

# The elution of aurocyanide from strong- and weak-base resins

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## SYNOPSIS

Results are presented on the elution of gold cyanide and base-metal cyanide complexes from strong- and weak-base resins. It is shown that thiocyanate anions, zinc cyanide anions, and thiourea in acid solution are effective eluants of strong-base resins, but that it is generally necessary for electrowinning to be incorporated in the elution cycle if fast rates of elution are to be achieved. Weak-base resins are eluted with sodium hydroxide solution, which is shown to be far simpler and far more effective than the elution of strong-base resins. The effects of parameters such as concentration of the eluant, temperature, and electrowinning efficiency on the rate of elution of the resins are examined.

## SAMEVATTING

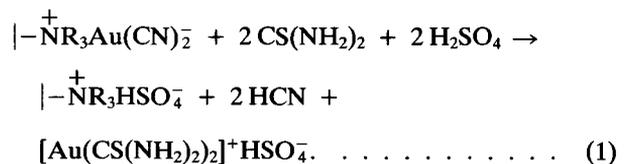
Resultate in verband met die eluering van goudsianied- en onedelmetaalsianiedkomplekse uit sterk- en swakbasisharse word aangebied. Daar word getoon dat tiosianaat- en sinksianiedanione en tio-ureum in 'n suur oplossing doeltreffende eluante vir sterkbasisharse is, maar dat elektrowinning gewoonlik by die elueersiklus ingesluit moet word om vinnige elueertempo's te kry. Die swakbasisharse word met 'n natrium-hidroksiedoplossing geëluëer en daar word getoon dat dit baie eenvoudiger en doeltreffender as die eluering van die sterkbasisharse is. Parameters soos die konsentrasie van die eluant, temperatuur en die doeltreffendheid van die elektrowinning word in verband met die elueertempo van die harse ondersoek.

## Introduction

In the first paper in this series<sup>1</sup>, the absorption of gold cyanide and other metal-cyanide complexes onto strong- and weak-base resins was examined. Results were presented showing that the rate of loading is similar for the two types of resin, but that the loading capacity of strong-base resins is some two to four times greater than that of weak-base resins. On the basis of loading capacity alone, therefore, strong-base resins would probably be preferred to weak-base resins.

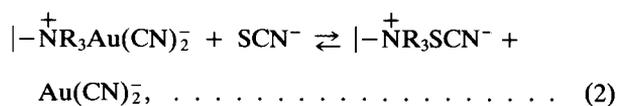
In the present paper, results are presented on the elution of metal-cyanide complexes from anion-exchange resins, and it is shown that weak-base resins are far more easily eluted than strong-base resins. A detailed pilot-plant investigation is currently under way in which pregnant solution from Durban Roodepoort Deep Gold Mine is being treated with strong- and weak-base resins in a NIMCIX column<sup>2</sup>, and it is hoped that the results of this campaign will allow these two factors in the performance of strong- and weak-base resins to be balanced from both the economic and the metallurgical standpoint.

In an examination of the chemistry of the interactions between the aurocyanide ion and anion-exchange resins<sup>1</sup>, it was shown that gold can be stripped from a strong-base resin either by ion exchange or by a chemical reaction. As an example of the latter reaction, the formation of a cationic complex in the reaction between gold and thiourea in acid solution was cited:

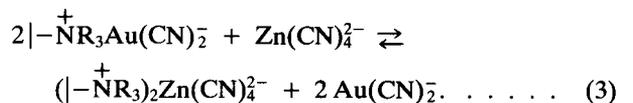


This method of elution of gold from strong-base resins has been described by Groenewald<sup>3</sup>, and is the method favoured by Russian hydrometallurgists, with a number of examples of its use in laboratory-, pilot-, and full-scale operations cited in the literature<sup>4</sup>.

In the ion-exchange method of elution, thiocyanate and zinc cyanide anions are both loaded strongly onto anion-exchange resins, effectively displacing gold cyanide under the correct conditions:



and



Zinc cyanide was first proposed as an eluant for gold cyanide on strong-base resins by Hazen<sup>5</sup>, and the thiocyanate anion has been tested by several investigators<sup>6-9</sup> over the years. It is interesting to note that the early South African work on thiocyanate elution<sup>8</sup> stemmed from the search for reagents that would regenerate strong-base resins that had been poisoned with cobaltcyanide during the extraction of uranium. It was noted that both gold cyanide and cobaltcyanide were effectively stripped

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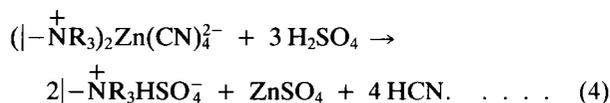
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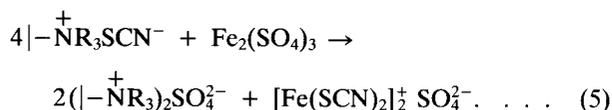
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from these resins with thiocyanate, and that gold could be recovered from the eluate either with activated carbon or by electrolysis.

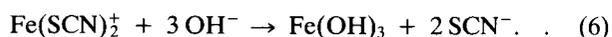
Because the thiocyanate and zinc cyanide anions are loaded so strongly, they have to be stripped and the resin has to be regenerated before it is returned to the next gold-absorption cycle. In the case of zinc cyanide, this can be achieved very efficiently with sulphuric acid or other mineral acids. The zinc cyanide complex decomposes in acid solution, producing hydrocyanic acid gas and zinc salt, which can be combined in alkaline solution to reconstitute the eluate:



Resin that has been eluted with thiocyanate can also be regenerated with mineral acids<sup>7</sup>, but the thiocyanate anion decomposes to elemental sulphur in strong acids. Alternatively, the resin can be regenerated with a ferric salt solution since a cationic ferric thiocyanate complex,  $\text{Fe}(\text{SCN})_2^+$ , which is readily washed from an anion-exchange resin, is formed:



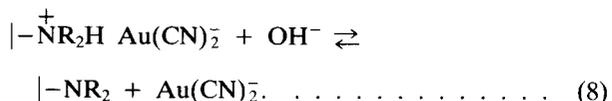
Thiocyanate can be recovered from the regenerant solution by the precipitation of ferric hydroxide:



Gold cyanide can be eluted from weak-base resins by each of the three techniques described above. However, the most efficient method for the elution of weak-base resins is the conversion of the functional groups of the resin to the free-base form; that is, in acid solution the equilibrium in equation (7) lies to the right-hand side, and the anion  $\text{X}^-$  in the following reaction is retained in the resin phase:



In alkaline solution, the equilibrium lies to the left-hand side, the ion exchange properties of the resin are lost, and the anion  $\text{X}^-$  returns to the bulk-solution phase. The equation for the elution of aurocyanide from a weak-base resin is



These three methods for the elution of strong-base resins and that for the elution of weak-base resins are examined in this paper, and the effects on the elution rate of gold of factors such as eluant concentration, temperature, and concentration of gold in solution are discussed.

Each method incorporates the continuous electrolytic recovery of gold in the elution cycle because, in the elution of gold from an anion-exchange resin, two opposing influences must be reconciled. The rate of elution is generally controlled by a combination of intraparticle diffusion and film diffusion. The rate of film diffusion is a function of the hydrodynamic conditions in the elution reactor, and an increase in the flowrate of eluate through the reactor will usually result in an increase in the film-diffusion coefficient, and therefore in an improvement in the overall rate of elution. However, because of the contribution from slow diffusion within the resin matrix, an increase in the flowrate of eluate will result in a decrease in the concentration of gold in solution, and in practice vast volumes of eluate, which are very dilute in gold, would be produced. It is difficult, therefore, for anion-exchange resins to be eluted efficiently by eluate that is pumped in a single-pass through a bed of resin, and the simplest way in which one can minimize film-diffusion effects while simultaneously minimizing the volume of eluate is to incorporate gold electrolysis in the elution cycle. The rapid pumping of solution through a bed of resin and through a cell minimizes film-diffusion effects and, provided the rate at which gold is deposited in an electrowinning cell exceeds the rate at which it appears in solution, the rate of elution will be maximized at the intraparticle-diffusion rate.

The results that are given here show that the rate of gold elution increases as the recirculating flowrate of the eluate increases, despite the fact that the single-pass extraction efficiency in the cell actually decreases with increasing flowrate. This is due to the fact that the overall rate of gold deposition on the cathode, which is a function of both the flowrate and the single-pass efficiency, actually increases with flowrate. Therefore, any increase in the flowrate or in the single-pass electrowinning efficiency (which would be achieved by the incorporation of more cells, for example) will result in an improvement in the rate of gold elution from the resin.

### Experimental Method

In the elution of strong-base resins with thiourea, commercial-grade thiourea was dissolved in Analar-grade sulphuric acid. For the zinc cyanide elutions, zinc sulphate heptahydrate was dissolved in sodium cyanide solution. Analar reagents were used, and the molar ratio of cyanide to zinc in solution was 4.5. In the elution of strong-base resin with thiocyanate, Analar-grade ammonium thiocyanate was used, Analar-grade sodium hydroxide being used to elute the weak-base resin. In all cases the chemicals were dissolved in water from a Millipore purification system.

Loaded strong- and weak-base resins from the NIMCIX pilot plant at Durban Roodepoort Deep Gold Mine<sup>2</sup> were used in this investigation. The strong-base resin was the Rohm & Haas product IRA 400UC, and the weak-base resin was the Duolite International product A7.

Elution tests were carried out in the apparatus shown in Fig. 1. Resin (200 ml) and eluate (1000 ml) were mixed in a cylindrical baffled glass reaction vessel with a variable-speed overhead stirrer. Solution was pumped continuously

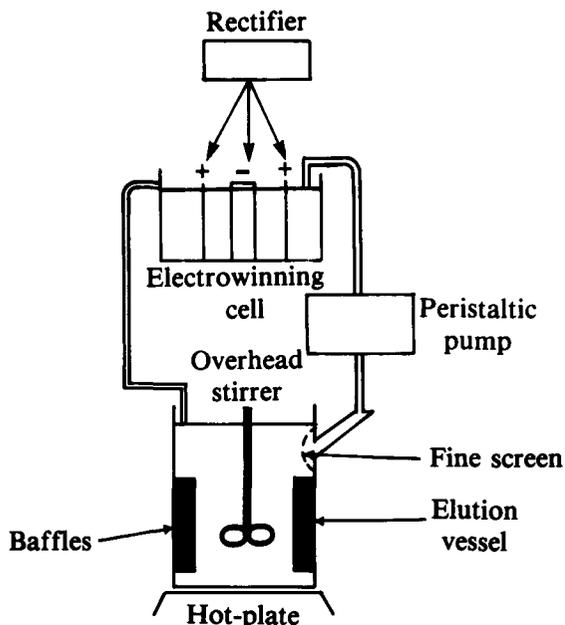


Fig. 1—Apparatus for the elution of anion-exchange resins

from the reaction vessel through an electrowinning cell and back by gravity to the elution vessel. The solution passed through a fine screen in the periphery of the elution vessel to prevent fine particles of resin from entering the pump and the electrowinning cell.

Electrolysis was carried out in a rectangular cell with one cathode between two anodes. The cathode was made of steel wool, which was contained inside a perforated polypropylene basket, and the anodes were either perforated lead sheeting (for the acid-thiourea and ammonium thiocyanate eluates) or stainless-steel mesh (for the zinc cyanide and sodium hydroxide eluates). The electrode dimensions were 0,45 by 0,6 dm, and the thickness of the cathode basket was 0,3 dm. A peristaltic pump delivered gold-bearing solution to the cell at flowrates between 2 and 14 l/h.

Each elution experiment was continued for a period of 24 hours. The rate of elution was monitored by periodic sampling and analysis of the resin for gold and various other elements by X-ray-fluorescence spectrometry. The efficiency of electrowinning was determined from periodic sampling of the solution entering and leaving the electrowinning cell and analysis for gold by atomic-absorption spectrometry.

### Treatment of Strong-base Resin with Zinc Cyanide

#### Elution and Electrowinning

Loaded strong-base resin, which had a gold concentration of about 5000 g/t, was treated with zinc cyanide solution under various conditions. The effects on the rate of gold elution of variations in the zinc cyanide concentration, the temperature, the current in the electrowinning cell, and the rate of recirculation of the eluate through the cell, were examined, and the results are summarized in Table I. In each experiment, one parameter was varied while the other parameters were maintained at the constant electro-elution

values. The elution efficiency (EE) represents the amount of gold eluted from the resin in 4 hours, this period being chosen because it allowed differences in rates of elution under various conditions to be detected. The single-pass extraction efficiency in the electrowinning cell (SPE) represents an average value over the first 4 hours of elution and gives a relative measure of the rate of gold extraction from the eluate by electrolysis. In all the experiments, elution continued for a period of 24 hours, after which more than 99 per cent of the gold had always been stripped from the resin, the concentrations of gold on the resin being less than 50 p.p.m.

The results indicate that the concentration of zinc cyanide has little effect on the elution rate and the electrowinning efficiency above about 0,15 M (10 g/l). A temperature of 50 °C had to be used for these experiments so that the crystallization of  $\text{Na}_2[\text{Zn}(\text{CN})_4]$  would be avoided (such crystallization would normally occur at room temperature from solutions containing more than 0,5 M zinc), and it is probable that the concentration of zinc cyanide would have a more pronounced effect on the rate of elution at lower temperatures. The equilibrium absorption of gold cyanide onto a strong-base resin in the presence of different concentrations of zinc cyanide is shown in Fig. 2. The results indicate that there should be significantly less residual gold on the resin when the zinc concentration is increased to 0,5 M, but that higher zinc concentrations will have little effect.

The effect of temperature on the rate of elution is more pronounced than the concentration of zinc cyanide, and an Arrhenius plot based on rate data over the first hour of elution gave an approximate activation energy for elution of  $26 \text{ kJ} \cdot \text{mol}^{-1}$ . This, coupled with the fact that the solubility of zinc cyanide increases with temperature, thereby permitting the use of more concentrated eluates, suggests that elevated temperatures (50 to 60 °C) should be

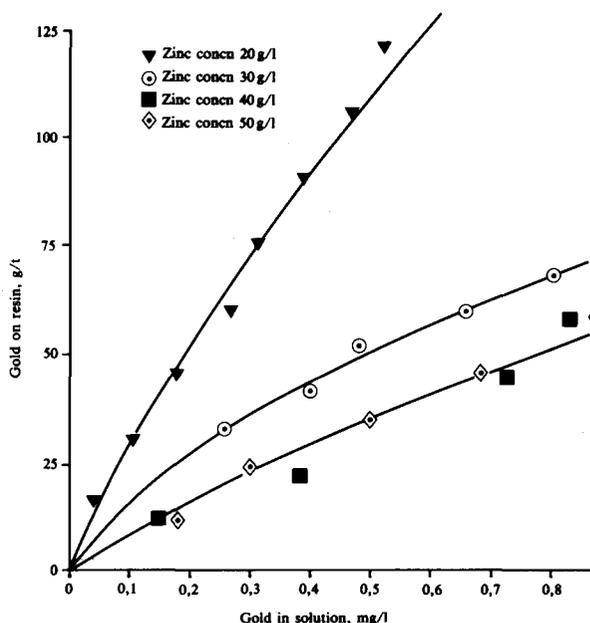


Fig. 2—Equilibrium absorption of aurocyanide on a strong-base resin (IRA 400) as a function of the concentration of gold in solution at different concentrations of zinc cyanide in solution

TABLE I

THE RATE OF ELUTION OF GOLD CYANIDE FROM A STRONG-BASE RESIN WITH ZINC CYANIDE UNDER VARIOUS CONDITIONS

## Standard electro-elution values:

Zn(CN) <sub>4</sub> <sup>2-</sup>			Cell current			1 A			Flowrate of eluate			14 l/h		
Temperature			0,46 M			20 °C								
Zn(CN) <sub>4</sub> <sup>2-</sup>	EE	SPE	Temp.	EE	SPE	Cell current	EE	SPE	Eluate flowrate	EE	SPE			
M	%	%	°C	%	%	A	%	%	l/h	%	%			
0,15	96	35	20	66	23	0,25	29	14	2	22	86			
0,30	96	36	30	64	31	0,50	51	25	5	46	49			
0,46	96	39	40	79	32	1,0	69	23	10	53	32			
0,61	95	39	50	96	39	2,0	61	31	14	66	23			
0,76	95	31	60	98	53									

\*Elutions done at 50 °C

EE = Elution efficiency after 4 hours

SPE = Average single-pass efficiency in electrowinning

TABLE II

EFFECT OF THE QUANTITY OF ACID ON THE STRIPPING OF ZINC FROM A STRONG-BASE RESIN PREVIOUSLY TREATED WITH ZINC CYANIDE

Concentration of H <sub>2</sub> SO <sub>4</sub>	Quantity relative to stoichiometric requirement	Analysis of final solution, g/l		Zinc on resin, g/t	
		H <sub>2</sub> SO <sub>4</sub>	Zinc	Column bottom	Column top
g/l	%				
10	33	0,8	0,3	5 000	115 000
15	50	0,7	1,4	5 800	128 000
25	83	10	4,3	1 300	75 000
30	100	13	6,5	1 000	2 900
50	166	22	7,1	300	600

TABLE III

THE RATE OF ELUTION OF GOLD CYANIDE FROM A STRONG-BASE RESIN WITH AMMONIUM THIOCYANATE UNDER VARIOUS CONDITIONS

## Standard electro-elution values:

NH <sub>4</sub> SCN			Cell current			1 A			Flowrate of eluate			10 l/h		
pH value			2 M			7								
Temperature			20 °C											
NH <sub>4</sub> SCN	EE	SPE	pH	EE	SPE	Temp.	EE	SPE	Cell current	EE	SPE	Eluate flowrate	EE	SPE
M	%	%		%	%	°C	%	%	A	%	%	l/h	%	%
0,5	42	11	2	19	≈0	20	95	19	0,25	74	14	4	57	33
1	72	19	3	64	21	35	≈100	14	0,5	87	14	6	75	24
2	95	16	4	83	18	45	≈100	24	1,0	95	19	10	95	19
5	99	19	5	90	19	60	≈100	25						
10	≈100	17	7	94	17									
			8	93	14									
			1M NaOH	90	17									
			2M NaOH	84	11									

EE = Elution efficiency after 4 hours

SPE = Average single-pass efficiency in electrowinning

TABLE IV

THE EFFECT OF FERRIC-ION CONCENTRATION ON THE STRIPPING OF THIOCYANATE FROM A STRONG-BASE RESIN

## Conditions:

Thiocyanate on resin 0,16 mol  
Ferric ions in regenerant solution 0,16 mol

Composition of regenerant solution		Thiocyanate on resin	Thiocyanate in regenerant solution	Efficiency of regeneration
Fe <sup>3+</sup> g/l	Volume litre	g/t	M	%
0	0	250 000		
2	10,0	9 800	0,04	96
8	2,5	20 500	0,11	92
20	1,0	22 800	0,35	91
40	0,5	26 100	0,63	90
100	0,2	36 250	1,12	86

employed with this elution technique. A further incentive for operation at higher temperatures is the fact that the rate of the electrolytic deposition of gold also increases with temperature, and this in turn enhances the rate of elution.

The removal rate of gold from solution by its deposition on the cell cathode can be increased by an increase either in the cell current or in the flowrate of recirculating eluate. The results in Table I indicate that increases in both these parameters enhance the rate of gold elution from the resin, and therefore, by implication, the rate of elution increases as the concentration of gold in the solution decreases. This would be predicted from a consideration of the exchange equilibrium shown in equation (3), where an increase in the concentration of gold cyanide in solution would shift the equilibrium to the left-hand side. The efficiency of single-pass extraction in the electrowinning cell increases with cell current but decreases with increasing flowrate. However, the net extraction of gold from the eluate, which is a function of both the flowrate and the efficiency of the single-pass extraction, actually increases with increasing flowrate, and this resulted in improved rates of elution.

#### *Regeneration*

On the basis of equation (4), the quantity of sulphuric acid required to regenerate the resin is 3 mol for every mol of zinc cyanide absorbed on the resin, i.e. 2 mol of acid is required for the destruction of the zinc cyanide complex, while the third mol of acid is extracted by the resin as the bisulphate ion. If the resin were converted to the sulphate rather than the bisulphate form, only 2 mol of acid would be required per mol of zinc. As confirmation of this point, sulphuric acid was pumped through a column of eluted resin, and the quantity of acid was varied from 30 to 160 per cent of the stoichiometric amount calculated on the basis of 3:1 molar; at the end of each experiment, the spent regenerant solution was analysed for zinc and sulphuric acid, and samples of resin from the bottom and the top of the column were analysed for zinc. The results (Table II) indicate that the reaction stoichiometry proposed in equation (4) is correct. In fact, the zinc on the resin should ideally be reduced to less than 1000 p.p.m. before the resin is recycled to absorption, and the results in the table indicate that a slight excess of acid would be necessary.

Another important requirement of the regeneration process is that the chemicals in the spent regenerant solution should be readily available for recycling. The hydrogen cyanide gas that is evolved during regeneration (equation (4)) can be collected in an aqueous solution of sodium or calcium hydroxide, which can either be utilized in leaching or combined with the zinc sulphate in the spent regenerant to reconstitute the zinc cyanide eluant. Ideally, the concentration of zinc in the spent regenerant should be at least 0,5 M, and the residual concentration of sulphuric acid should be as low as possible. It is likely that these objectives will best be realized when the regeneration column is operated in a countercurrent mode.

#### **Treatment of Strong-base Resin with Ammonium Thiocyanate**

##### *Elution and Electrowinning*

The effects on the gold elution and electrowinning rates

of variations in the ammonium thiocyanate concentration, the pH value of the eluate, the temperature, the cell current, and the flowrate of recirculating eluate were examined, and the results are summarized in Table III. Once again, these results represent the percentage of gold eluted from the resin after 4 hours and, in each experiment, one parameter was varied while the other parameters were maintained at the constant electro-elution values.

The rate of elution increased almost linearly with the concentration of ammonium thiocyanate, but from a practical point of view a concentration of about 2 M is probably optimum. The rate of elution by thiocyanate under the standard conditions was considerably faster than by zinc cyanide, an elution efficiency of 99 per cent being achieved in 6 hours.

The pH value of the eluate also had an effect on the rate of elution, with optimum results being achieved at a pH of 7 to 8. In strongly alkaline solution the slightly reduced elution efficiency could have been due to the increased viscosity of the eluate. In acidic solution there was much evidence of corrosion of the anodes and cathodes, and extensive precipitation occurred. The poor elution efficiency was therefore probably due to a combination of physical and electrochemical factors.

The rate of elution increased with temperature (activation energy approximately  $15 \text{ kJ} \cdot \text{mol}^{-1}$ ), but was so fast under the standard conditions that, from a practical point of view, the use of elevated temperatures would probably not be justifiable. The electrowinning efficiency also improved with temperature.

Finally, an increase in either the cell current or the flowrate of recirculating eluate also improved the rate of elution by increasing the extraction rate of gold from the eluate. This effect would be predicted on the basis of the ion-exchange equilibrium involved here (equation (2)), as was observed earlier in the case of zinc cyanide elution.

#### *Regeneration*

In the past, the major drawback in elution with thiocyanate has been the difficulty of the displacement of the thiocyanate anion from the resin after elution. This is an important aspect of the process for two reasons: firstly, the thiocyanate anion is not readily displaced by other anions, and therefore the anion-exchange capacity of the resin, if the resin is recycled to absorption, is significantly reduced; secondly, it is important from an economic point of view that a large percentage of the thiocyanate absorbed onto the resin during each elution cycle should be recovered and recycled to the next elution cycle. In an attempt to realize the first objective, samples of resin that had been eluted with ammonium thiocyanate were treated with 20 resin bed volumes of the following reagents: 1 M nitric acid, 2 M hydrochloric acid, 2 M sodium cyanide, 2 M sodium hydroxide, and 1 M sulphuric acid. The regenerated resin was washed thoroughly with water before being contacted with a synthetic aurocyanide solution and brought to equilibrium. The equilibrium isotherms are shown in Fig. 3, where they are compared with isotherms for fresh resin and for resin that had been eluted with thiocyanate but not regenerated. It can be seen that most of the loading

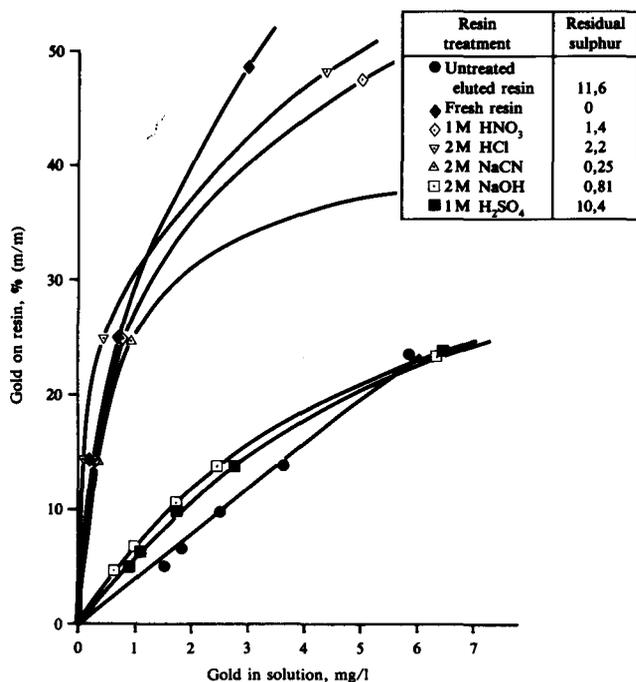


Fig. 3—Equilibrium absorption isotherms for the loading of gold cyanide on strong-base resin (IRA 400) that had been eluted with ammonium thiocyanate

capacity of the resin is lost after being eluted with thiocyanate and that treatment with sodium hydroxide or sulphuric acid restores little of the lost capacity. However, treatment with sodium cyanide, nitric acid, or hydrochloric acid restores the capacity of the resin almost to that of fresh resin.

However, for elution with thiocyanate to be viable on a large scale, a large percentage of the thiocyanate that is absorbed onto the resin during elution would have to be recovered and recycled. According to the method suggested by Davison<sup>7</sup>, eluted resin is treated with a mineral acid to displace the thiocyanate anions, and the mineral-acid solution is then treated with loaded resin to re-extract the thiocyanate from the acid solution. The consumption of thiocyanate in the subsequent elution step is then theoretically reduced by an amount equal to the amount of thiocyanate recovered from the mineral acid. This method was tested in the laboratory and was found not to be very efficient, the recovery of thiocyanate being only 30 to 40 per cent after the eluted resin had been treated with ten times its volume of mineral acid. The results were very similar for 1 M sulphuric, nitric, and hydrochloric acids. The instability of thiocyanate in acid solution, with fairly rapid decomposition to elemental sulphur, is another factor that counts against this technique.

A second method, which was developed at Mintek, involves treatment of the thiocyanate-loaded resin with a ferric salt. A relatively stable cationic complex,  $\text{Fe}(\text{SCN})_2^+$ , is formed that is readily eluted from the resin (equation (5)), and thiocyanate can be recovered from this solution by the use of hydroxide to precipitate iron as ferric hydroxide (equation (6)). To quantify the efficiency of the process, samples of resin loaded with thiocyanate were treated in a

column with ferric solutions of various compositions. The ferric solution flowed by gravity down through the column of resin, and the solution emerging was collected and analysed for thiocyanate. So that the quantity of ferric ions necessary to strip all the thiocyanate from a sample of resin could be determined, the ratio of ferric ions in the regenerant solution to thiocyanate on the resin was varied from the stoichiometric amount necessary to complex all the thiocyanate as the  $\text{Fe}(\text{SCN})_2^+$  complex to a 3,5-fold excess. The results (Fig. 4) indicate that about 70 per cent of the thiocyanate is stripped from the resin at a ferric-to-thiocyanate ratio of 0,5. This suggests that  $\text{Fe}(\text{SCN})_2^+$  is probably the dominant species in solution under these conditions, lesser amounts of the 1-to-1 complex  $\text{FeSCN}^{2+}$  also being present.

The concentration of ferric ions has a small but perceptible influence on the efficiency of thiocyanate stripping, as shown in Table IV. For these experiments, the quantity of ferric ions was kept constant while the concentration was varied from 0,035 to 1,80 M. The decrease in efficiency with increasing ferric ion concentration is probably due to slower mass transfer in the more concentrated solutions.

From a processing point of view, the establishment of the maximum concentration of thiocyanate that can be realized in the regenerant solution is also important. This is the concentration that would be obtained in a countercurrent stripping process, and indicates whether the final solution (after the precipitation of ferric hydroxide) would be suitable for direct recycling to elution without any preconcentration steps. These results are presented in Fig. 5, and indicate that the required concentration of thiocyanate for

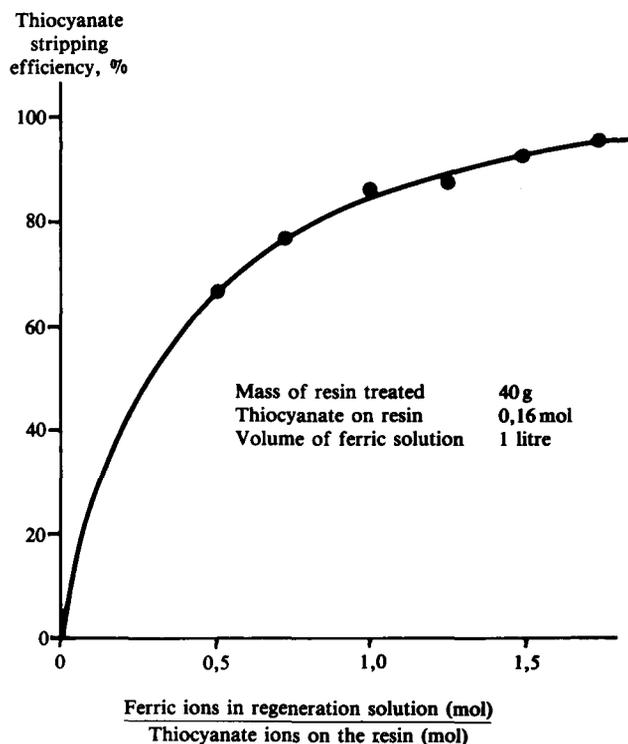


Fig. 4—The stripping of thiocyanate from a strong-base resin with ferric nitrate solutions of variable concentration

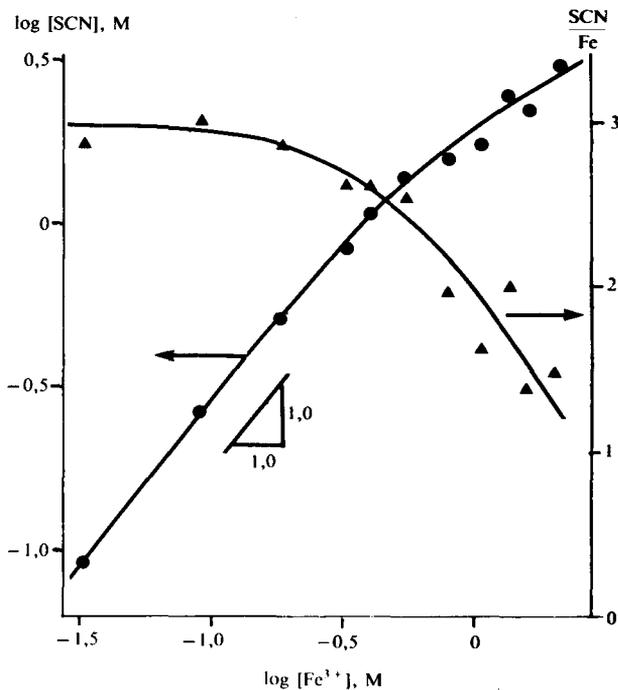


Fig. 5—The effect of the concentration of ferric ions on the concentration of thiocyanate in the spent regenerant solution

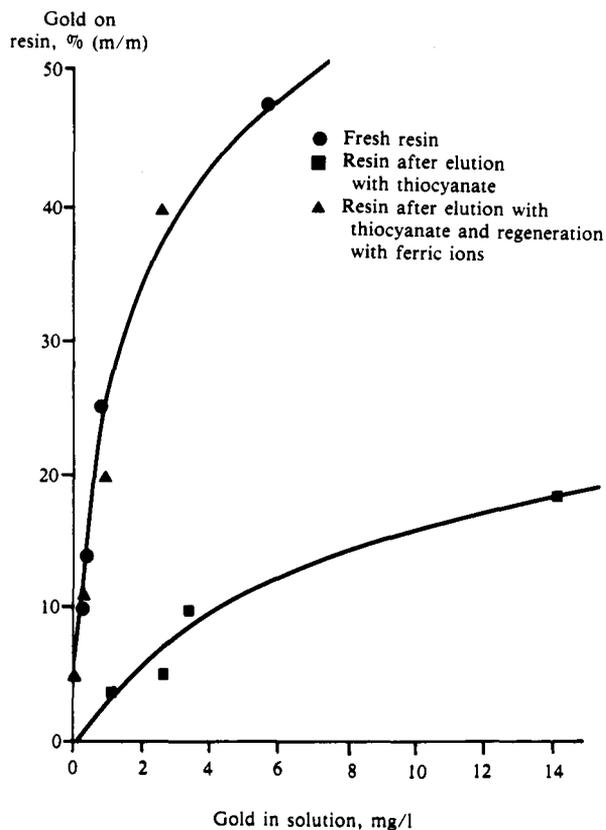


Fig. 6—The equilibrium loading of gold cyanide onto a strong-base resin from a synthetic solution containing only potassium aurocyanide

recycle (i.e. about 2 M) can be achieved at concentrations of ferric ions of greater than 1 M. It is interesting that the thiocyanate-to-ferric stoichiometry in the solution emerging from the column varies from about 3 (i.e.  $\text{Fe}(\text{SCN})_3$ ) at low concentrations of iron to almost 1 (i.e.  $\text{FeSCN}^{2+}$ ) at high concentrations of iron. Therefore, the utilization of ferric ions improves with decreasing concentrations, but the concentration of thiocyanate in the recycle solution also decreases; a measure of compromise would therefore be necessary.

Finally, the ion-exchange activity of the strong-base resin was determined both before and after ferric regeneration by the treatment of the resin with a gold cyanide solution. The results are shown in Fig. 6, and the equilibrium isotherms indicate that the ion-exchange capacity of the resin is completely restored by this treatment.

The above regeneration experiments were all carried out with the ferric nitrate salt. Tests were also conducted successfully with ferric sulphate but, owing to the competitive formation of sulphate complexes of ferric, a higher ferric-to-thiocyanate ratio (approximately 10) is necessary for complete regeneration.

#### Elution of Strong-base Resin with Thiourea

The effects, on the rate of gold cyanide elution and electrowinning, of variations in the concentrations of thiourea and sulphuric acid, the temperature, the cell current, and the flowrate of recirculating eluate are shown in Table V. In each experiment, one parameter was varied while the other parameters were maintained at the constant electro-elution values.

The rate of elution increased linearly with thiourea concentration up to 1 M, and also increased with increasing sulphuric acid concentration up to 1 M; at higher concentrations there was little improvement in the rate, and 1 M concentrations of each of these reagents were therefore used in the standard conditions. The efficiency of single-pass extraction in the electrowinning cell also increased with thiourea concentration, but there was very little change over the range of sulphuric acid concentrations studied.

The effect of temperature on the rate was intermediate between the results for zinc cyanide and those for thiocyanate, with an activation energy of approximately  $19 \text{ kJ} \cdot \text{mol}^{-1}$ . The electrowinning efficiency also improved with temperature.

The effects of cell current and flowrate of recirculating eluate on the rate of elution are rather small, but this is not unexpected because the thiourea-elution reaction (equation (1)) is irreversible, and therefore the concentration of gold in solution should theoretically have no effect on the rate.

A major problem with the thiourea method of elution is the decomposition of thiourea, which occurs fairly rapidly in strongly acidic solutions. Fig. 7 shows the rate of decomposition of thiourea in 100 g/l sulphuric acid. In this experiment, 500 ml of resin was treated initially with 3000 ml of solution containing 0.4 M thiourea. After 24 hours, the resin and the eluate were separated, and the eluate was

re-used with a second 500 ml batch of resin. This was then repeated a third time. It can be seen from the curves in Fig. 7 that there was an initial rapid decomposition of thiourea when the eluate was brought into contact with fresh loaded resin, but that, after the first 5 to 6 hours, the rate of decomposition was very low. As the amount of thiourea required to form a complex with the metal on the resin is very small (less than 1 per cent of the thiourea in solution), the initial rapid drop in concentration cannot be attributed to that cause. It seems rather to be due to some sort of resin-catalysed degradation reaction as proposed by Groenewald<sup>3</sup> or to oxidation at the anodes in the cell.

Apart from the cost of the reagent lost due to degradation, a secondary disadvantage is the fact that one of the degradation products is elemental sulphur, which forms a scum during elution. This scum may cause problems, especially if physically entrained in the electrowinning cell, and facilities for the periodic removal of scum would probably be required.

#### Elution of Weak-base Resin with Sodium Hydroxide

The effects, on the elution and electrowinning rates of gold from the weak-base resin, of variations in the concentration of sodium hydroxide, temperature, cell current, and flowrate of recirculating eluate are shown in Table VI. In each experiment, one parameter was varied while the other

parameters were maintained at the constant electro-elution values. The rate of elution was considerably faster than with the three strong-base resin techniques discussed above, and the elution efficiencies in Table VI refer to the extent of elution after a reaction time of only 15 minutes. Under the standard elution conditions, the concentration of gold on the resin was reduced from 1800 g/t to less than 10 g/t in 1 hour. The observation that gold can be stripped from the weak-base resin to very low residual values is consistent with earlier studies<sup>1</sup>, which indicated that this resin has practically no strong-base groups in the resin matrix. Strong-base groups, which can comprise 15 per cent or more of the ion-exchange capacity of a weak-base resin, load anions even in very strongly alkaline solution.

The results in Table VI show that the rate of elution increases with sodium hydroxide concentration up to 0,5 M. At higher concentrations, there is an apparent decrease in the rate of elution; this could be due either to poor mass transfer in the more viscous concentrated solutions, or it could be due to precipitation of the weaker metal-cyanide complexes (such as zinc) as hydroxides within the pores of the resin, resulting in physical entrapment of the gold in the resin.

The rate of elution increased with temperature, but the rate was so fast at elevated temperatures that it was not possible for the activation energy of the reaction to be

TABLE V

THE RATE OF ELUTION OF GOLD CYANIDE FROM A STRONG-BASE RESIN WITH MIXTURES OF THIOUREA AND SULPHURIC ACID UNDER VARIOUS CONDITIONS

Standard electro-elution values:

CS(NH<sub>2</sub>)<sub>2</sub> 1 M Cell current 2 A  
H<sub>2</sub>SO<sub>4</sub> 1 M Flowrate of eluate 10 l/h  
Temperature 20 °C

CS(NH <sub>2</sub> ) <sub>2</sub>			H <sub>2</sub> SO <sub>4</sub>			Temp.	EE		SPE		Cell current	EE		SPE		Eluate flowrate l/h	EE		SPE	
M	%	%	M	%	%		%	%	%	%		A	%	%	%		%	%	%	%
0,50	32	15	0,50	57	22	20	71	27	0,5	63	14	5	72	47						
0,75	49	22	0,75	63	31	35	84	32	1,0	63	27	7	70	42						
1,00	65	27	1,00	71	27	45	96	37	1,5	65	23	10	74	27						
1,25	68	30	1,25	70	25	58	~100	52	2,0	70	35	14	76	25						
1,50	71	31	1,50	71	33															

EE = Elution efficiency after 4 hours

SPE = Average single-pass efficiency in electrowinning

TABLE VI

THE RATE OF ELUTION OF GOLD CYANIDE FROM A WEAK-BASE RESIN WITH SODIUM HYDROXIDE UNDER VARIOUS CONDITIONS

Standard electro-elution values:

NaOH 0,5 M Cell current 1 A  
Temperature 20 °C Flowrate of eluate 9 l/h

NaOH			Temp.	EE		SPE		Cell current	EE		SPE		Eluate flowrate l/h	EE		SPE	
M	%	%		%	%	%	A		%	%	%	%		%	%	%	
0,1	18	~0	20	94	8	0,25	89	5	3	88	29						
0,2	48	~0	40	95	8	0,50	90	8	5	87	37						
0,5	93	8	50	98	23	0,75	90	9	7	92	23						
1	94	8	60	~100	36	1,00	94	8	9	94	8						
2	92	11															
5	88	19															
10	80	13															

EE = Elution efficiency after 15 minutes

SPE = Average single-pass efficiency in electrowinning

TABLE VII

THE ELUTION OF VARIOUS ANIONIC METAL-CYANIDE COMPLEXES FROM ANION-EXCHANGE RESINS USING ZINC CYANIDE, THIOCYANATE, THIOUREA, AND SODIUM HYDROXIDE UNDER STANDARD CONDITIONS

Metal ion	Elution efficiency, %			
	Strong-base resin			Weak-base resin
	Zn(CN) <sub>4</sub> <sup>2-</sup>	SCN <sup>-</sup>	CS(NH <sub>2</sub> ) <sub>2</sub>	
Silver	≈100	≈100	≈100	70
Copper	≈100	≈100	53	≈100
Cobalt	87	63	0	78
Nickel	85	58	≈100	66
Zinc	n.d.	0	0	0
Iron	90	87	0	58

n.d. = Not determined

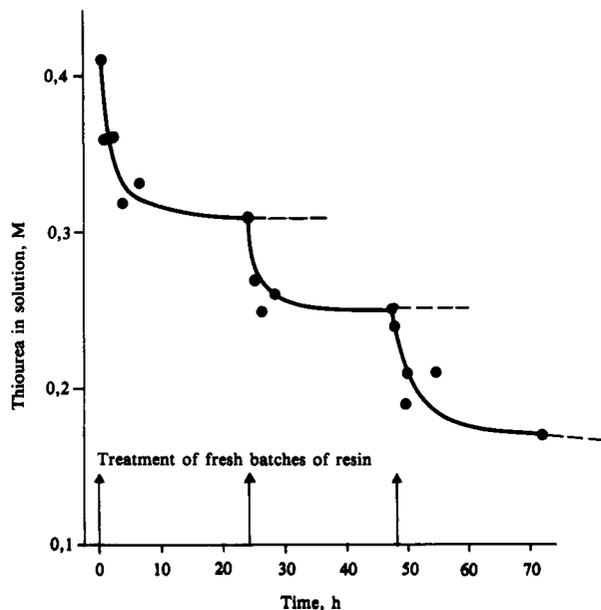


Fig. 7—The rate of decomposition of thiourea in 100 g/l sulphuric acid during the electro-elution of gold from a strong-base resin

determined under the experimental conditions with any degree of precision. It is unlikely that elevated temperatures would be necessary or justifiable in practice.

The effects of cell current and flowrate of recirculating eluate on the rate of elution are small, as might be expected for the equilibrium shown in equation (8). At high pH values, this equilibrium will lie to the right-hand side and, with the resin predominantly in the free-base form, the concentration of gold in solution should have a minimal effect on the rate of elution.

#### Elution of Other Cyanide Complexes from Anion-exchange Resins

This is a most important aspect of any elution process because it determines whether an additional chemical treatment is required in the elution cycle or, in the case of poisoning, whether it is necessary for resin to be discarded periodically. The elution efficiencies for a number of common metal-cyanide complexes of the four techniques described above are given in Table VII.

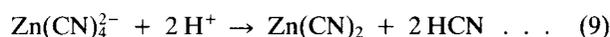
The best results were obtained with zinc cyanide. The concentration of all the metals on the resin was reduced by more than 85 per cent during the elution and, in a period of continuous operation on a pilot plant<sup>10</sup>, no element accumulated on the resin during cyclic operation. Results are not reported for zinc because zinc cyanide is absorbed onto the resin in this elution technique.

In elution with thiocyanate, silver, iron, and copper are eluted efficiently, cobalt and nickel are eluted moderately well, and zinc is not eluted at all. The elution of cobalt is slow and, given sufficient time, the elution efficiency can be improved to more than 90 per cent. The poor elution characteristics of zinc and nickel are believed to be due to the formation of anionic thiocyanato complexes of these

metals, which are absorbed onto the resin. These metals do not build up on the resin in cyclic operation (i.e. an equilibrium with the cyanide complexes is re-established when the eluted resin is returned to absorption), and it is not envisaged that problems would be experienced in continuous operation.

The elution characteristics with thiourea are not good, and poisoning is likely to be a major problem with this elution technique. The situation is particularly bad with cobaltcyanide, which, in the presence of sulphuric acid, forms polymeric species on the resin<sup>11</sup> that are extremely difficult to elute without destruction of the resin. The poor elution of copper, zinc, and iron is possibly associated with the formation of insoluble double-metal complexes of the type M<sub>2</sub>Fe(CN)<sub>6</sub> (where M is a divalent metal).

Of the various elements on the weak-base resin, only gold and copper were eluted efficiently. The poor elution of nickel, iron, silver, and zinc is believed to be due to precipitation within the resin matrix of insoluble metal-cyanide species in weakly acidic solution during the absorption. For example, the reaction



occurs between pH 5 and 7. The loaded resin for these tests was obtained from the NIMCIX pilot plant at Durban Roodepoort Deep Gold Mine<sup>2</sup>, for which the feed solution had been adjusted to a pH value of about 7. After contact with the weak-base resin in the protonated form, the solution emerging from the NIMCIX column had, on average, a pH value of about 4. It seems likely, therefore, that the weaker metal-cyanide complexes (i.e. zinc, nickel, silver, and lead) are loaded onto the resin by a normal ion-exchange mechanism and are then precipitated within the resin matrix as the pH value of the solution decreases. The precipitated species would no longer be bonded to the resin functional groups, and would therefore not be eluted when the functional groups are converted to the free-base form.

In more strongly acidic solution (with a pH value of less than 3), the cyanide complexes break down completely, and the metal cation is readily washed from the resin with water; for example, for zinc cyanide

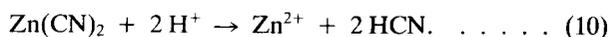


TABLE VIII  
THE STRIPPING OF METAL-CYANIDE ANIONS FROM A WEAK-BASE RESIN WITH VARIOUS REAGENTS

Metal ion	Loaded resin	Elution with 0,5 M NaOH	Elution with NaOH followed by regeneration with H <sub>2</sub> SO <sub>4</sub>	Elution with 0,5 M NaOH + 0,1 M NaCN
	g/t	g/t	g/t	g/t
Gold	1815	7	2	n.d.
Silver	500	150	195	<50
Copper	9900	390	<25	270
Cobalt	950	210	140	190
Nickel	5270	1780	<25	220
Zinc	2900	3000	<20	2980
Iron	850	360	255	130
Lead	710	750	470	n.d.

n.d. = Not determined

Support for this mechanism is seen in Table VIII; that is, by washing of the resin with sulphuric acid after elution, the stripping of nickel and zinc was improved to almost 100 per cent. When nitric acid was used instead of sulphuric acid, the concentrations of silver and lead on the resin were also reduced to less than 25 g/t.

Further evidence in support of this theory is the greatly improved efficiency of the elution of silver, nickel, and iron that is obtained when sodium cyanide is added to the eluate (Table VIII). Increased concentrations of cyanide in solution would oppose reactions (9) and (10) and should therefore result in enhanced elution efficiency.

#### Discussion

The relative rates of elution and electrowinning under standard conditions for the four eluants are compared in Figs. 8 and 9. The curves highlight the significant superiority of the weak-base resin process from both the elution and electrowinning standpoints, and this must be a major factor in favour of weak-base resins for this application. Of the three elution techniques for strong-base resins, the treatment with thiocyanate yielded the fastest elution kinetics and good electrowinning characteristics. The results for all four eluants show that the concentration of gold in the solution entering the electrowinning cell decreases systematically after the first 10 minutes of elution. This indicates that the rate of gold deposition on the cathode exceeds the rate of gold elution, which is the most important requirement of the electro-elution procedure.

The requirement in plant practice would be to reduce the concentration of gold on the resin to less than about 25 g/t. The relative rates of elution and electrowinning, translated into these practical terms, indicate that an elution cycle of between 1 and 2 hours would be adequate for the weak-base resin under standard conditions, whereas 6 to 10 hours would be required for the elution of a strong-base resin with thiocyanate, and about 24 hours for the elution with zinc cyanide and thiourea. It should be borne in mind, however, that the elution cycle for the latter two processes could also be reduced to about 6 hours by the use of elevated temperatures (50 to 60 °C).

A number of other advantages and disadvantages of the four eluants are summarized in Table IX. It can be seen that the thiourea method suffers from a number of serious draw-

backs, while possessing few advantages over the other elution systems. The most serious drawbacks are the decomposition of thiourea, which imposes high operating costs on the process<sup>10</sup>, and poisoning by cobaltcyanide<sup>11</sup>, which effectively precludes any solution with a higher concentration of cobalt than about 1 mg/l. Despite these disadvantages, this method appears to be favoured in the U.S.S.R., where pioneering work has been conducted on the large-scale application of resin-in-pulp for gold. A minor drawback with thiourea is the corrosive nature of the 1 M sulphuric acid solution. Several cathode materials were tested in the course of the present investigation to establish which would be most suitable in a strongly acidic medium. Graphite chips worked well but were discarded

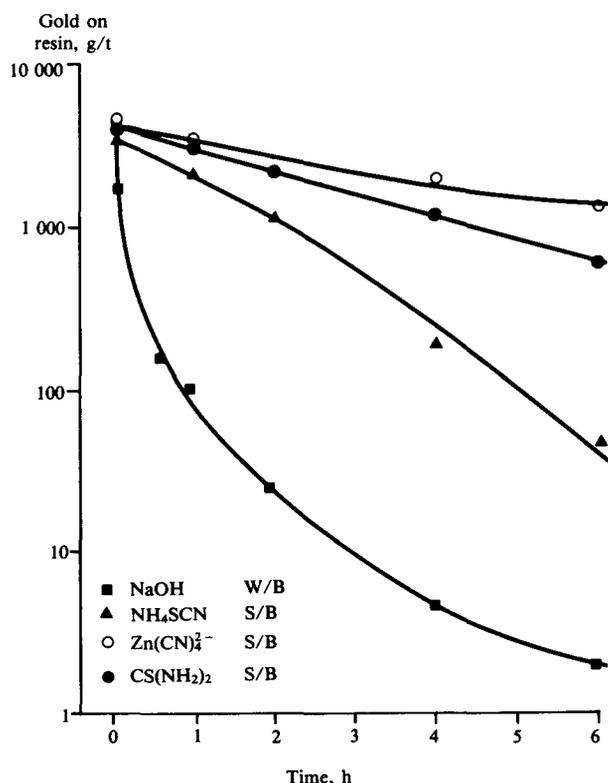


Fig. 8—Relative rates of gold elution from strong-base (S/B) and weak-base (W/B) resins under the standard electro-elution conditions

owing to difficulties involved in the final recovery of the gold. Stainless-steel wool was not sufficiently pliable to make a good packing material for the cathode boxes, while the low surface area of stainless-steel mesh resulted in low single-pass extraction efficiencies. Brass wool was also

tested, but the potential assumed by the wool was not sufficiently cathodic and the cathode dissolved in 100 g/l sulphuric acid in several hours. The best results were obtained with a coarse-fibred steel wool, and this material was used throughout. In all cases the anodes were made of lead sheet.

In view of the above factors, it is unlikely that thiourea will compete seriously with the other two eluants for strong-base resins in any future applications of resin technology for the recovery of gold. In fact, the potential for the efficient recycling of chemicals when zinc cyanide or thiocyanate is used as the eluant reduces the operating costs for both processes to between 5 and 15 cents per gram of gold recovered<sup>10</sup>, which compares very favourably with the current process of zinc cementation.

The elution process for weak-base resins is superior from all points of view, but there is a trade-off in that the ion-exchange capacity of weak-base resins is lower than that of strong-base resins at the pH values typical of cyanide-leach liquors<sup>1</sup>. Therefore, the lower operating costs for elution would have to be balanced against the higher resin inventories and more extraction stages in the absorption; but this is an exercise beyond the scope of the present paper.

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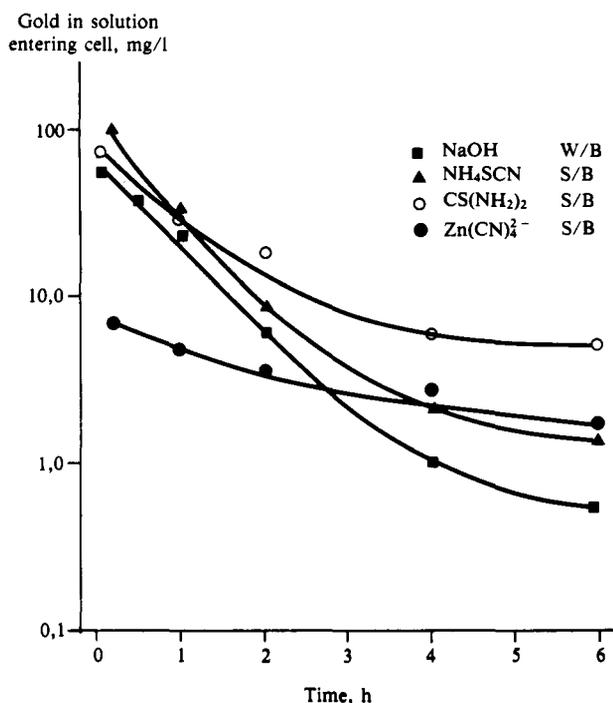


Fig. 9—Relative rates of gold recovery by electrolysis under the standard electro-elution conditions for the three strong-base (S/B) resin eluants and the one weak-base (W/B) resin eluant

TABLE IX

ADVANTAGES AND DISADVANTAGES OF VARIOUS PROCESSES FOR THE ELUTION OF STRONG- (S/B) AND WEAK-BASE (W/B) RESINS

Zn(CN) <sub>4</sub> <sup>2-</sup> (S/B)	SCN <sup>-</sup> (S/B)	CS(NH <sub>2</sub> ) <sub>2</sub> (S/B)	NaOH (W/B)
<b>Advantages</b> All anionic cyanide complexes eluted efficiently	All anionic cyanide complexes stripped in elution-regeneration		All anionic cyanide complexes stripped in elution and regeneration
Resin can be regenerated to full capacity each cycle with efficient recycle of chemicals	Resin can be regenerated to full capacity each cycle with efficient recycle of chemicals Non-toxic chemicals for elution and regeneration Fast elution kinetics	Resin does not have to be regenerated after elution Non-toxic chemicals for elution	Resin can be regenerated to full capacity each cycle with inexpensive chemicals Non-toxic chemicals for elution and regeneration Fast elution and electrowinning kinetics
No problems with materials of construction in elution and electrowinning			No problems with materials of construction in elution and electrowinning
<b>Disadvantages</b> Resin has to be chemically regenerated after elution Elution kinetics slow Toxicity of hydrocyanic gas produced during regeneration	Resin has to be chemically regenerated after elution Slight corrosion of electrodes in electrowinning cell	Elution kinetics slow Corrosion of electrodes in acidic eluate Poisoning of resin by cobalt-cyanide Decomposition of thiourea in acidic solution	Resin should be treated with acid after elution

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