

# The mechanism in the poisoning of anion-exchange resins by cobalt cyanide

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## SYNOPSIS

The complex responsible for the poisoning of anion-exchange resins is identified as the anionic cobaltic pentacyanide mono aquo species. It is shown that, at high concentration, this species polymerizes in solutions of pH less than 9. A mechanism for poisoning is presented that involves adsorption of anionic cobalt cyanide by a normal ion-exchange process, followed by polymerization within the resin matrix to form complexes that are too large to diffuse readily through the resin pores.

The effects of resin structure and functionality on the extent of cobalt poisoning are examined, and the effect of cobalt poisoning on the kinetics and equilibrium loading of uranium is discussed.

## SAMEVATTING

Die kompleks wat vir die vergiftiging van anioonruilharse verantwoordelik is, word geïdentifiseer as die anioniese kobalt-pentasianiedmonoakwospesie. Daar word getoon dat hierdie spesie by 'n hoë konsentrasie in oplossings met 'n pH-waarde van minder as 9 polimeriseer. Daar word 'n meganisme vir onomkeerbare vergiftiging aan die hand gedoen wat die adsorpsie van anioniese kobaltsianied deur 'n gewone ionruilproses gevolg deur polimerisering binne die harsmatriks om komplekse te vorm wat te groot is om maklik deur die harsporieë te diffundeer, behels.

Die uitwerking van die harsstruktuur en funksionaliteit op die omvang van die kobaltvergiftiging word ondersoek en die uitwerking van kobalt-vergiftiging op die kinetika en ewewigslading van uraan word bespreek.

## Introduction

A major feature of ion-exchange resins for the recovery and upgrading of soluble metal ions is their insolubility in aqueous solutions and the fact that, in principle, these materials can be regarded as a capital investment with an almost indefinite life. In practice, however, this ideal is seldom approached, and one of the main factors contributing to this altered economic picture is 'poisoning' of resin by the species that are not eluted under normal stripping conditions. These species accumulate on the resin, and the capacity of the resin for the desired metal ion gradually diminishes.

This problem was first encountered in South African uranium processing about thirty years ago on a pilot plant at the Western Reefs Gold Mining Co. Ltd. In experiments carried out on samples of poisoned resin at the Government Metallurgical Laboratory<sup>1</sup>, it was found that one of the species responsible for the poisoning of the resin was an anionic cobalt cyanide complex. The origin of the complex was readily explained since cobalt is a common constituent of Witwatersrand ores and cyanide is carried over from the cyanidation process for the extraction of gold.

Robinson's studies<sup>1</sup> indicated that the adsorption of one equivalent of cobalt on the resin reduced the ion-exchange capacity of the resin by three equivalents. Moreover, analytical results for the elements showed that the ratio of excess nitrogen to cobalt on the poisoned resin was about 6 to 1. On this basis, it was concluded that cobaltic hexacyanide,  $[\text{Co}(\text{CN})_6]^{3-}$ , was the responsible anion. However, although Burstall *et al.*<sup>2</sup> had produced evidence to show that  $[\text{Co}(\text{CN})_6]^{3-}$  that had been adsorbed on a resin could be eluted easily with a 2M solution of ammonium thiocyanate, this treatment had little effect on samples of poisoned resin from the pilot plant.

Two investigations carried out in an attempt to reconcile these differences led to the postulation of two new complexes as the species responsible for poisoning the resin:  $[\text{Co}(\text{CN})_4\text{2H}_2\text{O}]^{3-}$  (by West Rand Consolidated Mines<sup>3</sup>) and  $[\text{Co}(\text{CN})_5]^{3-}$  (by Pearson *et al.*<sup>4</sup>).

No further work was undertaken on this problem, and the situation remained in the unsatisfactory state that no agreement had been reached on the species responsible for the poisoning, and no concrete ideas or evidence had been presented on the mechanism of poisoning.

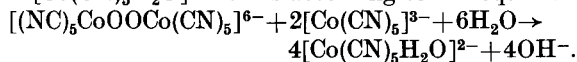
Interest was renewed in the problem recently as a result of work on the relative rates of poisoning of weak- and strong-base resins. It was felt that problems might be experienced with cobalt poisoning in the continuous ion-exchange treatment that was to be applied in the reclamation of relatively cobalt-rich dumps and slimes. Also, the extent to which high-density resins are poisoned by cobalt is of some interest in view of recent developmental work on the use of these resins to improve extraction performance with respect to parameters such as the flow-rate of leaching solution through a continuous ion-exchange column, and the pulp density of the leaching solution in the treatment of unclarified liquors.

This paper reports on the identification of the cobalt cyanide species responsible for poisoning resins. Advantage has been taken of the fairly comprehensive literature that has been published in recent years on the chemistry of the cobalt cyanide system. For example, in a review article, Chadwick and Sharpe<sup>5</sup> point out that cobalt(0)-cyanide and cobalt(I)-cyanide have been prepared, but that these species are stable only in a strongly reducing medium such as potassium in ammonia. It seems unlikely, therefore, that much credibility can be attached to the postulation<sup>3</sup> of the cobalt(I) species as being responsible for poisoning. Furthermore, a number of authors<sup>5-9</sup> have noted not only that the green cobaltous pentacyanide solution,  $[\text{Co}(\text{CN})_5]^{3-}$ , is

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rapidly oxidized by air, but that it also ages, a solution staying 'fresh' for a matter of seconds only. It therefore seems unlikely that the species postulated by Pearson *et al.*<sup>4</sup> is present in leach liquors in significant concentrations. Under normal conditions, and in the absence of competing ligands in high concentration,  $[\text{Co}(\text{CN})_5]^{3-}$  is the only cobalt(II) complex that can be expected to exist in uranium leach liquors.

The principal product of the rapid oxidation of the  $[\text{Co}(\text{CN})_5]^{3-}$  ion is a peroxo adduct of the cobalt(III) pentacyanide dimer,  $[(\text{CN})_5\text{CoOOC}(\text{CN})_5]^{6-}$ . The binuclear peroxo compound is moderately stable at 0°C, but at room temperature it oxidizes the  $[\text{Co}(\text{CN})_5]^{3-}$  ion and  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  forms according to the equation



When air is passed slowly through a solution containing the  $[\text{Co}(\text{CN})_5]^{3-}$  ion at 25°C, the binuclear peroxo compound is not detected and only  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  is formed. At a high CN-to-Co ratio, a percentage of the cobalt is converted to the hexacyanide ion  $[\text{Co}(\text{CN})_6]^{3-}$ , but at room temperature this is always a minor product since the uptake of the sixth cyanide is a slow process. However, at 95°C the conversion to  $[\text{Co}(\text{CN})_6]^{3-}$  is rapid.

An aqueous solution of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  has an absorption maximum at 380 nm, which is constant in the pH range 1 to 10. In 1M KOH the band moves to 371 nm, corresponding to the formation of  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$ . After aging or drying, the band at 380 nm is replaced by one at 350 nm, which is believed to be due to a polymeric anion. In the presence of excess cyanide, the band at 380 nm is slowly replaced by one at 310 nm, which corresponds to the hexacyanide complex  $[\text{Co}(\text{CN})_6]^{3-}$ . This is the ultimate product of reaction between cobalt and cyanide, and is the most stable anionic form in which cobalt can exist in uranium leach liquors.

As a result of the work reported in this paper and of previous work, it is now apparent that the cobalt cyanide on a resin is in one of two forms. The two forms are distinguished below in some detail, and are loosely termed 'reversible' and 'poisonous' cobalt. However, it should be borne in mind at the outset that even the reversible cobalt constitutes a poison in normal plant operation since it is not eluted by the eluants in common use.

### Experimental Solutions and Materials

All chemicals used in the preparation of the cobalt cyanide complexes and eluant solutions were of Analar Grade, and high-purity water from a Millipore purification system was used.

The  $[\text{Co}(\text{CN})_5]^{3-}$  and  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{6-}$  were prepared as described before<sup>6, 7</sup>, the  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  was prepared as described by Haim and Wilmarth<sup>6</sup>, and the  $[\text{Co}(\text{CN})_6]^{3-}$  was obtained by the method of Bigelow and Bailar<sup>10</sup>. In addition, a cobalt cyanide complex was prepared as follows under simulated plant conditions: an excess of cyanide was added to cobalt in aqueous solution and, while air was bubbled through the solution, the pH was lowered from 11, which is the pH value of the solution after cyanidation, to 1.8, which is the pH value of the uranium leach liquor.

The cobalt cyanide complexes that were prepared were characterized by ultraviolet spectroscopy. Absorption spectra of the complex solutions were recorded on a Beckman Acta MIV spectrophotometer, and reflectance spectra of the complexes and resins in the solid state were obtained on a Carl Zeiss RA3 single-beam spectrophotometer.

The resins that were studied were screened to a size range of minus 589 plus 500  $\mu\text{m}$  unless otherwise stated, and were converted to the sulphate form by treatment with 1M  $\text{Na}_2\text{SO}_4$ . The resins BRS76, WBR1, and WBR6 are experimental high-density resins produced at the National Institute for Metallurgy. The other resins that were studied (IRA400, A101DU, and XE299) are commercial anion-exchange resins.

### Batch Tests

The extent of poisoning on resins was determined in batch tests in which 1 ml samples of various resins were treated with 10 ml aliquots of solution containing cobalt cyanide, and were agitated for 16 to 24 hours. The cobalt in solution was determined by atomic-absorption spectrophotometry both before and after the solution had been contacted with the resin, and the amount of cobalt cyanide adsorbed on the resin was obtained by subtraction. The concentration of cobalt before the solution was contacted with the resin was generally 10 mg per 10 ml of solution, and this represents about 25 per cent of the capacity for cobalt of most of the resins studied (approximately 40 g per litre of wet-settled resin).

After being loaded, the resin was washed with distilled water and was then treated with a 10 ml aliquot of 2M  $\text{NH}_4\text{SCN}$ . This reagent is sufficiently strong to elute the reversible or ionically bonded cobalt cyanide, but has no effect on poisonous cobalt. The resin was subjected to successive stripping treatments with 2M  $\text{NH}_4\text{SCN}$ , each treatment being followed by a wash with water. The treatment was continued until no cobalt appeared in the strip liquor, and it was found that equilibrium on each stripping treatment was attained in 2 to 6 hours.

Finally, the resin was treated first with hot 50 per cent  $\text{NH}_4\text{SCN}$  for 16 hours and then with a hot solution of 10 per cent bromine in concentrated hydrochloric acid for about 4 hours. This treatment eluted the poisonous cobalt from the resin.

All the strip liquors were analysed for cobalt.

### Continuous Tests

The continuous tests were designed to measure the kinetics of adsorption of the anionic cobalt and uranium on the resins, and the capacity of the various resins for these metal anions. The experiments were conducted in the all-glass fluidized-bed reactor described by Harris and Finkelstein<sup>11</sup> and illustrated in Fig. 1. An all-glass centrifugal pump circulates solution through the reactor to fluidize the resin, which then passes through an optical flowcell located in the sample compartment of a Beckman DK2A spectrophotometer. The cobalt or uranium solution is introduced from reservoir S and the resin through the holding tube R, which is calibrated to hold 2.1 ml of wet-settled resin. Before resin is admitted to the reactor, the wavelength of the spectrophotometer is

adjusted to give a convenient absorbance with the desired uranium or cobalt solution circulating in the apparatus. After the resin enters the reactor, the absorbance (due to the metal ion) decreases as a result of ion exchange, and sufficient concentrated uranium or cobalt solution is added from a Mettler automatic burette (M) to restore the original concentration and absorbance level. The volume of concentrated solution added as a function of time therefore results in a kinetic profile of the reaction.

The maximum loading of metal ions is obtained by the reaction being continued to equilibrium.

All the solutions were adjusted to a pH of 1,8 and had a sodium sulphate concentration of 30 g/l. The uranium solutions contained 0,20 g/l uranium (as uranyl sulphate), and the uranium concentration in the automatic burette was 20 g/l. In the cobalt experiments, the reservoir contained cobalt at 0,10 g/l and the burette at 1,0 g/l.

### Results and Discussion

The complexes  $[\text{Co}(\text{CN})_6]^{3-}$ ,  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ ,  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{6-}$ , and  $[\text{Co}(\text{CN})_6]^{3-}$  and the simulated plant solution were tested with the heavy strong-base resin BRS76 to show which, if any, were responsible

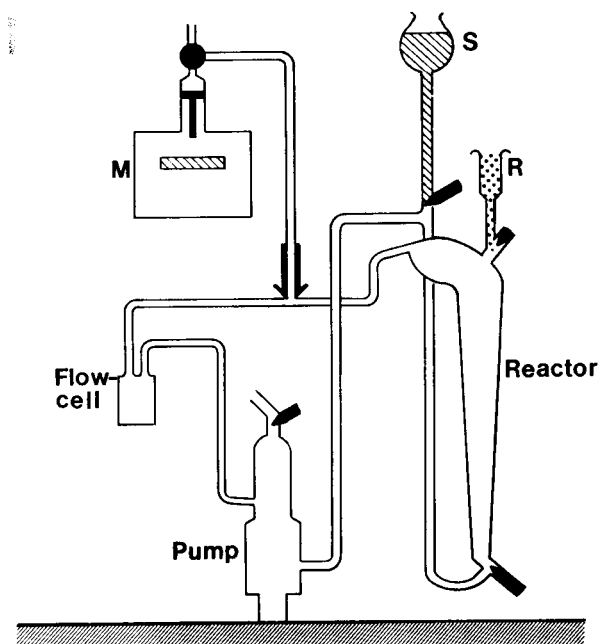


Fig. 1—An all-glass fluidized-bed reactor for the measurement of the kinetics of ion exchange

for poisoning the resin. The results are presented in Table I.

An ultraviolet spectrophotometer analysis of the five compounds indicated that the fresh simulated plant solution contained about 90 per cent  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  and about 10 per cent  $[\text{Co}(\text{CN})_6]^{3-}$ . This result and the results presented in Table I indicate that the species responsible for resin poisoning is  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ . Moreover, since  $[\text{Co}(\text{CN})_6]^{3-}$  oxidizes rapidly to  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ , and  $[(\text{CN})_5\text{CoO}_2\text{Co}(\text{CN})_5]^{6-}$  hydrolyses rapidly to  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ , the poisoning levels of 1 and 2 per cent respectively in these two cases (Table I) probably represent conversion to  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$ .

The complete elution of  $[\text{Co}(\text{CN})_6]^{3-}$  with 2M  $\text{NH}_4\text{SCN}$  agrees with the findings of Burstall *et al.*<sup>2</sup>

Unless otherwise stated, the experiments below refer to the  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  ion.

#### Effect of Eluant

Two high-density resins, strong-base BRS76 and weak-base WBR1, were loaded with  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  to about 10 g/l cobalt and then subjected to four batch-type treatments with various eluants. By the fourth elution in each case, very little cobalt appeared in the eluate. The results are listed in Table II.

These results show that the conventional reagents  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  have little effect on anionic cobalt cyanide adsorbed on a strong-base resin. Similarly,  $\text{H}_2\text{SO}_4$  and  $\text{NaCl}$  have little effect on the cobalt adsorbed on a weak-base resin, although  $\text{NaOH}$  is apparently effective.

The results for 2M  $\text{NH}_4\text{SCN}$  indicate that about 7 per cent of the cobalt initially loaded was converted to

TABLE II  
THE ELUTION OF  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  FROM STRONG- AND WEAK-BASE RESINS WITH VARIOUS ELUANTS

Resin	Eluant	Cobalt loaded on resin	Cobalt stripped from 1 litre of resin in 4 treatments	Total eluted
		g/l	g	%
BRS76	1M NaOH	10,40	0,14	1,3
BRS76	1M $\text{H}_2\text{SO}_4$	10,40	0,23	2,2
BRS76	2M $\text{NH}_4\text{SCN}$	10,40	9,62	92,5
WBR1	1M NaCl	9,89	0,72	7,3
WBR1	1M $\text{H}_2\text{SO}_4$	9,89	1,15	11,6
WBR1	1M NaOH	9,89	7,28	73,6
WBR1	2M $\text{NH}_4\text{SCN}$	9,89	9,23	93,3
WBR1	50% $\text{NH}_4\text{SCN}$ , $\text{Br}_2$ in HCL	9,89	10,35	104,7

TABLE I

THE LOADING AND STRIPPING BEHAVIOUR OF COBALT CYANIDE COMPLEXES ON STRONG-BASE RESIN BRS76

Cobalt cyanide complex	Cobalt loaded on 1 litre of resin	Cobalt stripped from 1 litre of resin				Cobalt poisoning resin
		2M $\text{NH}_4\text{SCN}$			50% $\text{NH}_4\text{SCN}$ $\text{Br}_2$ in HCL	
		1st	2nd	3rd		
	g	g	g	g	g	%
$[\text{Co}(\text{CN})_6]^{3-}$	28,36	26,00	1,80	0,27	0,33	1,2
$[(\text{CN})_5\text{CoOOC}(\text{CN})_5]^{6-}$	32,63	29,50	2,60	0,32	0,68	2,1
$[\text{Co}(\text{CN})_6]^{3-}$	10,19	9,06	1,25	0,47	0,04	0,4
$[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$	10,55	7,90	0,88	0,31	1,42	13,5
Simulated plant solution	10,30	7,40	0,81	0,11	1,85	18,0

the poisonous form (i.e. only 93 per cent can be eluted with 2M NH<sub>4</sub>SCN). The results for the other eluants (H<sub>2</sub>SO<sub>4</sub>, NaOH, and NaCl) therefore refer to the elution of predominantly reversible, or ionically bonded, cobalt cyanide. In normal plant operation, therefore, not even the reversible cobalt is eluted, and the practical implications of this are discussed below. (It should be noted that NaOH, H<sub>2</sub>SO<sub>4</sub>, and NaCl have absolutely no effect on poisonous cobalt, even after treatment for about three weeks.)

As expected, the treatment with hot 50 per cent NH<sub>4</sub>SCN followed by Br<sub>2</sub> in hydrochloric acid elutes both the reversible and the poisonous cobalt.

*The Effect of Resin Poisoning on the Kinetics and Equilibrium Loading of Uranium*

Four samples of a conventional strong-base resin, A101Du, were poisoned to different extents by being treated with solutions containing different concentrations of [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> for about three weeks. After this treatment, the reversible cobalt was eluted with 2M NH<sub>4</sub>SCN, and the adsorption behaviour of these samples was compared with that of a sample of unpoisoned A101Du. In these experiments the resin was screened to a size of plus 589 μm.

The results are shown in Table III.

The rate of approach to equilibrium was determined by a quadratic driving-force equation derived by Ver-

TABLE III

THE EFFECT OF COBALT POISONING ON THE KINETICS AND EQUILIBRIUM LOADING OF URANIUM ON A101Du

Cobalt poison on resin g/l	Uranium loaded on resin g/l	Initial rate g/l/min	Rate of approach to equilibrium s <sup>-1</sup> × 10 <sup>6</sup>
0	44,0	0,95	45,3
0,27	43,0	0,54	8,2
0,49	38,0	0,45	9,1
1,35	34,0	0,24	4,7
10,02	22,5	0,08	1,1

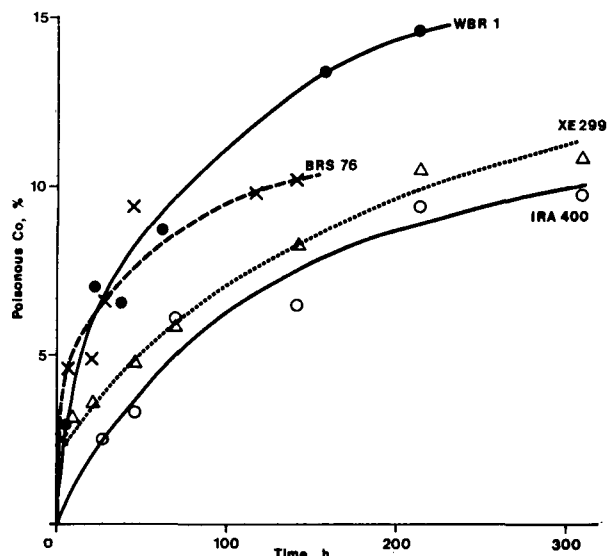


Fig. 2—The effect of resin density and functionality on the rate of cobalt poisoning (total cobalt on resin = 10 g/l)

TABLE IV

THE EFFECT OF RESIN DENSITY AND FUNCTIONALITY ON THE CAPACITY FOR URANIUM AND POISONOUS COBALT

Resin	Gel-type resin	Metal loaded on resin at equilibrium		Rate of approach to equilibrium	
		Cobalt g/l	Uranium g/l	Cobalt s <sup>-1</sup> × 10 <sup>6</sup>	Uranium s <sup>-1</sup> × 10 <sup>6</sup>
IRA400	Conventional strong-base	37,2	45,8	19	43
BRS76	High-density strong-base	46,8	45,0	26	56
XE299	Conventional weak-base	29,8	28,3	17	31
WBR6	High-density weak-base	45,2	30,7	12	33

meulen<sup>12</sup> and used by Hendricksz<sup>13</sup>, in terms of which the rate can be expressed as

$$\frac{d[U]}{dt} = \frac{D\pi^2}{r^2} \frac{[U]_e - [U]_t}{2[U]_t - [U]_0} \quad \dots \dots \dots (1)$$

where *D* is an average interdiffusion coefficient, *r* is the radius of the resin bead, and [U]<sub>0</sub> the concentration of uranium in the resin at time *t*=0. For [U]<sub>0</sub>=0 and [U]<sub>e</sub> a constant, the integration of equation (1) yields

$$\log \{[U]_e^2 - [U]_t\} = \frac{D\pi^2}{r^2} t + \text{constant} \quad \dots \dots \dots (2)$$

The rate data in Table III refer to the term *Dπ<sup>2</sup>/r<sup>2</sup>* in equation (2).

*The Effect of Resin Density and Functionality on Cobalt Poisoning*

The results plotted in Fig. 2 show the effect of resin density and functionality on the rate of cobalt poisoning, i.e., the rate at which ionically bonded cobalt is converted to poisonous cobalt. The time axis in Fig. 2 refers to the period of time between the loading of [Co(CN)<sub>5</sub>H<sub>2</sub>O]<sup>2-</sup> onto the resin and the first batch-type elution with 2M NH<sub>4</sub>SCN. The results indicate that the following gel-type resins are all poisoned by cobalt: strong-base (IRA400 and BRS76), weak-base (XE299 and WBR1), conventional (XE299 and IRA400), and high-density (BRS76 and WBR1).

The capacity of the resins for poisonous cobalt and the rate of approach to this poisoning equilibrium were also determined in the fluidized-bed reactor. These results are given in Table IV, where they are compared with results for uranium. The latter, of course, reflect simple ion-exchange equilibria.

The results show that the two strong-base resins have about 50 per cent greater capacity for uranium than the two weak-base resins, and that the rate of extraction is also about 50 per cent faster in the strong-base resins. This is to be expected in ion-exchange equilibria since the strong-base quaternary-amine functional group will have a greater force of attraction for anionic uranium than will the weak-base tertiary-amine functional group.

The situation is different with cobalt poisoning in that the weak- and strong-base resins are poisoned to an approximately equal extent. The high-density resins are apparently poisoned more than the conventional resins, and this effect remains unexplained. The fact that resin functionality has little influence on the final

concentration of cobalt poison suggests strongly that the cobalt, in its poisonous form, is not formally bonded to the functional group either ionically or covalently.

A distinction between the fast ion-exchange 'pseudo equilibrium' and the slow poisoning equilibrium is shown in Fig. 3. Thus, in a plot of  $\log \{[M_e]^2 - [M_t]^2\}$  against time using equation (2), the data for uranium fall on a single straight line whereas the data for cobalt are linear only in the initial stages of reaction. The data for cobalt in Table IV refer to the rate of attainment of the fast ion-exchange 'pseudo-equilibrium' (i.e., the slope of the linear portion of Fig. 3). It is not surprising to find that in this region the kinetics are faster for the strong-base resins than for the weak-base resins, as is the case with uranium.

#### The Effect of Resin Structure on Cobalt Poisoning

The effect of resin structure was examined in a comparison of three strong-base resins that contained respectively 2, 4½, and 8 per cent divinylbenzene (DVB). An increase in the percentage of DVB increases the cross-linking in the resin, which increases the density of

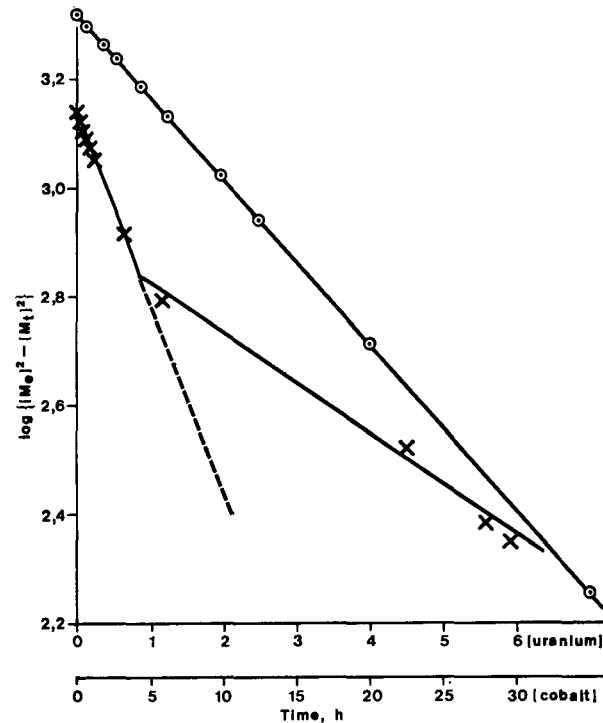


Fig. 3—The rate of approach to an equilibrium adsorption of uranyl sulphate (O) and cobaltic pentacyanide (x) on the strong-base anion-exchange resin IRA400

TABLE V

THE EFFECT OF RESIN STRUCTURE ON THE CAPACITY FOR URANIUM AND POISONOUS COBALT

Resin (conventional strong-base)	Metal loaded on resin at equilibrium		Rate of approach to equilibrium	
	Cobalt g/l	Uranium g/l	Cobalt $s^{-1} \times 10^6$	Uranium $s^{-1} \times 10^6$
2 DVB	29,8	15,7	68	437
4,5 DVB	37,2	27,6	57	176
8 DVB	33,0	42,9	14	79

functional groups in the resin and thereby increases its capacity for exchange ions. However, an increase in the density of the exchange sites in a resin decreases the interdiffusion coefficient,  $D$ , of exchange ions and this is reflected in poorer ion-exchange kinetics.

The results for the three resins are listed in Table V, and once again data for uranium are included for comparative purposes.

On the basis of the above arguments, the data for uranium are typical. Thus, with increasing DVB, the capacity of the resins for uranium increases whereas the kinetics of adsorption decrease. However, the content of DVB has little effect on the capacity of the resins for poisonous cobalt, and this result also indicates that cobalt, in its poisonous form, is not formally bonded to the exchange sites on the resin. Once again the kinetic data are parallel to those for uranium, and this too is to be expected since they represent the rate of approach to the 'pseudo' ion-exchange equilibrium and not the poisoning equilibrium.

#### Mechanism of Poisoning

The cobalt cyanide that is adsorbed on the resin could, theoretically, undergo one of two reactions that would convert the anion from a reversible to a poisonous species. Either the fairly weak ionic bond with the resin functional group could be replaced by a strong covalent bond, or the cobalt anions could polymerize, forming species too large to diffuse readily through the

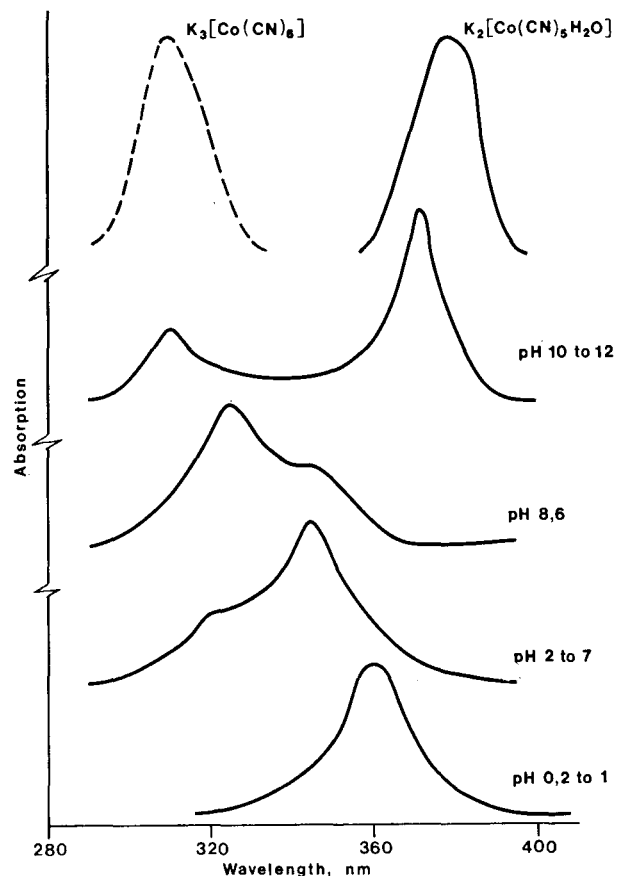


Fig. 4—The ultraviolet spectra of  $K_3[Co(CN)_6]$  and  $K_2[Co(CN)_5H_2O]^{2-}$  and of the cobaltcyanide complexes formed at high concentrations and at various pH values

resin pores. In the first case,  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  displaces a methyl group from the functional group, and in the second it displaces a water molecule from an adjacent  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  anion. Experience indicates that the latter reaction should have the lower activation energy. In addition, all the experimental evidence above suggests that the functional group plays little part in the poisoning mechanism.

The effect of the resin matrix upon individual anions is to bring them into very close proximity to one another by virtue of the high density of the exchange sites in the resin. Therefore, under normal conditions, the concentration of cobalt within the resin is considerably higher than in the bulk solution. In an attempt to simulate these conditions, a solution of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  was concentrated under vacuum at room temperature to 250 g/l cobalt. This was done at a number of pH values between 11 and 0,2, and the ultraviolet spectra of the concentrated solutions were recorded. These are presented in Fig. 4, along with the spectra of dilute solutions of  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  and  $[\text{Co}(\text{CN})_6]^{3-}$  as a comparison.

The spectra show that there is little change at pH values greater than 10. The band at 380 nm shifts to 372 nm, and this is consistent with the formation<sup>9</sup> of  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$ . A small amount of the hexacyanide compound is formed, but this is to be expected seeing that the  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$  solution contained a slight excess of cyanide.

At a pH value of 8,6 a new peak is observed at 325 nm, with a shoulder at 345 nm. The absence of absorption at 380 nm indicates complete conversion to the new species. Between pH values of 2 and 7, the species that absorbs at 345 nm predominates and there is a shoulder only at 325 nm. Finally, at pH values of less than 1 a new species is formed that absorbs at 360 nm.

Since  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  absorbs at 380 nm and  $[\text{Co}(\text{CN})_6]^{3-}$  at 310 nm, the replacement of the weak ligand  $\text{H}_2\text{O}$  by the strong ligand  $\text{CN}^-$  produces a blue shift of 70 nm in the ultraviolet spectrum. The peak at 325 nm corresponds to a blue shift of 55 nm from the spectrum for  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]$ . This suggests that the water molecule has been replaced by a ligand that is stronger than water yet weaker than cyanide. However, since there are no other ligands in solution besides  $\text{H}_2\text{O}$  and  $\text{CN}^-$ , the changes that occur in solution with increasing concentration can be attributed only to a change from C-bonded cyanide to N-bonded cyanide. This is consistent with a polymerization mechanism that involves the replacement of  $\text{H}_2\text{O}$  in  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  by an N-bonded cyanide of an adjacent  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  molecule, i.e., by the formation of cyanide bridges between adjacent cobalt atoms (Fig. 5). The existence of such polymeric species has been suggested before<sup>6, 7</sup>.

Bridging N-bonded cyanide is a weaker ligand than terminal C-bonded cyanide, and this is consistent with the red-shift from the spectrum for  $[\text{Co}(\text{CN})_6]^{3-}$ .

If it is assumed that the band at 325 nm corresponds to the linear polymeric species (I), which contains one N-bonded cyanide per cobalt unit,  $[\text{Co}(\text{CN})_5(\text{NC})]^{2-}$ , then, by an extension of the same argument, it seems likely that the bands at 345 nm and 360 nm correspond to polymeric species containing two and three N-bonded

cyanides per unit respectively. In these two cases polymerization takes place by way of the loss of cyanide, and not water as in polymer(I), and the fact that these species form only in fairly acid solution is therefore understandable. A summary of the spectral data for the monomeric cobaltic cyanide complexes and the proposed polymeric species is presented in Table VI.

In experiments similar to those described above, a solution of  $[\text{Co}(\text{CN})_6]^{3-}$  was concentrated to 250 g/l cobalt at various pH values between 11 and 0,5. There was no evidence of polymerization and, moreover, samples of resin that were loaded to capacity with  $[\text{Co}(\text{CN})_6]^{3-}$  showed no evidence of poisoning, even after four weeks of treatment.

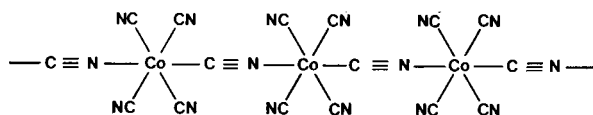


Fig. 5—Structure (I)

TABLE VI  
ABSORPTION MAXIMA OF VARIOUS COBALT CYANIDE COMPLEXES

Complex	Stable pH range	Wavelength at absorption maximum, nm
Polymeric $[\text{Co}(\text{CN})_6]^{3-}$	> 0,5	310
Polymeric $[\text{Co}(\text{CN})_5(\text{NC})]^{2-}$	7 to 9	325
Polymeric $[\text{Co}(\text{CN})_4(\text{NC})_2]^{-}$	2 to 7	345
Polymeric $[\text{Co}(\text{CN})_3(\text{NC})_3]$	0,2 to 1	360
$[\text{Co}(\text{CN})_5\text{OH}]^{3-}$	> 10	372
$[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$	1 to 10	380

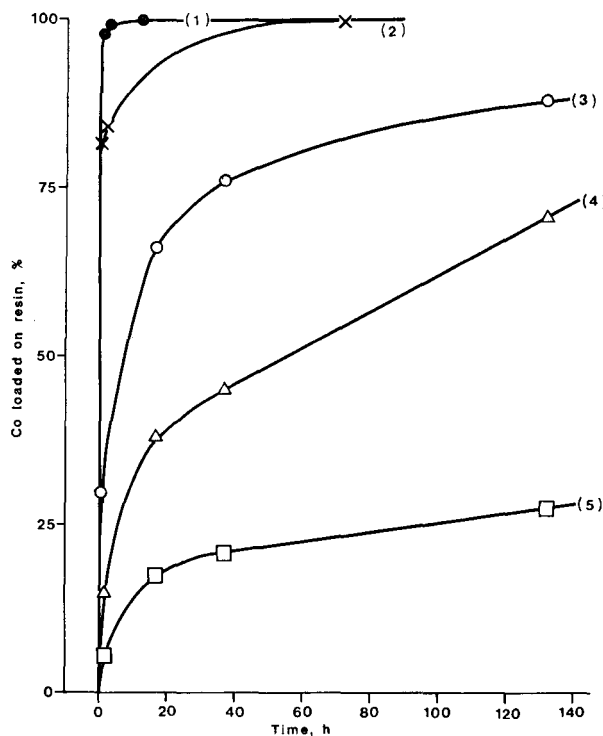


Fig. 6—The adsorption of cobalt cyanide onto BRS76 from solutions containing 250 g/l cobalt at various pH values: (1) pH 11,7 (2) pH 10,0 (3) pH 8,6 (4) pH 3,0 (5) pH 0,9

That the fourth and fifth cyanide ligands are displaced in the proposed polymers that absorb at 345 and 360 nm respectively, whereas the sixth cyanide in  $[\text{Co}(\text{CN})_6]^{3-}$  cannot be displaced, is not contradictory. This can be explained on the basis of a reduction in electrostatic repulsion in the former two complexes, which can give rise to differences of many orders of magnitude in the rate of polymerization<sup>14</sup>.

The ion-exchange properties of the proposed polymeric species were studied, and the results are shown in Fig. 6. It can be seen quite readily that the kinetics of loading decrease markedly as the extent of polymerization increases. By a logical extension, it can be predicted that, when polymerization takes place inside the resin and not in solution, the kinetics of elution will decrease similarly as the extent of polymerization increases. Confirmation of this mechanism was found in a study of the reflectance spectra of the various cobalt complexes in the solid state and adsorbed on a resin.

The three polymeric species were precipitated from their 250 g/l solutions by the addition of ethanol, and a reflectance spectrum of the mixture, with magnesium oxide as a reference, is presented in Fig. 7. The reflectance spectrum of a poisoned resin, with fresh resin as a reference, is also included in Fig. 7. The poisoned resin used for this spectrum was the sample of A101Du that contained 10 g/l poisonous cobalt (Table III).

The monomeric hexacyanide and pentacyanide complexes were also loaded onto samples of resin—the latter from a solution of pH 11 to ensure that no polymerization occurred. These spectra are included in Fig. 7 as a comparison, and the spectral evidence confirms

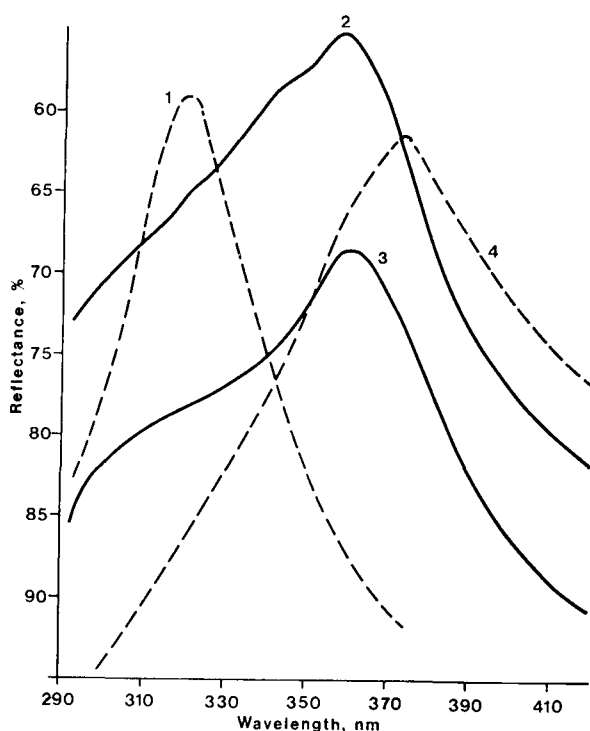


Fig. 7—The reflectance spectra of cobalt cyanide complexes: 1.  $[\text{Co}(\text{CN})_6]^{3-}$  adsorbed on a resin; 2. a mixture of cobalt cyanide polymeric species precipitated from aqueous solution with ethanol; 3. a resin that has been poisoned with cobalt; 4.  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$  adsorbed on a resin

that the poisoned A101DU resin contains polymeric cobalt cyanide.

These conclusions contradict the early observations that the cobalt anion on the resin is associated with six cyanide groups and has a triple negative charge. However, an examination of Robinson's data<sup>1</sup> shows that the proposed Co-to-CN ratio of 1 to 6 represents a maximum, whereas, if possible degradation of the resin is taken into account, the actual ratio could be as low as 1 to 3. Similarly, since the mechanism presented here shows that poisoning does not involve a simple 1-to-1 association of cobalt with the exchange site, it is not possible to deduce the charge on the cobalt complex from an analysis of the exchange capacity of the resin.

### Practical Implications

In the presence of excess cyanide, cobalt in solution will slowly be converted to its most stable form, which is the hexacyanide anion  $[\text{Co}(\text{CN})_6]^{3-}$ . Therefore, cobalt cyanide in solution, slimes, or dumps that have aged for a long time will be in the hexacyanide form and, when adsorbed on an anion-exchange resin, will not constitute a true poison, i.e., in the case of a weak-base resin, the cobalt will be eluted in the caustic regeneration cycle or, in the case of a strong-base resin, the cobalt can be eluted with ammonium thiocyanate.

In fresh solutions  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  predominates and will polymerize once adsorbed on the resin. The concentration of this species entering a uranium plant can be minimized either by water-washing of the filter cake after gold cyanidation and before acid leaching, or by treatment of the gold raffinate with an anion-exchange resin before recycling. This could perhaps even be done by a resin-in-pulp treatment during gold leaching. This resin would not be poisoned since, at the high pH value of the gold leach, the cobalt is in the  $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$  form.

The kinetics of polymerization are very slow. Therefore, if a weak-base resin were used instead of a strong-base resin, most of the  $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{2-}$  would be eluted in the caustic-regeneration step before it had time to polymerize.

Once a resin is poisoned it can still be regenerated by being treated with hot 20 per cent ammonium thiocyanate (which breaks the polymer) and eluted with strong acid. This treatment reduces the capacity of the resin slightly and should therefore be used infrequently.

### Acknowledgement

This paper is published by permission of the National Institute for Metallurgy.

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## Metallurgical slags

An International Symposium on Metallurgical Slags, sponsored by the Basic Sciences Section of the Metallurgical Society of the Canadian Institute of Mining and Metallurgy (CIM), will be held in Halifax, Nova Scotia, from 24th to 28th August, 1980.

The Symposium will be an integral part of the 19th Annual Conference of Metallurgists of the CIM. It is expected to be a three-day symposium with six sessions, which will run concurrently with the other sessions planned for the Conference as a whole.

Papers are being solicited on all aspects of the physics and chemistry of metallurgical slags, with particular emphasis on the following:

—Thermodynamics and constitution of slags

—Kinetics and equilibria of slag-metal reactions

—Transport, viscosity, and other properties

—Physical chemistry of copper-smelting slags, electro-slugs, and cryolite-alumina melts.

The proceedings will be published, and manuscripts of contributed papers will be subject to standard refereeing procedures. Interested participants should communicate in the first instance with the Symposium Chairman, Dr C. R. Masson, National Research Council of Canada, 1411 Oxford Street, Halifax, N.S., B3H 3Z1, Canada.

The deadline for titles and short abstracts is 1st December, 1979. The deadline for complete manuscripts, in a form suitable for publication, is 1st April, 1980.

## Design awards

Manufacturers are invited to enter products for the 1979 Design Institute/Shell Design Awards.

The Awards are nationally and internationally recognized accolades given to the manufacturers of South African products considered by an independent panel of judges to be outstanding examples of South African product design.

The commercial benefits to the manufacturer of an award-winning product are considerable; past recipients have reported significant increases in their sales, locally and overseas. The award emblems may be used on products, on advertisements, in sales literature, and at exhibitions.

There are three broad categories in which products may be entered for an award: engineering products and components intended for use in general industry, agriculture, mining, medicine, transportation, communication, and any other appropriate area of engineering

activity; consumer products intended for purchase by members of the general public for use in their domestic, working, or recreational pursuits; and contract products intended for use in the equipping and furnishing of public and commercial premises and environments.

The 1979 awards are open to the manufacturer of any product that is designed and manufactured in South Africa.

The Design Institute and the sponsor of the awards are committed to promoting the award-winning products by means of national and international press releases to selected media. The Design Institute publishes a full colour edition of its monthly journal *Brief*, in which the award-winning products are prominently featured, and arranges exhibition displays.

Applications for entry forms for the Design Institute/Shell Design Awards 1979 should be made to the Manager, Design Institute, Private Bag X191, Pretoria, 0001.