SELECTIVE RECOVERY OF GOLD CYANIDE FROM SLURRIES USING HIGHLY SALINE WATER

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ABSTRACT

Due to the increased processing of ores that have a low grade and a complex mineralogy, the current challenge is to develop new technology that will revolutionise the gold industry. The use of alternative sorbents to carbon which have higher loading capacities, greater selectivity for gold cyanide and the ability to enhance the extraction of gold from refractory and preg-robbing ores is sought. The present study demonstrates that ion exchange resins can be used to selectively extract gold cyanide from saline solutions without compromising the loading capacity of the resin for gold. Using Raman spectroscopy, it has been established that the selective sorption of gold cyanide by ion exchange resins is due to the preferential formation of the tetrahedrally shaped \([\text{Cu(CN)}_4]^2-\) complex in saline solutions that contain free cyanide. The present study also demonstrates that saline water can be used to selectively elute copper cyanide and iron cyanide from resins. Conventional eluants, including KSCN and zinc cyanide, have also been investigated in order to determine the effect of functional group structure on the elution of metal cyanide complexes. The results of the present study suggest that a two stage stripping process for resins can be developed incorporating an inexpensive saline water elution step followed by the conventional zinc cyanide or KSCN elution method to selectively recover the valuable gold cyanide complex. The selective elution procedure allows for the recycling of cyanide that is bound to the copper and iron cyanide complexes.

INTRODUCTION

Over the last 25 years the carbon-in-pulp (CIP) process has become accepted as the main technology in the Western World for the recovery of gold from low grade and complex ore types. However the resin-in-pulp (RIP) process for precious metals recovery has been practised widely in the former Soviet Union, and in fact, the world’s first commercial application of RIP technology for gold recovery occurred at one of the largest gold mines in the Soviet Union in 1978 (Fleming, 1982).

Resins are more versatile substrates than activated carbon because specific functional groups can be introduced onto the resin matrix during synthesis to alter their sorptive properties. In addition, it has been demonstrated that resins in comparison to carbon have superior kinetics and greater equilibrium loading capacity of gold cyanide (Fleming and Cromberge, 1984a). It has also been proposed that ion exchange resins have the potential to minimise the effects of the re-adsorption of gold onto the ore (preg-robbing) during the leaching stage (Lukey, 2000).

A recent review considers the development of various types of ion exchange resins that have been investigated for their gold sorption properties (Lukey, 2000). It has been reported that the gold loading on resins decreases with increasing ionic strength (Fleming and Cromberge, 1984a). This is attributed to the increase in competition of anions such as chloride and sulphate for active sites on the resin that occupy the gold cyanide complex. In contrast, further studies have reported no change in gold sorption with strong-base resins (Hla, 1991). Similar work has also shown that the selectivity of resins is improved slightly in saline solutions (Hla, 1992). However no explanation was offered for the observed sorption behaviour of the metal cyanide complexes on the resins studied.

The stripping and regeneration procedure that was used in the former Soviet Union was complicated and time-consuming (Bolinski and Shirley, 1996). The typical stripping process required the selective removal of copper and iron by the use of NaCN followed by the elution of zinc and nickel by H_2SO_4. Thiourea was then used to remove the silver and gold that was loaded on the resin. Regeneration of the resin using sodium hydroxide at elevated temperatures (50°C - 60°C) was also necessary. The elution procedure subjected the resin to wide fluctuations in pH and consequently degradation of resin due to osmotic shock was an important consideration.

The recovery of gold cyanide from ion exchange resins has been the focus of many investigations in the
Western World (Hosking, 1984). From this work several suitable eluants have been proposed for the efficient recovery of gold and other metal cyanide complexes, including ammonium thiocyanate, thiourea and zinc cyanide (Fleming and Cromberge, 1984b).

The former Golden Jubilee Mine in South Africa initially used thiourea to remove metals from the resin (Seymore and Fleming, 1989). However, the use of an acidic reagent caused the precipitation of insoluble double metal complexes such as ZnFe[Fe(CN)$_6$] and Fe$_4$[Fe(CN)$_6$]$_3$ within the resin pores. The elution reagent was changed to alkaline zinc cyanide and good elution of all metal cyanide complexes was achieved. Zinc cyanide is also used as the eluant for the recovery of metal cyanide complexes from the recently piloted Vitrokle™ resin (Imperial Mining, 1998).

It has also been established that efficient elution of iron cyanide from strong-base resins is accomplished with a 2 M NaNO$_3$ solution. However, gold cyanide is also partially eluted in this process which makes the eluant impracticable (Riveros et al., 1993). It has also been shown that concentrated sodium chloride solutions are able to efficiently elute both copper and iron cyanide complexes from ion exchange resins (Leão et al., 1998). The focus of this investigation was on the recovery and recycling of cyanide from tailings streams. Therefore, the resins investigated were only loaded with copper, iron and nickel because these metals are high consumers of cyanide.

The behaviour of ion exchange resins in saline solutions is of interest to Australian mining companies because of the unusually highly saline process water used on the goldfields of Western Australia. The salinity of the available ground water at these locations is reported to be 200 g/l of total dissolved solids. The present study investigates the effect of saline solutions on the capacity and selectivity of ion exchange resins that contain different functional groups. The ability of saline solutions to selectively elute copper cyanide and iron cyanide from each resin will also be examined. It is proposed that the concentrated copper cyanide and iron cyanide eluate can be fed to a conventional AVR (acidification-volatisation-reneutralisation) or Cyanisorb process for the recovery and recycling of cyanide.

The elution of metal cyanide complexes using conventional eluants, KSCN and zinc cyanide, has also been investigated. It has been established that the ionic density and structure of the functional group do not significantly affect the elution of metals from resins using a KSCN eluant. However, it has been found that the zinc cyanide complex is not a good eluant for gold selective resins because gold cannot be significantly recovered from resins that have a low ionic density or large bulky functional groups.

Furthermore a sequential elution procedure is proposed whereby the elution of copper and iron cyanide is achieved by saline water, and conventional eluants such as thiocyanate or zinc cyanide are used to efficiently elute the gold cyanide complex. The resin can then be regenerated using conventional acid treatments.

EXPERIMENTAL METHODS

Ion exchange resins

The two ion exchange resins used in this study were synthesised using the procedure described by Lukey (2000). These resins are referred to as trimethylamine and dimethylamine, respectively. The trimethylamine resin contains trimethylammonium functional groups attached to a polystyrene-divinylbenzene matrix. The dimethylamine resin contains predominantly weak-base groups as well as some strong-base groups. The proposed structure of the functional groups on the dimethylamine resin is shown in Figure 1.

Figure 1 – Possible structures of the dimethylamine functional group. Adapted from Lukey et al. (1999b).

Equilibrium sorption tests using saline solution

Sorption tests were performed using the method and equipment previously described by Lukey et al. (1999a). Unless otherwise stated, the metal cyanide concentration used for each experiment was 5 mg/L Au and Ag, 15 mg/L Cu, and 10 mg/L Zn and Fe. The free cyanide concentration in each container was adjusted to approximately 200 mg/L prior to the addition of the
RESULTS AND DISCUSSION

The sorption of metal cyanide complexes from saline solutions

The results obtained for the sorption of a mixture of metal cyanide complexes in KCl solutions of varying salinity onto the trimethylamine and dimethylamine resins are presented in Figure 2 and Figure 3 respectively. Comparing Figure 3 with Figure 2, it is evident that when the total ionic strength of the solution is not adjusted, the dimethylamine resin loads less copper cyanide and iron cyanide than the trimethylamine resin. As a result, the equilibrium loading of the linear [Au(CN)2]− complex and the [Ag(CN)2]− complex is slightly greater on the dimethylamine resin. The decrease in the sorption of copper and iron on the dimethylamine resin in non-saline solutions can be explained in terms of the differences in structure of the functional group and the strong-base capacity of each resin (Lukey et al., 1999a).

It has been determined previously by Lukey (2000) that the strong-base capacity of the dimethylamine resin is lower than that for the trimethylamine resin. As a result it can be assumed that the ionic density (the number of ‘active sites’ per unit volume of resin) of the dimethylamine resin is lower than that for the trimethylamine resin. The decrease in ionic density (or the separation of ‘active’ sites on the resin) has been studied previously and has been shown to enhance the selectivity of strong-base resins for gold cyanide (Riveros, 1993). These results can be explained in terms of the valence of each metal cyanide complex and the number of functional groups required for sorption to occur.

As shown by Figure 4, the copper cyanide species exists in non-saline ([KCl] = 0) cyanide solution as [Cu(CN)2]2− and [Cu(CN)4]3−. It follows then that the copper cyanide complex requires two or three active functional groups to be in close proximity and of the right stereochemistry for sorption to take place. A decrease in the ionic density of the resin has the effect of increasing the distance between functional groups on the resin matrix and therefore decreasing the number of ‘active sites’ that are of the right size and geometry for sorption of copper cyanide complexes. This phenomenon has the effect of decreasing the loading of multivalent cyanide complexes such as copper and iron and to a lesser extent zinc, thereby increasing the selectivity of the resin for univalent anions such as gold and silver cyanide because these complexes only require a single functional group for sorption to occur.
Increasing the total ionic strength of solution by the addition of KCl has the effect of significantly increasing the selectivity of each resin studied. Figures 2 and 3 show that as the chloride concentration is gradually increased to 3 M, the loading of gold cyanide onto the trimethylamine and dimethylamine resin remains unchanged. In contrast, the loading of copper cyanide is significantly decreased. At a chloride concentration of 3 M, copper cyanide did not load onto either resin studied. Similar trends were observed for the iron cyanide complex.

Figure 2 - The effect of chloride concentration (by KCl addition) on the selectivity of the trimethylamine resin.

Figure 3 - The effect of chloride concentration (by KCl addition) on the selectivity of the dimethylamine resin.

It has been established by Lukey et al. (1999a) that the same loading profiles were obtained for each resin regardless of whether the chloride concentration was adjusted using KCl, NaCl or MgCl₂. It is then clear that univalent and bivalent cations (K⁺, Na⁺, Mg²⁺) do not significantly affect the sorption of metal cyanides onto each resin. In contrast, the chloride anion does have an effect on the sorption of metal cyanides.

Figure 4 shows that without the addition of KCl three peaks are observed in the Raman spectra for copper cyanide. The existence of three peaks in the spectra is consistent with previous work (Kappenstein et al., 1978). As the concentration of KCl is increased it is observed that the peak at 2108 cm⁻¹ gradually disappears. Therefore, the distribution of copper cyanide complexes changes in saline solution, preferentially forming [Cu(CN)₄]³⁻ when the free cyanide concentration is not limiting. Work by Lukey et al. (1999c) supports this contention. Consequently, it is proposed that the increase in selectivity of the trimethylamine and dimethylamine resins for gold cyanide over copper cyanide in saline solutions is due to the predominant formation of [Cu(CN)₄]³⁻ in solution. This complex is tetrahedral in geometry and is tri-valent. Consequently, the [Cu(CN)₄]³⁻ complex is unable to closely associate with the functional groups on either resin studied.

The elution of metal cyanide complexes using saline solutions

It is shown in Figures 5 and 6 that copper and iron cyanide are selectively eluted from the trimethylamine and dimethylamine resins using a 2 M KCl eluant containing 200 mg/L cyanide as KCN. The combined elution of gold cyanide and zinc cyanide from the
trimethylamine resin after the passing of 16 BV of eluant was less than 7%. It is important to note that this saline elution work has been extended to include resins having tripropylamine and dipropylamine functional groups (Lukey, 2000).

Structure ‘A’ is the weak-base form of the dimethylamine group. Structures ‘B’ and ‘C’ represent quaternary ammonium functional groups and consequently contain a fixed positive charge. Although it is very difficult to establish experimentally, it is possible that different copper cyanide complexes would tend to associate with different structures of the same functional group (either structures ‘B’ or ‘C’ in Figure 1) on the resin. Consequently, these differences in sorption of different species would affect the elution of copper cyanide from the resin.

It has been established by Lukey (2000) that similar elution profiles are obtained for each resin regardless of whether the saline eluant was prepared from KCl or MgCl₂. However, it appears from the work of Lukey (2000) that the kinetics of elution are slightly enhanced using the KCl eluant, which can be attributed to the easier diffusion of the univalent potassium cation into the resin pores than the divalent magnesium cation.

The elution of metal cyanide complexes using KSCN or [Zn(CN)₄]²⁻

The elution of metal cyanide complexes from the trimethylamine and dimethylamine resins using 2.0 M KSCN containing 200 mg/L cyanide (as KCN) is shown in Figures 7 and 8. As shown by Figure 7, greater than 95% of iron, copper and silver has been eluted from the trimethylamine resin within the first 8 bed volumes of the 2.0 M KSCN eluant. A similar elution profile is also obtained for the dimethylamine resin (Figure 8). It is important to note that the strongly sorbed gold cyanide and zinc cyanide complexes are slower at being eluted. It appears that the structure of the functional group has no substantial influence on the elution of metal cyanide complexes from ion exchange resins using a potassium thiocyanate eluant.

The elution profiles for trimethylamine and dimethylamine resins using a 0.5 M zinc cyanide eluant are presented in Figures 9 and 10. For the macroporous trimethylamine resin, all of the iron, copper and silver were eluted from the resin within the first 4 bed volumes of eluant. The elution of gold from the trimethylamine resin is also similar to that observed for the potassium thiocyanate eluant (Figure 7).

Recent work by has shown that as the length of the alkyl chain of the functional group is increased the elution of gold from resins using zinc cyanide is substantially decreased, while the elution of other metals seems to be affected to a lesser extent (Lukey, 2000). Figure 10 shows that the poor elution of gold using zinc cyanide is observed for the dimethylamine resin. As stated previously, this is a weak-base resin that contains
a small amount of strong-base functional groups. Consequently, the dimethylamine resin has a low ionic density. It is proposed that the poor elution of gold from resins of a low ionic density is predominantly due to the stereochemistry and charge of the tetrahedral [Zn(CN)₄]²⁻ complex. For the zinc cyanide complex to load onto the resin and therefore elute the loaded gold cyanide complex it requires at least two functional groups of the correct size and spatial geometry to satisfy electroneutrality. This requirement is less easily satisfied for resins of a low ionic density because the functional groups are not close together and consequently poor elution of gold is observed.

**Figure 7** - Percentage elution of metals from trimethylamine resin using 2.0 M KSCN. [CN⁻] = 200 mg/L, pH = 12.2. Elution temperature of 22°C.

Figure 8 - Percentage elution of metals from dimethylamine resin using 2.0 M KSCN. [CN⁻] = 200 mg/L, pH = 12.6. Elution temperature of 22°C.

**Figure 9** - Percentage elution of metals from trimethylamine resin using 0.5 M zinc cyanide. pH approximately 10.7. Elution temperature of 50°C.

**Figure 10** - Percentage elution of metals from dimethylamine resin using 0.5 M zinc cyanide. pH approximately 10.6. Elution temperature of 50°C.

Zinc cyanide is the preferred eluant for the recovery of metals from ion exchange resins and it has been successfully used at the former Golden Jubilee mine in South Africa. However the results of the current study show that the ability of the eluant to simultaneously recover metals from the resin is dependent upon the charge and consequently the hydration of the eluant species (thiocyanate or zinc cyanide), the type of functional group attached to the resin matrix, and also the strong-base capacity of the resin. Therefore, potassium thiocyanate can be used to recover metals from all types of strong-base resins studied because it has a univalent charge and as a result is less hydrated than the divalent zinc cyanide complex. In contrast, the [Zn(CN)₄]²⁻ complex can only be used to elute metals from a resin that has a high strong-base capacity and preferably a functional group with a short alkyl chain such as trimethylamine. These resin features lower the hydrophobic nature of the resin and as a result the
conditions within the resin are more favourable for the hydrated zinc cyanide complex.

The results of this study show that a suitable eluant is yet to be proposed that can rapidly (< 10 BV) and completely elute all metals from a variety of strong-base ion exchange resins. However, two suitable options still exist and have yet to be exploited. Firstly, it has been shown that a non-selective resin (e.g. trimethylamine) selectively sorbs the gold cyanide complex in saline solutions. The gold loaded on the resin could then be eluted using 0.5 M zinc cyanide as reported in this study. Essentially then, in saline solutions a gold selective resin exists that has the physical properties (high ionic density, short alkyl chain on functional group) of a non-selective resin. Consequently, zinc cyanide can be used as an efficient eluant.

However, if the salinity of the leaching solution is not high enough so that selective sorption of gold cyanide can be achieved, another process option is available. The results of the current study and that by Lukey (2000) have established that saline solutions can be used to selectively elute iron and copper from ion exchange resins containing different functional groups. The eluted resin that is still loaded predominantly with gold could then be returned to the sorption circuit, whereby the loading of gold on the resin could be gradually increased. A thiocyanate eluant could then be used to recover the gold loaded onto the resin.

CONCLUSIONS AND SIGNIFICANCE

Increasing the salinity of solution during sorption increases the selectivity of anion exchange resins without adversely affecting the loading capacity for gold cyanide. Using Raman spectroscopy, it has been established that the selective sorption of gold cyanide by ion exchange resins is due to the preferential formation of the tetrahedrally shaped \([\text{Cu(CN)}_4]^{3-}\) complex in saline solutions that contain free cyanide. This complex requires at least three active sites of the correct size and spatial geometry for sorption to occur. Consequently, other anions are able to successfully compete for sorption sites on the resin.

It has also been established that saline solutions can be used to selectively elute iron cyanide and copper cyanide complexes from the resins studied. Negligible elution of gold cyanide and zinc cyanide complexes with saline eluants was observed. It has been shown that a significant amount of copper is eluted from resins that have a high ionic density using saline KCl solutions. This is due to the ability of the chloride anions to compete with the tetrahedral \([\text{Cu(CN)}_4]^{3-}\) complex that predominantly loads onto resins that have a high ionic density.

This study has also compared the elution performance of potassium thiocyanate and zinc cyanide eluants for the trimethylamine and dimethylamine resins. The concentration of cyanide in each eluant was approximately 200 mg/L. It was established that a potassium thiocyanate eluant at pH more than 12 can be used to simultaneously recover all metals from each resin. This result is in accordance with previous studies and is attributed to the highly polarised thiocyanate anion having a stronger affinity for the resin partly due to its univalent charge, linear geometry and degree of hydration. However, the zinc cyanide eluant was unable to significantly elute the gold cyanide complex from the dimethylamine resin. This was attributed to the low ionic density of this resin, and consequently, the inability of the divalent and tetrahedral zinc cyanide complex to associate closely with the functional group to replace the linear gold cyanide complex.

The combined results of the current study suggest that a novel sorption and elution procedure can be proposed for the recovery of gold using ion exchange resins. These alternative processes make use of saline water to either selectively sorb the gold cyanide complex from solution or to selectively elute copper and iron cyanide from the resin. Conventional eluants such as zinc cyanide or thiocyanate could then be employed to recover the gold that is predominantly loaded onto the resin with a high degree of purity.

The proposed two-stage elution process is cost-effective particularly in areas where the salinity of available ground water is 200 g/L (Western Australia). In this instance the reagent cost is considerably decreased because only a small portion of thiocyanate would be required to recover the gold. Furthermore, the selective elution procedure allows for the recycling of cyanide that is bound to the copper and iron cyanide complexes. This leads to a significant reagent cost reduction.

REFERENCES


