect on the recovery of zinc cyanide from polyacrylic-based resins was significant. It was also found that for polystyrene-based resins temperature significantly affected the elution of iron cyanide, especially at lower concentrations of both thiocyanate and nitrate. The effectiveness of elution relied on the features of the resin as well as the eluant. It was shown that commercially available strong base resins can be used for efficient recovery of base metal cyanocomplexes. Notwithstanding, cyanide recovery with resins is site specific and a sound judgment based on the features of both the effluent to be treated and the resin is necessary for choosing the most suitable option. As demonstrated in this work, the nature of the resin and the eluant defines the patterns during elution and it is not possible to identify a priori the best combination.

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