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The Effect of Functional Group Structure on the Elution of Metal Cyanide Complexes from Ion-Exchange Resins

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ABSTRACT

Previous investigations have established that the thiocyanate anion and the zinc cyanide complex are suitable eluants for the simultaneous recovery of metal cyanide complexes from ion-exchange resins. However, the effect of the ionic density of the resin and the stereochemistry of the functional group on metal recovery has never been systematically studied. The present study investigated the elution properties of five experimental resins that have the same type of resin matrix but contain different aliphatic amino functional groups. It is shown that ammonium thiocyanate is not a suitable eluant because iron and zinc are not completely eluted from any of the resins studied. It has been proposed that this is due to the precipitation of $Zn_2[Fe(CN)_6]$ and possibly $Fe_4[Fe(CN)_6]_3$ within the resin pores. It has been established that potassium thiocyanate at a pH greater than 12 can be used to recover more than 80% of copper, zinc, and iron within the first 10 bed volumes of eluant for most resins. The recovery of gold from each resin using potassium thiocyanate has been shown to be considerably slower than that of other metals, with approximately 60% recovered after 20 bed volumes of eluant. It has been found that the length of the alkyl chain of the functional group does not significantly affect the elution of metal cyanide complexes from the resins studied using the thiocyanate eluant. The elution of metals from all resins has been found to be superior when using a 0.5 M zinc cyanide eluant at a temperature of 50°C. More than 90% of copper, silver and iron were recovered from most resins within 4 bed volumes of eluant. However, the recovery of gold using a zinc cyanide eluant is dependent upon the ionic density of the resin and also the stereochemistry of the attached functional group. The results of this study show that zinc cyanide is not a suitable eluant for gold-selective ion-exchange resins.

Key Words. Ion exchange; Cyanidation; Elution; Thiocyanate; Zinc cyanide; Selective; Gold

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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 (1, 2). However the resin-in-pulp (RIP) process for precious metals recovery has been practiced widely in the former Soviet Union for many years (3) and 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 (4).

The RIP process involves the contact of ion-exchange resins directly with cyanide-leached pulp in countercurrent flow. The gold loaded onto the resin is later recovered by elution once the resin has been separated from the pulp by screening. If necessary, the resin is regenerated after gold elution is complete. The adoption of the CIP process in the Western world can be partly attributed to the complicated and time-consuming stripping and regeneration procedure that at the time was required for the recovery of gold from ion-exchange resins (3). 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 were loaded on the resin. Regeneration of the resin using sodium hydroxide as well as elevated temperatures (50–60°C) was also necessary. The elution procedure subjected the resin to wide fluctuations in pH and consequently loss of resin due to osmotic shock was an important consideration.

The recovery of gold cyanide from anion-exchange resins has been the focus of many investigations in the Western world (5). From this work, several suitable eluants have been proposed for the efficient recovery of gold and other metal cyanide complexes, including ammonium thiocyanate, zinc cyanide, or thiourea (6). Other reagents have also been investigated, including a combination of mineral acids and polar solvents such as acetone (7, 8) or organic–water mixtures (9). A recent study (10) has also established that highly saline solutions can be used to selectively elute copper cyanide and iron cyanide complexes from a variety of ion-exchange resins containing different aliphatic amino functional groups.

The thiocyanate anion and the zinc cyanide complex have more affinity for the resin than the gold cyanide complex, and thus under the correct conditions are able to displace the gold cyanide complex (6). Mineral acids such as sulfuric acid can be used to regenerate the resin, but in strong acids the thiocyanate anion can decompose to form elemental sulfur, which may poison the resin (1). An alternative approach involves complexing the thiocyanate anion with ferric ions to form a cationic complex that will not be bound to the resin (11).

The former Golden Jubilee Mine in South Africa initially used thiourea to remove metals from the resin. This elution method had the advantages of fast kinetics, simplicity of operation, and regeneration of the resin was unnecessary (12, 13). However the use of an acidic reagent caused the precipitation of insoluble double metal complexes such as $Zn_2[Fe(CN)_6]$ and $Fe_4[Fe(CN)_6]_3$ within the resin pores. Consequently, with the exception of copper, very few metals were stripped from the resin, and as a result the capacity of the resin for gold substantially decreased. The elution reagent was changed to alkaline zinc cyanide and good elution of all metal cyanide complexes was achieved. However, with this method the resin needed to be regenerated uisng 1 M H_2SO_4. Zinc cyanide is also used as the eluant for the recovery of metal cyanide complexes from the recently piloted Vitrokele™ resin (14).

The present study determines the effect of the ionic density and hydrophilicity of the resin and also the stereochemistry of the functional group on the elution of metal cyanide complexes using the thiocyanate anion as well as the zinc cyanide complex as eluants. It has been established that the efficient elution of zinc and iron from ion-exchange resins is dependent on the pH of the thiocyanate eluant. As a consequence, the present study shows for the first time that ammonium thiocyanate is not a good eluant for ion-exchange resins that contain significant quantities of zinc and iron. In addition, the current study shows that the ionic density and structure of the functional group do not significantly affect the elution of metals from ion-exchange resins using a potassium thiocyanate eluant. However, it has been established 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.

EXPERIMENTAL PROCEDURES

Ion-Exchange Resin Synthesis and Preparation

Macroporous chloromethylated polystyrene (D2780) spherical beads (the polymer substrate) were obtained from Purolite International Ltd, United Kingdom. The beads were off-white in appearance and had a particle size of 500–800 microns. The beads had a reported chlorine content from the manufacturer of 22%, and the crosslinking by divinylbenzene was approximately 10%. Based on elemental analysis, the chloromethyl group content was determined to be 6 mmol/g of resin.

Ion-exchange resins were synthesized by the method previously reported (15). Unless otherwise stated, all ion-exchange resins were in the chloride form following synthesis. The commercial strong-base resin Amberjet 4400 (chloride form) was obtained from Rohm and Haas, France. Amberjet 4400 contains trimethylamine functional groups affixed to a gelular polystyrene–divinylbenzene matrix. Amberjet 4400 has superseded Rohm and Haas's resin IRA 400.

Determination of Resin Strong-Base Capacity

The strong-base capacity (the number of quaternary ammonium groups) of each resin was determined in a recent study (15). Each resin (in the chloride form) was treated with an excess of sodium hydroxide solution in a column for up to 5 hours. This treatment causes the strong-base groups on the resin to load hydroxide ions, while the weak-base groups on the resin revert to the free-base form. Each resin was then washed with distilled water for up to 2 hours to remove free hydroxide ions from within the resin pores. Excess sodium chloride was used to elute the hydroxide ions from the resin until no change in the pH entering or leaving the column was observed. The effluent was then titrated with dilute hydrochloric acid (0.01 M) to determine the concentration of hydroxide ions that were loaded onto the resin. The strong-base capacity of each resin studied is presented in Table 1.

Determination of Cyanide in Solution

The silver-nitrate-titrimetric method of cyanide determination was used for all measurements of the cyanide anion. Note that cyanide that is not complexed with a metal atom is commonly referred to as “free” or “excess” cyanide. This method is based on the formation of $[Ag(CN)_2]^-$ as silver nitrate is added to a cyanide solution. The end point of the titration is reached when a silver-sensitive indicator detects an excess of silver. Unless otherwise stated, rhodinine (para-dimethylaminobenzylidene, supplied by Rowe Scientific, AR Grade) was used as an indicator. The end point was taken to be the final color change from canary yellow to salmon. The presence of labile copper cyanide interferes with the end point by the loss of cyanide associated with the copper complex. Therefore an increase in the value of free cyanide is ob-

TABLE 1
Comparison of the Loading of Each Metal on Ion-Exchange Resins Containing Different Functional Groups

Resin	Strong base capacity (mmol/mL)	Metal loading (mg/mL)				
		Au	Ag	Cu	Zn	Fe
Experimental						
Trimethylamine	0.86	4.42	3.18	13.77	9.36	4.23
Tripropylamine	0.35	4.85	4.27	6.62	9.75	0.05
Dimethylamine	0.33	4.80	3.61	5.35	2.93	0.27
Dipropylamine	0.10	4.84	3.47	1.77	4.58	0.57
Commercial						
Amberjet 4400	1.33	4.81	3.78	17.73	9.81	6.69

tained. This effect was minimized by the dilution of all samples as well as by titrating past the first color change until the solution retained the salmon hue.

Sorption of Metal Cyanides onto Ion-Exchange Resins

Sorption tests were performed in baffled 1-PVC containers that were attached to an overhead stirrer bench that had the capacity to stir 28 containers. Each container was immersed in a water bath at a constant temperature of 22°C. Each resin was loaded with gold, silver, copper, zinc, and iron as cyanide complexes by contacting 5 × 20 mL portions of wet settled resin with 1 L of solution. The composition of this mixture was 100 ppm Au, 100 ppm Ag, 400 ppm Cu, 200 ppm Zn, and 200 ppm Fe. The concentration of free cyanide in each container was determined by the method previously stated and then adjusted to approximately 200 ppm prior to sorption. Each container was stirred for 72 hours at 200 rpm. Loss of solution due to evaporation was negligible. Samples (3 mL) of the solution in each container were taken at the beginning and end of each experiment. The loading of each metal on the resin was determined by mass balance. After sorption, each portion of loaded resin was separated from the metal cyanide solution and washed with distilled water (pH of 7). These portions were combined for each type of resin, and the total metal loading estimated by averaging the metal loading of each combined portion. No attempt was made to analyze each resin for metal content. The metal content of each resin used in the elution is shown in Table 1.

Preparation of Eluant Solution

Unless otherwise stated, eluant solutions were prepared from NH_4SCN, KSCN, and $Zn(CN)_2$ obtained from Ajax Laboratory Chemicals. The concentration of the thiocyanate anion in both NH_4SCN and KSCN eluants was 2.0 M. The free cyanide concentration of each thiocyanate eluant was adjusted to approximately 200 ppm by the addition of KCN. The zinc cyanide eluant (0.5 M Zn) was prepared by the addition of $Zn(CN)_2$ powder to a cyanide solution (as KCN) at a CN:Zn molar ratio of 2.5. The free cyanide concentration of the zinc cyanide eluant was not adjusted. The pH of KSCN eluant was adjusted to 12 using KOH to ensure that no precipitation of metals occurred during the elution experiment. The pH of the NH_4SCN eluant was buffered at approximately 7. All thiocyanate elutions were carried out at 22°C. However, it was necessary to use a temperature of 50°C for the zinc cyanide eluant.

Elution Apparatus and Procedure

All elution experiments were conducted in a glass column with an internal diameter of 12 mm. The piping and associated connections were made from polyethylene tubing. Unless otherwise stated, a water jacket was used to maintain a constant and uniform temperature of 22°C or 50°C throughout the resin bed. The resin (15 mL wet settled volume) was dropped into the glass column containing half a bed volume of distilled water at the elution temperature. This action minimized the air bubbles in the column. Subsequent removal of air bubbles that formed in the column was achieved by inserting a thin glass rod into the resin bed.

The resin bed was washed with distilled water for 1 hour in situ prior to elution. No loss of metal was reported during this washing time. The eluant was passed downwards through the column at a flow rate of 1.4–1.5 mL/min by a positive displacement pump. This flow rate corresponds to approximately 5 BV/h (where 1 BV is defined as the empty volume of the reactor that is occupied by the packed bed of ion-exchange resin). This flow rate was chosen because it enabled efficient sampling of the eluate to fully determine the elution profile of each element. Unless otherwise stated, samples of the eluate were taken over a 2 minute period. The flow rate of the eluant was monitored periodically and no change was observed throughout the course of the elution experiment.

Determination of Metals in Solution

The concentration of each metal in solution was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Metal cyanide solutions were prepared as described previously and were used as metal calibration standards (16). Unless stated otherwise, the same standards were used for all results reported in this study. To ensure that the metal value reported is absolute, a sample of each standard was acidified with aqua regia and the metal content analyzed by ICP-OES using certified standards obtained from Merck Australia Pty Ltd.

RESULTS AND DISCUSSION

The results obtained for the elution of Amberjet 4400 and the dimethylamine resin using 2.0 M NH_4SCN containing initially 200 ppm cyanide are presented in Figs. 1 and 2. The elution of metals from the same resins using 2.0 M KSCN containing 200 ppm cyanide is presented in Figs. 3 and 4. The elution results obtained for the other resins studied are summarized in Table 2.

It is shown for Amberjet 4400 and the dimethylamine resin that copper cyanide and silver cyanide are completely eluted within 10 bed volumes of eluant (Figs. 1 and 2). At least 18 bed volumes of eluant are required to achieve an elution of greater than 80% of the gold cyanide complex from each resin. A previous study has shown that the elution of gold from ion-exchange resins was slow and inefficient using 2.0 M NH_4SCN (1). For both resins the

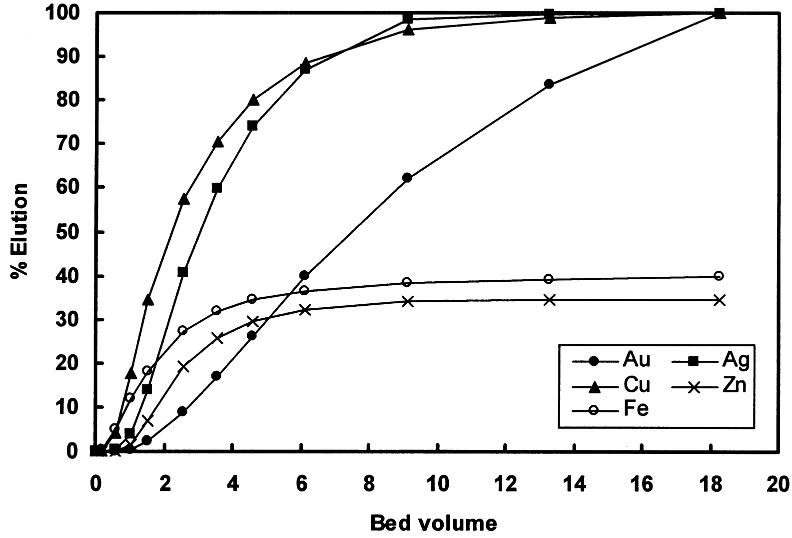

FIG. 1 Percentage of elution of metals from Amberjet 4400 resin using 2.0 M NH_4SCN. Concentration of free cyanide in eluant is approximately 200 ppm. pH = 7. Elution temperature of 22°C.

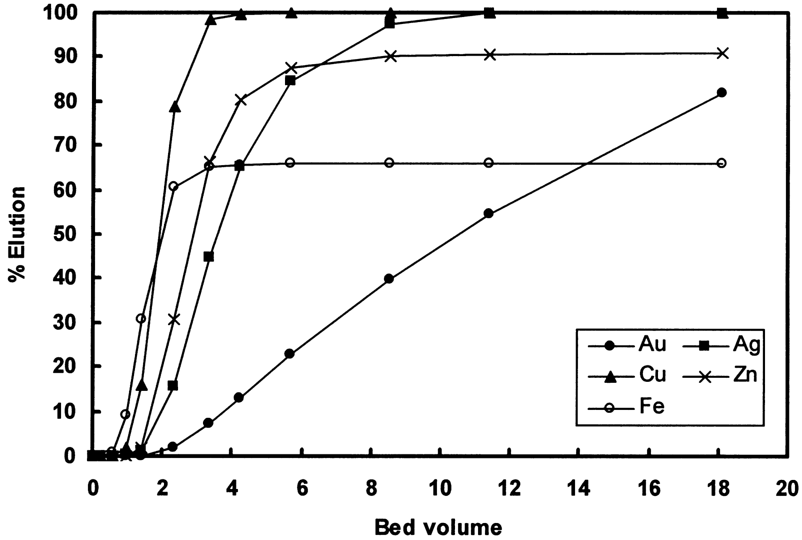

FIG. 2 Percentage of elution of metals from dimethylamine resin using 2.0 M NH_4SCN. Concentration of free cyanide in eluant is approximately 200 ppm. pH = 7. Elution temperature of 22°C.

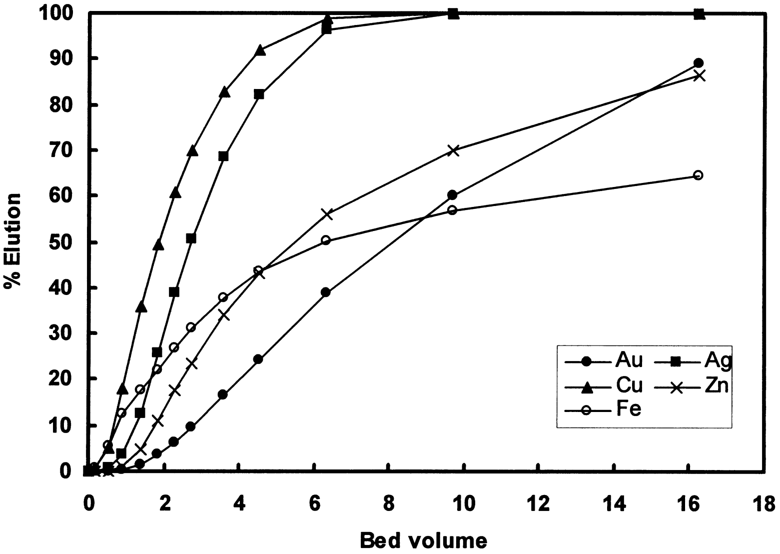

FIG. 3 Percentage of elution of metals from Amberjet 4400 resin using 2.0 M KSCN. Concentration of free cyanide in eluant is approximately 200 ppm. pH = 12.6. Elution temperature of 22°C.

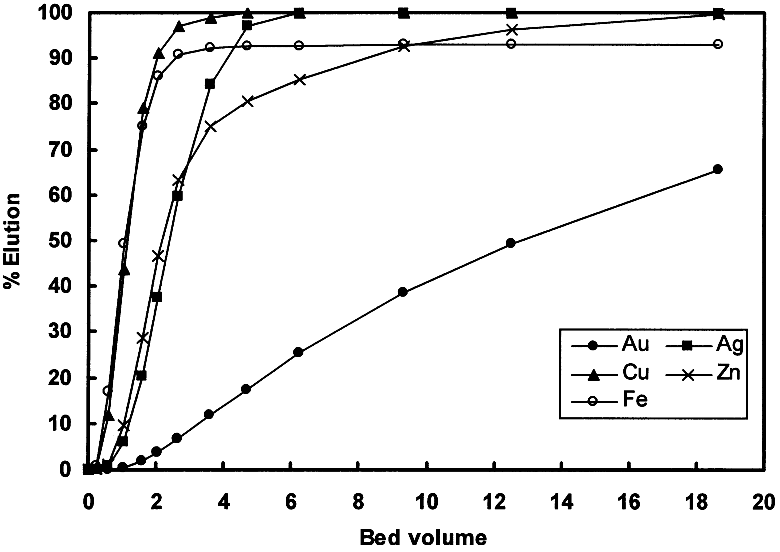

FIG. 4 Percentage of elution of metals from dimethylamine resin using 2.0 M KSCN. Concentration of free cyanide in eluant is approximately 200 ppm. pH = 12.6 Elution temperature of 22°C.

incomplete elution of zinc cyanide and iron cyanide is observed using 2.0 M NH_4SCN. In particular, less than 40% of zinc or iron were eluted from Amberjet 4400 (Fig. 1). Comparing Figs. 3 and 4 with Figs. 1 and 2, it is shown that a substantial increase in the elution of zinc and iron is observed for both resins using a 2.0 M KSCN eluant containing 200 ppm cyanide. The elution of other metals remains the same for both eluants.

These results indicate that ammonium thiocyanate is not a suitable eluant for ion-exchange resins that contain significant quantities of iron cyanide or zinc cyanide. This observation contradicts previous studies indicating that ammonium thiocyanate is an efficient reagent for the elution of gold cyanide from ion-exchange resins (6). However, it is important to note that much of this work was performed on resins only loaded with the gold cyanide complex.

It is proposed that the poor elution of iron and zinc from the resins studied is due to the formation and subsequent precipitation of double metal complexes of the type $Zn_2[Fe(CN)_6]$ or $Fe_4[Fe(CN)_6]_3$ within the resin bead pores. The formation of these types of species has been postulated previously using an ammonium thiocyanate eluant (17). The precipitation of these types of double metal complexes is also often reported when thiourea is used as an eluant (13). Furthermore, it was observed that as the ammonium thiocyanate elution progressed for each resin, a white precipitate formed in the column. This is further evidence of the presence of the zinc ferrocyanide double metal complex.

It has been shown that the formation of zinc ferrocyanide complexes is dependent on the pH of the solution as well as the zinc-to-iron ratio (18). The zinc ferrocyanide complex is insoluble in an acidic medium. The constant addition of alkali to the ammonium thiocyanate eluant was undesirable, and as a result the pH of the eluant was unable to be maintained at a pH greater than 7 because of the rapid formation of the hydronium ion in solution that lowers the pH (Eq. 1).

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + NH_3\ (aq) \qquad (1)$$

As the pH of the ammonium thiocyanate eluant decreases because of the formation of hydronium ions in solution, the loss of cyanide due to volatilization of HCN increases dramatically. It has previously been established that at a pH of 7, almost 100% of cyanide is in the HCN form (19). Consequently, it is possible that the white precipitate that forms is due to the formation of CuSCN in very low cyanide concentrations (20). However, it has been established that concentrated solutions of thiocyanate dissolve CuSCN (20). In addition, it was observed that the white precipitate turned a reddish brown with time. This is an indication of iron hydroxide formation. This observation provides further evidence for the formation of $Zn_2[Fe(CN)_6]$.

A similar double metal complex is known to occur between ferricyanide and ferrous ions in solution, forming the well known Prussian Blue complex,

TABLE 2
Elution of Metal Cyanide Complexes from Ion-Exchange Resins Using 2.0 M KSCN. Concentration

	Metal					
	Au			Ag		
Resin	2 BV	8 BV	16 BV	2 BV	8 BV	16 BV
Trimethylamine	3.92	50.01	74.83	23.18	98.85	100.0
Tripropylamine	3.81	28.53	54.94	47.28	100.0	100.0
Dimethylamine	3.54	32.88	58.41	36.10	99.95	100.0
Dipropylamine	6.80	37.38	66.56	83.40	99.91	99.94
Amberjet 4400	4.58	49.27	88.03	30.54	98.24	100.0

$Fe_4[Fe(CN)_6]_3$ (21). This complex is also insoluble in an acidic medium and therefore it is possible that it could precipitate within the pores of the resin causing the poor elution of iron.

In strongly alkaline conditions ($pH > 12$), zinc ferrocyanide complexes are soluble (18). As a result, their formation was not observed for the 2.0 M KSCN eluant because the pH could be maintained higher than 12 using KOH. As shown by Table 2, greater than 95% of iron, copper, and silver were eluted from the trimethylamine and tripropylamine resin within the first 8 bed volumes of the 2.0 M KSCN eluant containing a concentration of approximately 200 ppm cyanide. The strongly adsorbed gold cyanide and zinc cyanide complexes were substantially slower at being eluted. It is also shown by Table 2 that the large octahedrally shaped iron cyanide complex and the trigonal planar and tetrahedral copper cyanide complex are more easily eluted from each resin than the highly polarized linear gold cyanide complex. Therefore, it appears that the length of the alkyl chain of the functional group has no substantial influence on the elution of metal cyanide complexes from ion-exchange resins using a potassium thiocyanate eluant. Instead, the relative affinity that each complex has for the resin is important.

From Table 2 it can be seen that very poor elution of zinc and copper is observed for the dipropylamine resin using the potassium thiocyanate eluant. However, the elution of gold, silver, and iron at 8 and 16 bed volumes, respectively, was similar to that obtained for the tripropylamine resin. The dipropylamine resin has a low strong-base capacity compared with the other resins studied; thus the ionic density (the number of "active sites" per unit volume) of the resin is also significantly lower (Table 1).

A previous study has established, using CP/MAS ^{13}C-NMR and FTIR, that the speciation of copper cyanide on the dipropylamine resin is different than of Free Cyanide in Eluant is Approximately 200 ppm. pH 5 12.2–12.6. Eluant temperature 5 22°C

eluted [%]								
Cu			Zn			Fe		
2 BV	8 BV	16 BV	2 BV	8 BV	16 BV	2 BV	8 BV	16 BV
70.24	100.0	100.0	11.74	80.40	94.78	96.17	100.0	100.0
90.47	100.0	100.0	27.71	76.23	87.39	70.41	99.37	100.0
90.10	100.0	100.0	45.27	89.45	98.18	85.32	92.87	93.13
37.23	45.70	50.08	33.40	52.89	61.23	77.24	87.26	89.57
53.69	99.49	100.0	13.36	62.89	86.01	23.73	53.43	64.19

that for the other resins studied. In particular, the dipropylamine resin loads the linear $[Cu(CN)_2]^-$ complex as well as $[Cu(CN)_3]^{2-}$ on the resin. It was also shown that the tetrahedral $[Cu(CN)_4]^{3-}$ complex does not load on the dipropylamine resin (15). This was attributed to the spacing of ionic groups on the resin due to the low strong-base capacity of the dipropylamine resin. Therefore it would be expected that the elution profile of copper cyanide from the dipropylamine resin would be different from the other resins studied because of the difference in copper cyanide speciation on the resin. However, it is shown in Table 2 that the linear gold cyanide complex was displaced from the resin using 2.0 M KSCN, so it would be expected that $[Cu(CN)_2]^-$ would also be eluted. Although not observed in the copper cyanide speciation study (15), it is possible that $[Cu(CN)_2]^-$ loaded on the resin partly decomposes to form insoluble CuCN, thereby causing the poor elution of copper from the dipropylamine resin. In addition to conventional ion exchange, it is also possible that some metal cyanide complexes may adsorb onto the dipropylamine resin by the formation of ion pairs similar to that proposed for activated carbon (22). This sorption mechanism has been proposed previously to explain the unexpected sorption behavior of some experimental weak-base resins (23). Consequently, such species would not be significantly eluted using a thiocyanate eluant.

The elution profiles for Amberjet 4400, trimethylamine, and dimethylamine resins using a 0.5 M zinc cyanide eluant are presented in Fig. 5 to 7. The elution results obtained for the other resins studied are shown in Table 3. Comparing Fig. 5 with Fig. 6, it is shown that similar elution profiles for each metal are obtained for Amberjet 4400 and the trimethylamine resin. 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. It is also shown

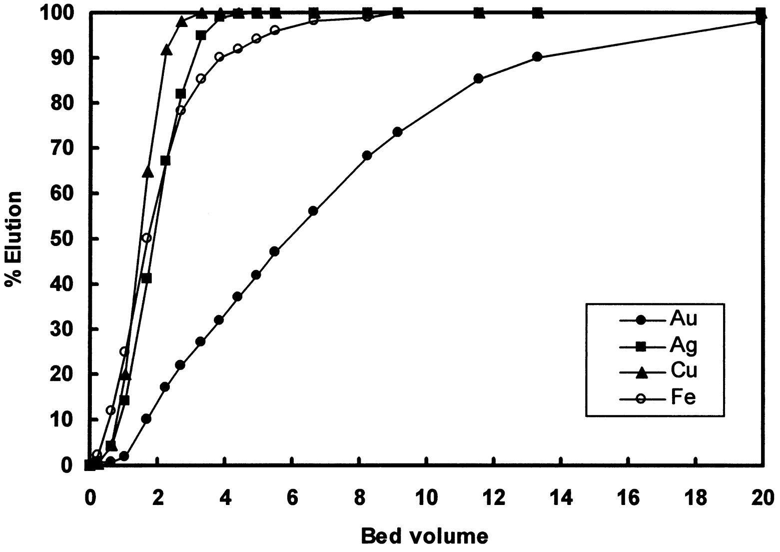

FIG. 5 Percentage of elution of metals from Amberjet 4400 resin using 0.5 M zinc cyanide. pH approximately 10.7. Elution temperature of 50°C.

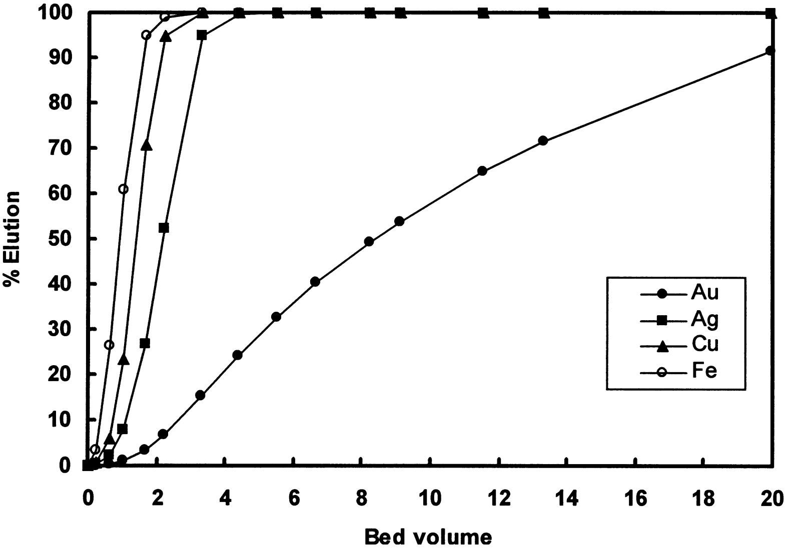

FIG. 6 Percentage of elution of metals from trimethylamine resin using 0.5 M zinc cyanide. pH approximately 10.7. Elution temperature of 50°C.

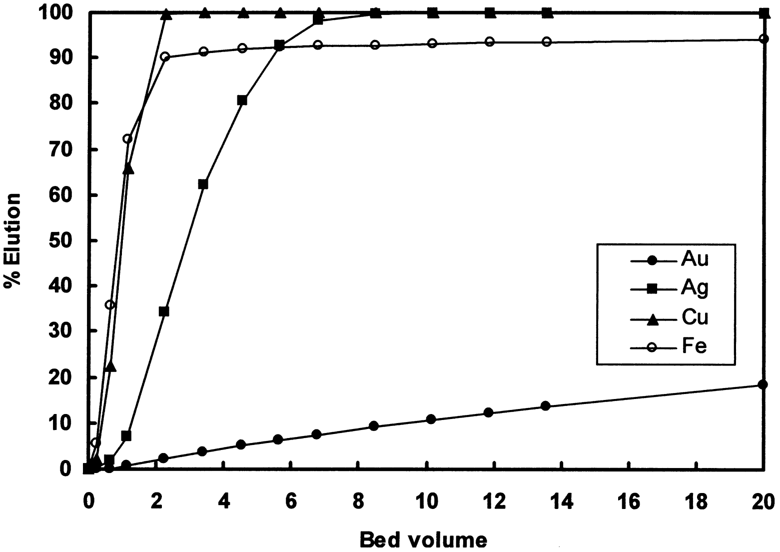

FIG. 7 Percentage of elution of metals from dimethylamine resin using 0.5 M zinc cyanide. pH approximately 10.6. Elution temperature of 50°C.

that the elution of the large octahedrally shaped iron cyanide complex is slower for the Amberjet 400 resin which has a gelular matrix structure. This phenomenon has recently been observed for the same resin using a highly saline eluant (10). Therefore it appears that large complexes diffuse more slowly from gel-type matrices than from the macroporous counterparts, such as the trimethylamine resin. The elution of gold from both resins was also similar to that observed for the potassium thiocyanate eluant (Tables 2 and 3).

From Table 3 it can be seen that as the length of the alkyl chain of the functional group is increased the elution of gold from the resin is substantially decreased. The elution of the other metals seems to be affected less by an increase in the length of the alkyl chain. The poor elution of gold using zinc cyanide is also observed for the dimethylamine and dipropylamine resins. As stated previously, these are predominantly weak-base resins that contain a small amount of strong-base functional groups. Consequently, the dimethylamine and dipropylamine resins have 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 eas-

TABLE 3
Elution of Metal Cyanide Complexes from Ion-Exchange Resins Using

						Metal
	Au			Ag		
Resin	2 BV	8 BV	16 BV	2 BV	8 BV	16 BV
Trimethylamine	5.20	49.36	79.7	41.24	100.0	100.0
Tripropylamine	1.43	7.150	13.52	30.97	100.0	100.0
Dimethylamine	1.79	8.652	15.34	28.06	99.23	100.0
Dipropylamine	0.37	1.978	3.671	12.76	68.60	98.11
Amberjet 4400	13.98	68.21	93.27	55.80	100.0	100.0

ily satisfied for resins of a low ionic density because the functional groups are not close together, and consequently poor elution of gold is observed.

These results indicate that the zinc cyanide eluant is unable to recover gold from ion-exchange resins that contain large and bulky functional groups or resins that possess a low ionic density, such as tripropylamine and dipropylamine. A previous study has shown that resins that have a high ionic density exhibit nonselective adsorption properties and that by increasing the distance between ‘active sites’ (decreasing the ionic density) multivalent complexes such as $[Fe(CN)_6]^{4-}$ and $[Cu(CN)_4]^{3-}$ are unable to load onto the resin (24). As shown by Table 1, as the strong-base capacity of the resin is decreased, the loading of iron cyanide and copper cyanide is decreased. The ionic density of the resin does not affect the loading of the univalent gold cyanide complex. Therefore, the use of a gold-selective ion-exchange resin is highly desirable in a RIP process because the resin potentially has a greater loading capacity for the valuable gold species and also gold of a higher purity can be obtained after elution. In addition, the potential of fouling the resin due to the formation of precipitates is dramatically decreased.

Comparing the percentage of elution values at 2 bed volumes presented in Table 3 with those in Table 2 it is found that copper, silver, and iron are eluted faster from most resins using the zinc cyanide eluant. This has been reported previously (6) and is possibly due to the higher temperature of the zinc cyanide eluant (50°C) as well as the divalent charge of the zinc cyanide complex compared to the univalent thiocyanate ion. It is noteworthy that the poor elution of copper cyanide from the dipropylamine resin was also observed using the zinc cyanide eluant (Table 3).

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

0.5 M $[Zn(CN)_4]^{2-}$ Eluant. pH = 10.4. Eluant temperature = 50°C

eluted [%]

Cu			Fe		
2 BV	8 BV	16 BV	2 BV	8 BV	16 BV
84.48	100.0	100.0	97.27	100.0	100.0
99.49	100.0	100.0	96.03	100.0	100.0
91.99	100.0	100.0	86.06	92.72	93.62
42.66	52.92	53.86	69.33	83.86	91.98
80.37	100.0	100.0	59.68	99.79	100.0

ability of the eluant to recover metals from the resin is dependent on 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 favorable for the hydrated zinc cyanide complex.

Presented in Fig. 8 to 11 are the concentration profiles of each metal in the eluate as each elution proceeded using the potassium thiocyanate or zinc cyanide eluant. Comparing Fig. 8 with Fig. 9, it is observed that the order that each metal is eluted from each resin is the same. Therefore, it appears that the strong-base capacity or the ionic density of the ion-exchange resin does not affect the sequence in which different metals are eluted from each resin. The strong-base capacity of the trimethylamine resin is considerably larger than the strong-base capacity of the dimethylamine resin (Table 1). The peak concentration of iron cyanide in the eluate appears first, followed by the peak for copper cyanide. The shape of both of these peaks is sharp and no tailing of the curve is evident. After the passing of 3 bed volumes of the 2.0 M KSCN eluant, it is observed that the concentration of iron and copper in the eluate is approximately zero. This point corresponds to an elution of greater than 90% iron and copper from both resins.

The rapid elution of iron and copper from each resin is expected and attributed to the geometry and hydration of each complex. As explained previ-

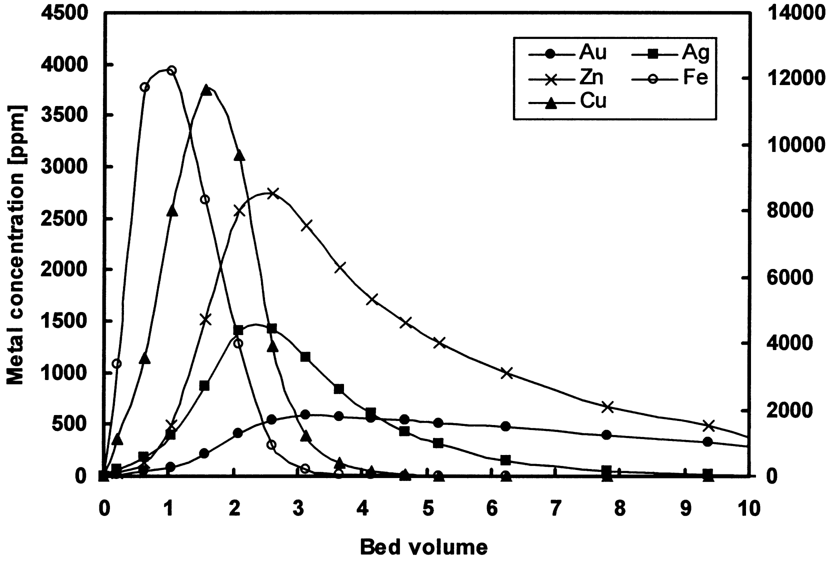

FIG. 8 Elution profile of trimethylamine resin using 2.0 M KSCN. Concentration of free cyanide in eluant is approximately 200 ppm. pH = 12.5. Elution temperature 22°C.

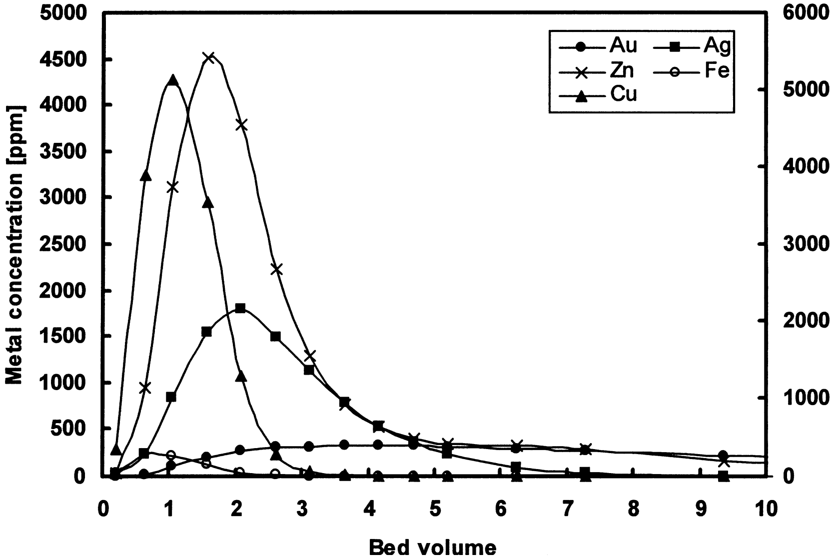

FIG. 9 Elution profile of dimethylamine resin using 2.0 M KSCN. Concentration of free cyanide in eluant is approximately 200 ppm. pH = 12.6. Elution temperature 22°C.

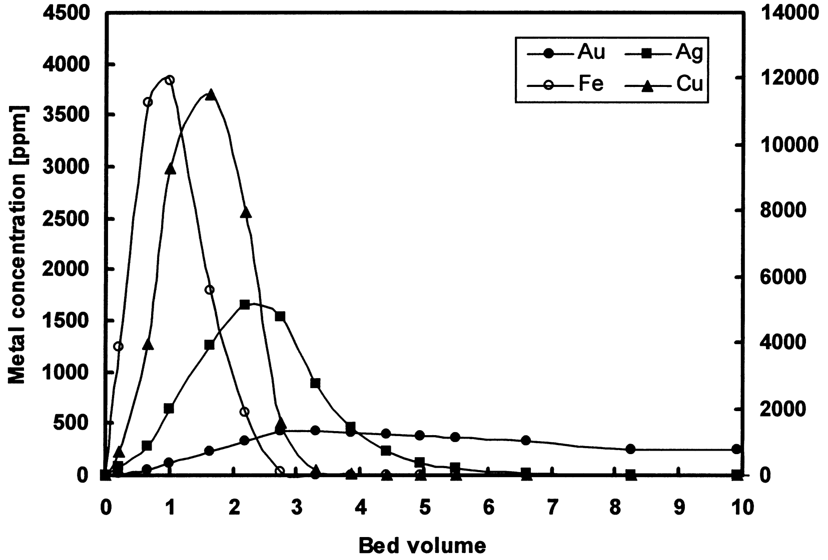

FIG. 10 Elution profile of trimethylamine resin using 0.5 M zinc cyanide. pH = 10.7. Elution temperature 50°C.

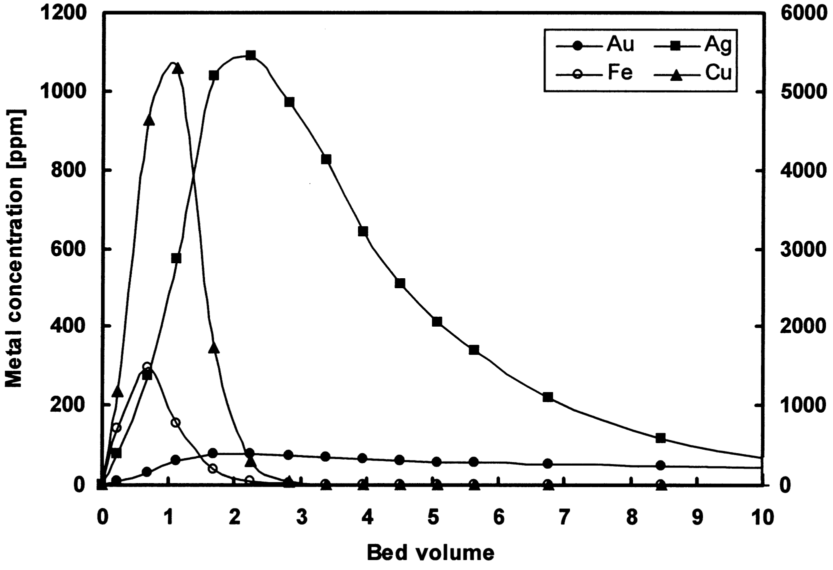

FIG. 11 Elution profile of dimethylamine resin using 0.5 M zinc cyanide. pH = 10.6. Elution temperature 50°C.

ously, the iron cyanide complex is octahedrally shaped, and the copper cyanide complex is predominantly trigonal planar. Consequently, these complexes are unable to closely associate with the functional groups on the resin. Furthermore, these complexes are more hydrated than the univalent gold and silver cyanide complexes, and as a result they are more strongly rejected by the hydrophobic resin matrix.

The peaks in concentration of zinc cyanide and silver cyanide in the eluate are more broad than those observed for iron and copper, and they also occur after the majority of iron and copper has been eluted from the resin (approximately 2 bed volumes). The long tail observed in the elution profile for zinc cyanide from the trimethylamine resin and to a lesser extent from the dimethylamine resin indicates that the concentration of zinc in the eluate does not rapidly decrease as the elution progresses. It is also observed that the elution profile for the gold cyanide complex exhibits a broad peak with a long tail. These observations support previous results indicating that zinc cyanide and gold cyanide bind strongly to ion-exchange resins (6).

Similar elution profiles were obtained for both resins using the zinc cyanide eluant (Figs. 10 and 11). Comparing Fig. 10 with Fig. 11, it is shown that the concentration of silver in the eluate decreases more rapidly for the trimethylamine resin than the dimethylamine resin. This can be attributed to the divalent zinc cyanide complex requiring at least two functional groups of the correct size and spatial geometry to be in close proximity for sorption of the zinc cyanide complex to occur and consequently elute the univalent silver cyanide complex. These requirements are not as easily satisfied by the dimethylamine resin because it has a lower ionic density than trimethylamine resin. Consequently, a longer time is required for silver cyanide to be eluted from the dimethylamine resin. Although a similar elution profile for gold cyanide is observed for both resins using a zinc cyanide eluant (Figs. 10 and 11), the recovery of gold from the resin is significantly different (Table 3).

These results show that both the 2.0 M potassium thiocyanate and the 0.5 M zinc cyanide eluant simultaneously recover metal cyanide complexes from ion-exchange resins that possess high or low ionic densities. However, it is important to consider that the effect of the concentration or the temperature of the eluant has not been considered in this study and it may be possible that the selective elution of metals from each resin could be achieved using a lower eluant concentration or possibly different eluant temperatures.

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, combining the results of the current study with those recently published (10), it can be concluded that two suitable options still exist and have yet to be exploited. It has been reported that a commercially available nonselective resin (Amberjet 4400) selectively adsorbs the gold cyanide complex and also the zinc cyanide complex in highly saline solutions (25). The gold loaded on the resin could then be eluted using 0.5 M zinc cyanide as reported in this study. Essentially then, in highly saline solutions a gold-selective resin exists that has the physical properties (high ionic density, short alkyl chain on functional group) of a nonselective 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 adsorption of gold cyanide can be achieved, another process option is available. It has been recently established that highly saline solutions can be used to selectively elute iron and copper from a variety of ion-exchange resins containing different aliphatic amino functional groups (10). The eluted resin that is still loaded predominantly with gold could then be returned to the adsorption 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. The elution of gold using thiocyanate is slow and requires a large number of bed volumes (ca. 20 BV). However, given that the loading of gold on the resin would be very high, this process could be economically feasible. A similar process has been tested in pilot-plant conditions and shown to be highly successful (26).

CONCLUSIONS

This study has compared the elution performance of ammonium thiocyanate, potassium thiocyanate, and zinc cyanide eluants for five ion-exchange resins that have the same resin matrix but contain different aliphatic amino functional groups. The concentration of cyanide in each eluant was approximately 200 ppm.

It was found that iron and copper cyanide were poorly eluted from each resin using an ammonium thiocyanate eluant at a pH of 7. It was proposed that this was due to the formation of insoluble double metal cyanide complexes of the type $Zn_2[Fe(CN)_6]$ or $Fe_4[Fe(CN)_6]_3$ within the pores of the resin. It was established that a potassium thiocyanate eluant at a pH of 12 can be used to simultaneously recover all metals from the ion-exchange resins studied, except the dipropylamine resin. This result is in accordance with previous studies and is attributed to the highly polarized thiocyanate anion having a stronger affinity for the resin, partly due to its univalent charge, linear geometry, and degree of hydration. However, the recovery of gold from all resins studied required at least 20 bed volumes of the potassium thiocyanate eluant, which is economically unfavorable.

It was also found that the zinc cyanide eluant was unable to significantly elute the gold cyanide complex from resins that have a low strong-base capacity. This was attributed to the low ionic density of these resins 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. Therefore, the results of this study show that zinc cyanide cannot be used as an eluant for the recovery of gold from gold-selective resins.

Two novel adsorption and elution procedures have been proposed that combine recently reported observations with the results presented in the current study. These alternative processes make use of highly saline water to either selectively adsorb the gold cyanide complex from solution or to selectively elute copper and iron cyanide from the resin. Zinc cyanide or thiocyanate could then be used to recover the gold that is predominantly loaded onto the resin.

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