The extraction of gold from cyanide solutions by strong- and weak-base anion-exchange resins

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SYNOPSIS
This paper describes the extraction of gold, as the anionic aurocyanide complex, from solution by strong- and weak-base anion-exchange resins. The effects, on the rate of extraction and the loading capacity for gold, of parameters such as pH, temperature, ionic strength, agitation, and the presence of competing anions are reported.

The elution and regeneration of strong- and weak-base resins will be examined in a second paper. A third paper in this series will present the results of several small-scale pilot-plant investigations carried out with strong- and weak-base resins in cyanide pulps from various South African gold mines, and will compare the metallurgical performance of resin-in-pulp with that of the carbon-in-pulp process.

SYNOPSIS
Hierdie referaat beskryf die ekstraksië van goud, as die anoniëse ourosianied-kompleks, uit 'n oplossing met sterk- en swakbasis-anion-ruilharse.

Die uitwerking van parameters soos die pH, temperatuur, loonsterkte, roering en die aanwesigheid van mededingende anionie op die ekstraksië-tempo en die laaivermoë vir goud word aangegaan.

Die eluering en regenerasie van sterk- en swakbasisharse sal in 'n tweede referaat ondersoek word; 'n derde referaat in die reeks sal weer die resultate aangee van verskeie kleinskaalse proefaanlegondersoek wat met sterk- en swakbasisharse uitgevoer is in sianiedpulp afkomstig van verskillende Suid-Afrikaanse goudmyne, en die metalurgiese werkverrigting van die hars-in-pulpproses met dié van die koosloof-in-pulpproses vergelyk.

Introduction
Resin-in-pulp as an Alternative to Carbon-in-pulp

Much attention has been focused at the Council for Mineral Technology (Mintek) on the carbon-in-pulp (CIP) process for the extraction of gold from cyanide media. The successful development of this process led to a decision that the resin-in-pulp (RIP) process should be examined as a possible alternative to CIP for gold recovery, because resins have several characteristics that make them more attractive than activated carbon. The following are examples.

(a) Anion-exchange resins are superior to currently available activated carbons with respect to the rate and equilibrium loading of aurocyanide. This means that either the resin inventory or the plant will be smaller in the RIP process than in the CIP process.

(b) Resins can be eluted at room temperature, whereas the elution of carbon has to be carried out at high temperatures, preferably around 120 to 130°C, in a pressure vessel.

(c) Activated carbon requires periodic thermal reactivation for the removal of adsorbed organic materials—a step that is unnecessary with resins. (This factor and (b) could contribute to reduced capital and operating costs in an RIP application.)

(d) Resins do not load calcium carbonate to the same extent as activated carbon, and the acid-washing step in the CIP process will therefore probably be unnecessary in an RIP application.

(e) Resins do not appear to be 'poisoned' by organic species such as flotation reagents, machine oils and lubricants, or solvents, all of which can severely inhibit the loading of gold onto activated carbon. Similarly, species such as hematite and shales or clay-type minerals depress the loading of gold onto carbon but have little effect on resins.

(f) A possible further advantage of RIP is that South Africa has developed a resin-manufacturing facility, whereas the long-term supply of activated carbon is less assured.

To be weighed against these advantages of resins over activated carbon are the following disadvantages.

(i) Anion-exchange resins are less selective than activated carbon for gold cyanide over the base-metal cyanides that are prevalent in cyanide leach liquors.

(ii) The particles of resin are smaller than those of carbon. Consequently, in RIP the pulp has to be screened at about 35 mesh with 28-mesh interstage screening, whereas in CIP the pulp is screened at 28 mesh with 20-mesh interstage screening.

(iii) The physical strength of resins and their resistance to attrition and abrasion in the absorption tanks are largely unknown.

(iv) Resins are less dense than activated carbon and tend to accumulate at the surface of the pulp unless it is agitated efficiently.

In its project on RIP, Mintek aims to weigh the advantages and disadvantages of RIP and CIP one against the other, and to establish whether there is a place for RIP in the South African gold-mining industry.

Historical Background

The use of resins to extract gold from cyanide solutions and pulps was first investigated in South Africa as early as 1961, although the U.S. Bureau of Mines conducted an even earlier investigation. In the latter study, the use of weak-base resins to recover gold...
cyanide solution was examined, but the process failed owing to the inability of weak-base resins to extract anions efficiently at the high pH values of cyanide leach liquors.

The use of resins for the recovery of gold was also advanced by Burstall et al.3 and Burstall and Wells4 in the early 1950s. In those studies, it was observed that gold in cyanide solution could readily be absorbed onto strong-base anion-exchange resins together with the complex cyanides of many other metals. By using a series of selective eluting agents, they4,4 found it possible to remove the various metals successively and to obtain a number of discrete eluates containing relatively high concentrations of the various metals. One of the eluates was an organic liquid that carried virtually all the silver and gold present in the original impure cyanide pregnant solution that had been treated.

Davey et al., using strong-base resins, also demonstrated the potentiality of the RIP process, and expressed the view that it could compete with the conventional cyanide-precipitation process provided that the pregnant solution was high in gold and relatively free of competing metal cyanide complexes. Their design philosophy was the extraction of the aurocyanide as selectively as possible in the absorption stages, followed by non-selective elution of the resin. Pure gold was recovered from the eluate by electrolysis. The most efficient recovery of gold was obtained when the elution and electrolysis were carried out in a continuous and closed 'electroelution' cycle. Acidified thiourea and ammonium thiocyanate were successfully tested as non-selective eluants.

More recent progress in the development of RIP for gold extraction has been made in the Soviet Union and Roumania5-8, and a 1978 report4 indicates that one of the largest gold mines in the Soviet Union is using an anion-exchange resin to extract aurocyanide by an RIP process. This is believed to have been the world's first application of RIP to the extraction of gold, although RIP is now used widely for gold extraction in the Soviet Union. In their process, non-selective absorption is followed by selective elution. Zinc, nickel, and cyanide are eluted first by dilute mineral acid. This is followed by the elution of copper with an ammoniacal solution of ammonium nitrate and, finally, gold and silver are desorbed and electrowon continuously, with acidified thiourea as the eluant. The unattractive features of the process developed by the Russians are the following:

(i) its complexity, since three or four stages of elution are undesirable as regards capital and operating costs,
(ii) the use of acid in the first stage of elution, which converts iron and cobalt on the resin to complex species that desorb with difficulty, and
(iii) the significant percentage of thiourea (an expensive reagent) that is lost in each cycle.

The Canadians recently looked into the possibility of using strong-base resins to extract gold from cyanide solution9. They concluded that the non-selectivity of gold absorption, coupled with the high cost of elution (ammonium thiocyanate and acidified acetone were tested as eluants), rendered the process unfavourable as compared with zinc precipitation. In their study, only clarified solutions were investigated, and the economic benefits to be gained from the bypassing of filtration by an RIP application were not considered.

Mintek first became interested in resins for the extraction of gold in 1975, when RIP was applied to the recovery of soluble gold at Durban Roodepoort Deep Gold Mine10. Weak-base resin was tested in a solution whose pH value had been adjusted to 4, but the process was abandoned because of the massive formation of crystalline calcium sulphate at that pH value. Strong-base resin was also tested, and it was demonstrated that gold could be successfully absorbed and eluted. An elution procedure (which uses zinc cyanide as the eluant) proposed by Hazen11 was tested because of its compatibility with the processes used on most gold mines. That method uses a saturated solution of sodium zinc cyanide to elute gold from the resin, after which the gold cyanide passes through a bed of zinc powder. The gold gments onto the zinc, and the zinc cyanide that is generated is recycled to elution. It was reported11 that the concentration of zinc in a saturated solution of zinc cyanide was only 4 g/l and that, for this reason, vast volumes (320 resin bed-volumes) of eluate had to be used to elute the gold completely. Accordingly, the process was assessed unfavourably11. In fact, in the present study it is shown that, at ambient temperature, sodium zinc cyanide solution can be prepared that contains as much zinc as 30 g/l, which has placed the zinc cyanide elution procedure in a new perspective.

In the present study, which is described in a series of three papers, the whole question of RIP for gold recovery is re-examined in the light of the successful development of CIP; the advances in the technology of ion-exchange resins, and the changed economic situation brought about by high gold-bullion prices. A conventional CIP plant comprising absorption, elution, and electrowinning circuits should therefore be readily convertible to RIP if it can be demonstrated that the RIP process offers definite economic advantages. A further factor in the changed situation since the early RIP studies is the rapidly expanding resin market and the availability of a far wider range of strong- and weak-base resins suitable for use in an RIP application.

The design philosophy in the present study is simplicity, and the complex multi-elution procedure for strong-base resins proposed by earlier workers5-7 was therefore rejected. Efficient recoveries of gold and silver can be achieved by electrolysis, even when this is preceded by non-selective absorption and elution steps. Thus, the spent electrolyte contains the undesirable base-metal cyanides that can be discarded periodically or removed in a bleed stream to regenerate the eluate.

Extensive tests were carried out on a variety of strong- and weak-base resins. These tests included laboratory experiments, which are reported in this and the second paper in the series, and small-scale pilot-plant investigations, which are reported in the third. In the laboratory experiments, the effects on gold absorption of parameters such as the pH value of the solution, temperature, agitation, and the presence of competing ions were determined. In addition, several reagents were tested.
under various conditions to establish optimum elution procedures for both types of resin.

The Chemistry of Absorption and Elution

The functional group of a strong-base resin is a quaternary amine possessing a permanent positive charge. Gold cyanide and other anions are therefore extracted by an ion-exchange reaction, which is shown here for aurocyanide:

\[
\text{NR}_3 X^- + \text{Au(CN)}_2^- \rightleftharpoons \text{NR}_3 \text{Au(CN)}_2^+ + X^-. 
\]

where the symbol \( \rightleftharpoons \) denotes the inert backbone or matrix of the resin, which is generally polystyrene. Other anions that occur commonly in cyanide leach liquors are Ni(CN)_4^2-, Co(CN)_6^3-, Cu(CN)_2^-, Zn(CN)_4^2-, Fe(CN)_6^3-, Fe(CN)_3^-, all of which are extracted by a strong-base resin according to an ion-exchange reaction similar to that depicted in equation (1).

The complex metal cyanides on the resin can be eluted from the resin either by ion exchange, in which the equilibrium depicted in equation (1) can be forced to the left-hand side by an increase in the concentration of \( X^- \), or by conversion of the metal ions to non-anionic complex species. An example of the latter technique involves the thiourea ligand, which, in the presence of strong mineral acids, forms a cationic complex with gold, according to equation (2):

\[
\text{NR}_3 \text{Au(CN)}_2^- + 2(\text{NH}_2)\text{SO}_4^- \rightarrow \text{NR}_3 \text{Au}^{2+} + 2\text{NH}_2\text{SO}_4^- + 2(\text{NH}_2)\text{OS}^-. \]  

As examples of the ion-exchange elution technique, anions such as chloride, bisulphate, nitrate, thiocyanate, or cyanide can be used to reverse the ion-exchange equilibrium shown in equation (1). However, gold cyanide is loaded far more strongly than these anions and, for the equilibrium to be shifted to the left-hand side of equation (1), the activity of the eluant anion has generally to be increased by the addition of a polar organic solvent such as acetone or acetonitrile to the eluate. This forms the basis of the organic type of elution procedures that were tried in the past.

Alternatively, an anion can be chosen that is absorbed onto a strong-base resin more strongly than aurocyanide, in which case the equilibrium in equation (1) would lie naturally to the left-hand side. One such anion, which was tested and evaluated in this investigation, is the zinc cyanide anion \( \text{Zn(CN)}_4^2- \). Because this anion is absorbed so strongly onto a strong-base resin, the resin has to be regenerated before it is recycled to absorption. This can be carried out conveniently by treatment of the resin with a dilute mineral acid because the zinc cyanide anion decomposes in acid solution. The elution of a strong-base resin with zinc cyanide followed by acid regeneration of the resin is depicted in equations (3) and (4):

\[
2 \rightarrow \text{NR}_3 \text{Au(CN)}_2^- + \text{Zn(CN)}_4^2- \rightleftharpoons \text{NR}_3 \text{Zn(CN)}_4^2- + 2 \text{Au(CN)}_2^- \]  

Weak-base resins contain primary, secondary, or tertiary amine functional groups (or a mixture of these), and the ion-exchange properties of weak-base resins are governed by the pH value of the solution in contact with the resin, as can be seen from equation (5):

\[
\text{NR}_3 + \text{HX}^- \rightleftharpoons \text{NR}_3 \text{HX}^- \]  

In acid solution, the equilibrium lies to the right-hand side of equation (5), and the weak-base resin behaves like a strong-base resin, i.e., for the absorption of aurocyanide,

\[
\text{NR}_3 \text{Au(CN)}_2^- + \text{OH}^- \rightarrow \text{NR}_3 \text{Au}^{2+} + 2\text{NH}_2\text{SO}_4^- + 2\text{HCO}_3^- \]  

Weak-base resins can also be eluted in acid solution by an ion-exchange reaction similar to that depicted in equation (3), but in practice the reaction shown in equation (7) is very much more efficient and is also simpler and cheaper, and so would generally be preferred.

For most commercial weak-base resins, the pKa, which is defined as the pH value at which 50 per cent of the functional groups of the resin are protonated, is in the range 6 to 8. Therefore, in the pH range 10 to 11, which is common for most gold cyanide leach liquors, the equilibrium in equation (5) would be to the left-hand side, with the resin predominantly in the free-base form. In the past, this was the most serious limitation of the process using a weak-base resin, and required that the pH value of the cyanide solution in contact with the weak-base resin should be adjusted to a point where the equilibrium in equation (5) lies substantially to the right-hand side. In recent years, considerable success has been achieved in the development of new weak-base resins that absorb gold cyanide efficiently between pH values of 8 and 10, and this was one of the major factors that promoted re-examination of the RIP process based on the use of weak-base resins.

Gold and silver can be recovered from all these eluates by electrolysis with deposition of the metal (and the evolution of hydrogen) at a steel-wool cathode, and the evolution of oxygen either at a stainless-steel anode (for alkaline eluates) or at a lead anode (for neutral or acidic eluates).

Experimental Work

**Solutions and Materials**

In the experiments designed to show the effects of
temperature, pH, ionic strength, agitation, and gold concentration on the rate of loading and the equilibrium loading of aurocyanide on strong-base resins, a solution was prepared by the dissolution of potassium aurocyanide (supplied by Johnson Matthey Limited) in water from a Millipore purification system. Adjustments to the pH value of the solution were made with commercial-grade sulphuric or hydrochloric acids or sodium hydroxide, and adjustments to the ionic strength of the solution were made with sodium chloride. In the experiment designed to show the effect of competing ions on the equilibrium absorption of aurocyanide onto strong- and weak-base resins, pregnant solutions from the plants at Grootvlei and Durban Roodepoort Deep Gold Mines were used. Finally, in the experiment designed to show the selectivity of strong- and weak-base resins for gold cyanide over a variety of base-metal cyanide complexes as a function of pH, a stock solution was prepared that contained each of the following metal ions: gold, silver, copper, nickel, zinc, cobalt, and iron, and an excess of free cyanide ions, at a molarity of approximately $10^{-4}$. Aliquot portions of this solution were adjusted to pH values in the range 2 to 11, and all the base metals and silver were dissolved as the analar-grade metal nitrates.

Details of the various resins tested are given in Table I. Unless stated otherwise, the samples of resin were converted to the bisulphate form (by treatment with sulphuric acid) before use, and the temperature at which the experiments were carried out was 22°C.

**Batch Equilibrium Tests**

Equilibrium isotherms were determined under conditions that resembled, as closely as possible, those that would be encountered in a countercurrent RIP plant or in a continuous ion-exchange (CIX) column. In these applications, the ratio of the flowrate of solution to that of the resin is generally between 500 and 1000 to 1. This ratio was maintained in the batch equilibrium tests designed to show the effect of competing ions on the absorption of gold cyanide. To 5 to 10 ml of resin, 5 litres of a plant pregnant solution was added and brought to equilibrium overnight on a roller. The solution was analysed (by atomic-absorption spectrophotometry) for the various metals at the start of the reaction and again at equilibrium, the concentration of the metal ions on the resin being determined by difference. This gave one point on an isotherm for each of the metals. The same sample of resin was then added to 5 litres of fresh pregnant solution and brought to equilibrium once more, thus giving a second point on the isotherm. This procedure was repeated six or seven times to produce an isotherm covering the full range of metal-ion concentrations in solution and on the resin that would be found in a typical countercurrent application.

In the determination of the influence of solution pH on the selectivity of strong- and weak-base resins for aurocyanide, an excess of a stock solution containing equimolar concentrations of various metal cyanide complexes was pumped slowly in a single pass through a bed of resin in a column until equilibrium was attained. The solution and resin were then analysed so that the equilibrium loading could be determined. This experiment was repeated at various pH values in the range 2 to 11.

The strong-base content of weak-base resins was determined by treatment of the weak-base resins with an excess of sodium hydroxide. This treatment causes the strong-base groups to load hydroxyl ions while the weak-base groups revert to the free-base form. The hydroxyl ions are then eluted from the resin with sodium chloride and analysed by acid-base titration to give a measure of the strong-base capacity of the resin. The weak-base capacity of a resin was determined by protonation of the weak-base groups with a mineral acid, followed by titration of the resin with a standard sodium hydroxide solution.

**The Kinetics of Absorption**

The rate of loading and the equilibrium loading were measured under conditions simulating those in a countercurrent extraction process, i.e. conditions in which the concentration of gold cyanide in solution remains approximately constant as the loading of gold on the resin increases and approaches its equilibrium value. Details of the experimental technique have been described elsewhere for the loading of uranyl sulphate on a strong-base resin. Basically, the technique involves continuous monitoring of the concentration of gold in solution, gold being added to the reaction vessel from an external source at the same rate at which it is being extracted from solution by the resin, thus maintaining a constant concentration of gold in solution. The rate at which gold is added from the external source therefore yields a kinetic

### Table I

**Details of the Various Strong- and Weak-Base Resins Used in This Study**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Manufacturer</th>
<th>Functional group</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>IRA400</td>
<td>Rohm &amp; Haas</td>
<td>Quaternary amine</td>
<td>Poly styrene-DVB</td>
</tr>
<tr>
<td>A101DU</td>
<td>Diaprochin</td>
<td>Quaternary amine</td>
<td>Poly styrene</td>
</tr>
<tr>
<td>A7</td>
<td>Diaprochin</td>
<td>Secondary amine</td>
<td>Phenol formaldehyde</td>
</tr>
<tr>
<td>A30B</td>
<td>Diaprochin</td>
<td>Tertiary amine</td>
<td>Epoxy polyamine</td>
</tr>
<tr>
<td>A378</td>
<td>Diaprochin</td>
<td>Tertiary amine</td>
<td>Poly styrene-DVB</td>
</tr>
<tr>
<td>IRA60</td>
<td>Rohm &amp; Haas</td>
<td>Tertiary amine</td>
<td>Acrylic amine</td>
</tr>
<tr>
<td>IRA98</td>
<td>Rohm &amp; Haas</td>
<td>Tertiary amine</td>
<td>Poly styrene-DVB</td>
</tr>
<tr>
<td>A305</td>
<td>Ionac</td>
<td>Polyamine*</td>
<td>Epoxy amine</td>
</tr>
<tr>
<td>A560</td>
<td>Ionac</td>
<td>Polyamine*</td>
<td>Aliphatic amine</td>
</tr>
<tr>
<td>M61</td>
<td>Ionac</td>
<td>Polyamine*</td>
<td>Acrylic-DVB</td>
</tr>
</tbody>
</table>

* A mixture of primary, secondary, tertiary and, in some cases, small amounts of quaternary amine groups.

DVB = Divinylbenzene

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profile of the reaction, while the total amount of gold added from the external source yields a measure of the equilibrium loading. The strong absorption of the aurocyanide ion in the ultraviolet spectrum (239 nm) offers a convenient method for monitoring of the gold in solution at concentrations higher than 1 to 2 mg/l; for lower gold concentrations, a radioactive gold isotope and isotope-counting equipment were used.

Two reaction vessels were used: a column of 10 mm cross-sectional diameter in which the resin was fluidized by pumping of the gold cyanide solution in an up-flow direction through the bed, and a cylindrical, water-jacketed cell in which the resin was agitated by an impeller driven by a Heidolph RZR 50 variable-speed motor.

Absorption on Strong-base Resins

The Effect of Gold Concentration

The rate of extraction of gold cyanide over a range of concentrations of gold in solution was obtained from the following expression:

$$\frac{d[Au]_R}{dt} = \frac{[Au]_R^0 - [Au]_R}{t} = \frac{V_R C_R}{V_R}, \ldots (5)$$

where $[Au]_R$ and $[Au]_R^0$ are the concentrations of gold on the resin at time $t$ and $0$ respectively,

$V_R$ is the volume of concentrated gold solution added from the external source,

$C_R$ is the concentration of gold in the external source, and

$V_R$ is the volume of resin in the reaction vessel.

For the first 20 to 30 minutes of reaction, the rate was always constant and independent of the concentration of gold on the resin. The results given in Tables II to VI refer to this initial first-order reaction.

Results that show the rate of extraction and the loading capacity as a function of the concentration of gold in solution are given in Fig. 1. These show that the rate of loading is first-order in the concentration of gold in solution over the range of concentrations studied; they also show that extremely high gold loading can be achieved when no competing ions are present in solution.

The Effect of pH

The rate of loading and the equilibrium loading were examined at various pH values in the range 2 to 12. The solution contained potassium aurocyanide, and adjustments to the pH value were made with sodium hydroxide and hydrochloric acid. The ionic strength was kept constant at 0.01 M by the addition of sodium chloride. The results are presented in Table II and show that, over this range, the pH value has no effect on the rate or the equilibrium loading.

The Effect of Ionic Strength

The ionic strength of an aurocyanide solution was varied from near 0 to 0.05 M by the addition of sodium chloride, and the effect on the loading rate and the equilibrium loading was examined. The results (Table III) show that ionic strength has little effect on the rate of loading, but a fairly significant effect on the equilibrium loading. This is due to the increased competition between $Au(CN)_2^-$ and $Cl^-$ ions for active sites on the resin.

The Effect of Temperature

The loading of gold onto a strong-base resin was examined at various temperatures in the range 30 to 80°C. No background electrolyte was added to the neutral synthetic aurocyanide solution. The results (Table IV) show that the rate of loading increases with temperature.

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**Fig. 1—Rate of extraction and loading capacity of aurocyanide onto a strong-base resin (IRA400) as a function of gold in solution**
(an Arrhenius plot reveals an activation energy of 16.5 kJ/mol), while the loading at equilibrium is slightly exothermic in nature. However, this latter effect is small compared with the exothermic absorption of aurocyanide onto activated carbon, as shown in Table V.

### Table IV

**The Effect of Solution Temperature on the Loading of Aurocyanide onto a Strong-Base Resin (IRA 400)**

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Initial loading rate (g/l)/min</th>
<th>Loading capacity g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.33</td>
<td>107</td>
</tr>
<tr>
<td>40</td>
<td>0.43</td>
<td>110</td>
</tr>
<tr>
<td>50</td>
<td>0.49</td>
<td>104</td>
</tr>
<tr>
<td>60</td>
<td>0.62</td>
<td>87</td>
</tr>
<tr>
<td>70</td>
<td>0.76</td>
<td>97</td>
</tr>
<tr>
<td>80</td>
<td>0.84</td>
<td>84</td>
</tr>
</tbody>
</table>

### Table V

**The Effect of Solution Temperature on the Loading of Aurocyanide onto Activated Carbon (Metsorb 101)**

<table>
<thead>
<tr>
<th>Temperature°C</th>
<th>Initial loading rate (g/l)/min</th>
<th>Loading capacity g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>0.28</td>
<td>26</td>
</tr>
<tr>
<td>42</td>
<td>0.38</td>
<td>19</td>
</tr>
<tr>
<td>62</td>
<td>0.48</td>
<td>13</td>
</tr>
<tr>
<td>82</td>
<td>0.60</td>
<td>9</td>
</tr>
</tbody>
</table>

**The Effect of Agitation**

The influence of mixing efficiency on the rate of loading was examined in a fluidized-bed column and in a stirred cell. In the column, the solution was circulated at various flowrates, large-bead resin being used to maintain a stable fluidized bed over a wide range of flowrates as possible (Table VI). The dependence of the loading rate on the flowrate of the solution is indicative of a process controlled by film diffusion.

### Table VI

**The Effect of Solution Flowrate through a Fluidized-Bed Column on the Rate of Extraction of Aurocyanide by a Strong-Base Resin (IRA 400)**

<table>
<thead>
<tr>
<th>Flowrate of solution l/h</th>
<th>Initial loading rate (g/l)/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.14</td>
</tr>
<tr>
<td>0.60</td>
<td>0.21</td>
</tr>
<tr>
<td>1.40</td>
<td>0.49</td>
</tr>
<tr>
<td>2.50</td>
<td>0.87</td>
</tr>
<tr>
<td>4.90</td>
<td>1.74</td>
</tr>
<tr>
<td>5.70</td>
<td>2.02</td>
</tr>
<tr>
<td>6.20</td>
<td>2.19</td>
</tr>
</tbody>
</table>

In the stirred cell, the stirring speed, pH value, ionic strength, and concentration of gold in solution were varied. These variations enabled the isolation and identification of areas in which film-diffusion control on the one hand, or intraparticle-diffusion control on the other, are dominant. In this regard the following guidelines are relevant.

(a) For processes controlled by film diffusion, the rate increases with improved mixing efficiency, whereas under control by particle diffusion mixing has no effect on the rate.

(b) Under conditions of film-diffusion control there is a first-order dependence of the rate on the concentration of gold in solution; under particle-diffusion control, this dependence could be somewhat less than first-order.

(c) The pH value and the ionic strength of the solution will have little effect on the rate under conditions of film-diffusion control but could have a marked effect under conditions of particle-diffusion control.

The effect of the concentration of gold in solution on the initial rate of loading at different stirring speeds is shown in Fig. 2. The straight-line log-log relationships of unit slope indicate that the rate has a first-order dependence on the concentration of gold in solution between 0.08 and 100 mg/l, and that the rate increases with increasing stirring speed. These results point to film-diffusion control under these conditions.

The effect of stirring speed on the initial loading rate at different pH values and ionic strengths is shown in Fig. 3. Under each of the three sets of conditions, the rate increases with increasing stirring speed, once again pointing to at least a partial contribution from film-diffusion control. The dependence of the rate on stirring speed decreases with decreasing pH and with increasing ionic strength. (Particle-diffusion rates decrease under these conditions.)
conditions.) At 500 r/min the rate is apparently controlled entirely by film diffusion (since ionic strength and pH have little effect on the rate), whereas at 2000 r/min it is probable that both film and particle diffusion contribute to the loading rate.

The broad conclusion to be drawn from these results is that film diffusion influences the rate of gold extraction to a greater or lesser extent under all the conditions likely to be encountered in RIP. Efficient mixing is therefore a most important criterion in the design of large-scale mixers for RIP absorption.

The Effect of Competing Ions

The equilibrium loading of gold, silver, and several base metals in pregnant cyanide solutions from two gold mines onto two commercial strong-base resins is shown in Figs. 4 and 5. The trends in the two sets of isotherms are similar and indicate that copper, nickel, and zinc are more strongly absorbed than gold, whereas cobalt, silver, and iron are less strongly absorbed. The results in Figs. 4 and 5 are fairly representative of a general selectivity trend with minor variations that has been observed in the laboratory for a wide variety of plant pregnant solutions and different strong-base resins. The conclusions that can be drawn from this trend is that, for gold to be efficiently extracted from a plant pregnant solution, it is necessary for all the copper, nickel, and zinc in solution to be extracted. This was generally confirmed in the pilot-plant investigations.14

The stability of the gold cyanide complex, which is greater than that of most base-metal cyanide complexes, offers the possibility that the gold loading can be improved by selective precipitation of the base-metals from solution at low pH values. The order of stability15 of the cyanide complexes that are commonly found in gold leach liquors is Co3+(log β3 ≈ 64) > Au+(log β4 = 47) > Fe3+(log β5 = 44) > Fe2+(log β6 = 35) > Ni2+(log β7 = 30) > Cu2+(log β8 = 28) > > Zn2+(log β9 = 10). At pH values between 6 and 3, the cyanide complexes of zinc, nickel, and copper break
down to form insoluble neutral cyanide species in weakly acidic solutions, which then redissolve as the cationic metal salts in more strongly acidic solution. The results plotted in Fig. 6 show the effect of pH on the concentration of the anionic cyanide complex in solution.

The effect of selective base-metal precipitation on gold loading is shown in Fig. 7, where a synthetic solution containing a $10^{-4}$ M concentration of each metal in excess cyanide was adjusted to various pH values in the range 2 to 11 prior to equilibration with a strong-base resin. It can be seen that the loading of the gold improved significantly at pH values below 7. This is clearly not an effect of pH per se (Table II), and can be due only to the fact that there is less competition from the base metals that have precipitated. The sharp decrease in the zinc loading between pH values of 9 and 7 provides an explanation for the fact that zinc loads very strongly from the Grootvlei pregnant solution at a pH value of 11 (Fig. 4), but only marginally better than gold from the Durban Roodepoort Deep pregnant solution at a pH value of 7 (Fig. 5). The loading of iron is anomalously high compared with the loadings in Figs. 4 and 5. This is because the simulation of iron cyanide loading is difficult in the laboratory. It depends on the ratio of Fe(II) to Fe(III) also on the formation of double metal cyanide complexes, which occur at lower pH values and low concentrations of free cyanide.

**Absorption of Weak-base Resins**

*The Effect of pH on Absorption*

In most respects, a weak-base resin behaves similarly to a strong-base resin with the same matrix. This is true of parameters such as temperature, agitation, and ionic strength. However, the pH value of the solution, while playing little part in the mechanism of absorption on a strong-base resin, is the most important parameter in the determination of the ion-exchange characteristics of a weak-base resin. Moreover, the effect of pH on the ion-exchange properties of a weak-base resin varies considerably from one resin to another. This aspect of the performance of weak-base resins was therefore examined in some detail.

The effect of the pH value of the solution on the rate of loading and the loading capacity of aurocyanide onto a weak-base resin was determined in the following experiment. Resin was added to a synthetic gold cyanide solution in the stirred cell and, before the experiment started, the resin and solution were adjusted to the same pH value (in the range 2 to 10) to minimize drift in pH during the course of the experiment. Adjustments to the pH value were made with hydrochloric acid or ammonia, and the ionic strength was maintained at a constant level by the addition of ammonium chloride. (Ammonia was used rather than sodium hydroxide because the sodium ion interferes in the detection of gold by ultraviolet spectroscopy.) The effect of pH on the rate of loading and on the loading capacity onto two weak-base resins, A7 and MGI, was examined, and the results (Table VII) indicate that the rate of loading is more or less independent of the pH value of the solution at levels below about 8, and is similar to the rate of loading onto a strong-base resin under the same conditions (Table II).

In contrast, the loading capacity is strongly dependent on the pH value of the solution, increasing with increasing acidity, as might be predicted on the basis of equation (5). It is of interest that the maximum loading of gold onto A7, which occurs at a pH value of 6, is equal to about one-quarter of the loading onto a strong-base resin under

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**Fig. 6—Effect of acidity on the stability of various metal cyanide complexes in aqueous solution**

**Fig. 7—Effect of pH on the selectivity of a strong-base resin (AIOIDU) for metal cyanide complexes**
TABLE VII
THE EFFECT OF pH ON THE LOADING OF AUROCYANIDE ONTO WEAK-BASE RESINS

<table>
<thead>
<tr>
<th>Gold in solution</th>
<th>Initial loading rate (g/l)/min</th>
<th>Loading capacity g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>~0.42 mm</td>
<td>A7</td>
<td>MG1</td>
</tr>
<tr>
<td>10 mg/l</td>
<td>0.01 M</td>
<td>0.01 M</td>
</tr>
<tr>
<td>0.22</td>
<td>0.23</td>
<td>0.23</td>
</tr>
<tr>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>0.23</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>0.02</td>
<td>0.19</td>
<td>0.19</td>
</tr>
<tr>
<td>&lt;0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>9.4</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>15.5</td>
<td>7.4</td>
<td>7.4</td>
</tr>
<tr>
<td>30.0</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>17.7</td>
<td>11.0</td>
<td>11.0</td>
</tr>
<tr>
<td>3.5</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>2.0</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

The Effect of Strong-base Functional Groups

Another property of a weak-base resin, which can have a profound influence on its performance in this application, is the presence of strong-base functional groups within the weak-base resin. These are quaternary amine groups, and are formed when two adjacent tertiary amine groups cross-link. Their ion-exchange properties are the same as those of the functional groups in a strong-base resin, i.e. the absorption of anions on these groups is largely independent of the pH value of the solution. The implication is that the aurocyanide that is loaded onto the strong-base groups during absorption is not eluted by hydroxide ions in the elution cycle. This gold is therefore returned to the next absorption cycle, and this would result in poor extraction efficiency.

The weak-base and strong-base capacities of several commercial weak-base resins are shown in Table VIII. In the determination of the effect that the strong-base capacity of a weak-base resin has on the pH functionality of absorption and elution, the equilibrium loading of aurocyanide on the resins was determined as a function of the pH value of the solution. The results are shown in Figs. 9 and 10.

For the results shown in Fig. 9, the experimental con-
ditions were arranged so as to yield less than 1 per cent utilization of the capacity of the resin, and it can be seen that gold is loaded very selectively onto the strong-base groups under these conditions; in fact, to such an extent that resins IRA93 and A378 behave like strong-base resins, and the pH value has no effect on the loading of the gold. A7 is the only resin that would be fully eluted with sodium hydroxide (pH value greater than or equal to 13), and IRA68 would also exhibit good elution characteristics. This is consistent with the low strong-base contents of these two resins (Table VIII).

The results shown in Fig. 10 were obtained by the utilization of 5 to 10 per cent of the capacity of the resin. It can be seen that, at these higher loadings, the loading of gold onto each of the resins showed a dependence on the pH value of the solution. The magnitude of the potential problem is most evident, however, in the results for IRA93. Here the loading of about 30 000 g/t at high pH values, which is the amount of gold absorbed irreversibly with respect to pH, is some 5 to 10 times greater than the loading one would normally achieve in the treatment of pregnant solutions from gold plants. Moreover, the loading of 30 000 g/t represents only about 50 per cent utilization of the strong-base groups in this particular resin. This weak-base resin would therefore behave more like a strong-base resin in most applications, and the advantage of efficient, cheap elution would be lost entirely.

Experiments have shown that the cross-linking between adjacent tertiary or secondary amine groups, which creates the strong-base groups in a weak-base resin, can be partly eliminated by fairly simple chemical means. Thus, heating of IRA93 in 0.1 M sodium hydroxide solution at 70°C for 48 hours reduced the strong-base content of the resin from 5.8 to 2.0 per cent. It is significant that the weak-base capacity of the resin was not affected by this treatment, i.e. there was no evidence of degradation of the tertiary amine groups.

The Effect of Ionic Strength

The ionic strength of an aurocyanide solution was varied from 0 to 0.05 M by the addition of sodium chloride, and the effect on the loading rate and the equilibrium loading on A260 was examined. The results (Table IX) indicate that, as with strong-base resins, ionic strength has little effect on the rate but has a major influence on the loading capacity owing to the competition between chloride and aurocyanide ions for functional groups on the resin.

The Effect of Agitation

Aurocyanide solution was pumped up-flow at various flowrates through a column containing a fluidized bed of the resin A7, and the rate of gold extraction was measured as a function of flowrate. The results (Table X) show that the initial loading rate varies with agitation, which is consistent with a rate of loading controlled by film diffusion.
TABLE IX
THE EFFECT OF IONIC STRENGTH ON THE LOADING OF AUROCYANIDE ONTO A WEAK-BASE RESIN (A260)

<table>
<thead>
<tr>
<th>Particles size of resin</th>
<th>Gold in solution</th>
<th>pH value</th>
<th>Ionic strength M</th>
<th>Initial loading rate (g/l)/min</th>
<th>Loading capacity g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.50 &gt; 0.42 mm</td>
<td>10 mg/l</td>
<td>4</td>
<td>0</td>
<td>0.22</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td>0.28</td>
<td>91</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.01</td>
<td>0.20</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.21</td>
<td>10</td>
</tr>
</tbody>
</table>

As the gold loading approaches the equilibrium capacity of the resin, the contribution from slow particle diffusion to the rate of extraction increases. So that a distinction could be made between areas in which film-diffusion control and particle-diffusion control are dominant, the loading of gold onto MG1 was allowed to approach its equilibrium value in the stirred-cell reactor, and the rate of loading was monitored continuously. The results, which are given in Fig. 11, indicate that the loading is controlled by film diffusion at gold loadings of less than 4 g/l (about 30 per cent of the loading capacity under the chosen conditions). At higher loading, the rate decreases owing to an increasing contribution from slow particle diffusion in the loading mechanism.

TABLE X
THE EFFECT OF AGITATION ON THE RATE OF EXTRACTION OF GOLD CYANIDE BY THE WEAK-BASE RESIN A7

<table>
<thead>
<tr>
<th>Particles size of resin</th>
<th>Gold in solution</th>
<th>pH value</th>
<th>Column diameter</th>
<th>Flowrate of feed solution cm/s</th>
<th>Resin-bed expansion %</th>
<th>Initial loading rate (g/l)/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.50 &gt; 0.42 mm</td>
<td>10 mg/l</td>
<td>6</td>
<td>10 mm</td>
<td>0.53</td>
<td>50</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.04</td>
<td>100</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.58</td>
<td>150</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.21</td>
<td>250</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.44</td>
<td>300</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Interruption tests to provide evidence of this effect are a convenient way by which film diffusion and particle diffusion can be distinguished. During the loading cycle, the absorption process is interrupted for a period when the resin is separated from the feed solution. If the loading is under particle-diffusion control, the period of interruption allows time for the higher concentration of gold in the peripheral regions of the resin to be distributed evenly throughout the resin matrix. The rate of loading immediately after the interruption should therefore be faster than it was before. If, on the other hand, the loading is under film-diffusion control, the gold will always be evenly distributed throughout the resin matrix, and the period of interruption should have no effect on the rate of loading. Under the conditions of the experiment, the results in Fig. 11 are therefore consistent with particle-diffusion control at gold loadings greater than 4 g/l and with film-diffusion control at loadings below 4 g/l.

The Effect of Competing Ions
In an examination of the loading of gold and various base metals onto the weak-base resin A7, plant pregnant solutions from Durban Roodepoort Deep and Grootvlei Gold Mines were used, the isotherms being determined at a pH value of 7 (Figs. 12 and 13 respectively). The patterns of the isotherms are very similar to those obtained with strong-base resins, with zinc, copper, and nickel generally being loaded more strongly than gold, cobalt, iron, and silver, although the loading capacity of most of the metal complexes is about one-half of that for strong-base resins under the same conditions.

In a comparison of Figs. 4 and 12 with Figs. 5 and 13, it is interesting that cobalt was loaded far better from
the Grootvlei than from the Durban Roodepoort Deep pregnant solution. A possible reason for this could be that the Grootvlei solution was inadvertently allowed to ‘age’ for several weeks before the loading experiments were carried out, which would have increased the concentration of the Co(CN)$_3^-$ species in solution at the expense of the Co(CN)$_6^{3-}$ species.

It is also of interest that the selectivity of weak-base resins for gold and silver cyanide over other common metal cyanide complexes is greatly enhanced at high pH values, as illustrated by Table XI. For these results, a solution containing gold, silver, cobalt, copper, nickel, zinc, and iron (10$^{-4}$ M each), and an excess of cyanide was pumped through a column of resin until equilibrium was attained. The experiment was repeated on four weak-base resins and one strong-base resin (A101DU) at the two pH values of 11 and 6. The effect is best illustrated by the results for IRA93, which show that the distribution coefficients for gold and silver are very similar at both pH values, whereas the distribution coefficients for cobalt, copper, nickel, and iron are 10 to 20 times lower at a pH value of 11 than at a pH value of 6. These results form a contrast with those for the strong-base resin, A101DU, which shows no selectivity for gold or silver at either pH value. This effect might be due to a reduction in the charge (functional-group) density of the weak-base resins at high pH values, which would have less effect on the single-charged gold and silver cyanide anions than on the doubly and triply charged cyanide complexes of cobalt, nickel, copper, iron, and zinc. These latter ions require two or more positively charged functional groups to be in proximity to one another to achieve electrical neutrality. At pH values greater than about 13, all the weak-base functional groups will be in the free-base form, and the ion-exchange properties of the resin will be determined by the strong-base content of the resin.

On the basis of this argument, it should be possible for a resin with a low, optimum strong-base content that is evenly distributed throughout the resin matrix to achieve excellent selectivity for gold and silver cyanide. Russian workers have shown that good selectivity for gold cyanide can be achieved by a weak-base resin with a strong-base capacity of 16 per cent, whereas two other resins they examined (with strong-base capacities of 36 and 77 per cent) showed no selectivity whatsoever. The pH value of their feed solution was 10.6. It therefore seems to be technically feasible for both good ion-exchange capacity and good selectivity to be achieved for gold and silver in the pH range 10 to 11, which is typical of most plant pregnant solutions. With these objectives in mind, the further development of weak-base resins should be aimed at the optimization of the pKa of the weak-base groups and of their overall strong-base content.

**TABLE XI**

<table>
<thead>
<tr>
<th>Metal cyanide</th>
<th>A365</th>
<th>A368</th>
<th>A7</th>
<th>IRA93</th>
<th>A101DU</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D11</td>
<td>D6</td>
<td>D11</td>
<td>D6</td>
<td>D11</td>
</tr>
<tr>
<td>Gold</td>
<td>550</td>
<td>3440</td>
<td>1750</td>
<td>2340</td>
<td>710</td>
</tr>
<tr>
<td>Silver</td>
<td>70</td>
<td>320</td>
<td>150</td>
<td>165</td>
<td>90</td>
</tr>
<tr>
<td>Cobalt</td>
<td>50</td>
<td>4740</td>
<td>450</td>
<td>1770</td>
<td>120</td>
</tr>
<tr>
<td>Copper</td>
<td>30</td>
<td>1430</td>
<td>160</td>
<td>430</td>
<td>20</td>
</tr>
<tr>
<td>Nickel</td>
<td>80</td>
<td>11080</td>
<td>990</td>
<td>1480</td>
<td>10</td>
</tr>
<tr>
<td>Iron</td>
<td>140</td>
<td>2930</td>
<td>230</td>
<td>34600</td>
<td>115</td>
</tr>
<tr>
<td>Zinc</td>
<td>1760</td>
<td>2600</td>
<td>1070</td>
<td>2200</td>
<td>13370</td>
</tr>
</tbody>
</table>

**Conditions:**
- Ratio of solution to resin 1000:1
- pH value 7
- Temperature = 20°C

**Fig. 13—Equilibrium loading of various metal cyanide complexes from Durban Roodepoort Deep pregnant solution onto a weak-base resin (A7)**
Acknowledgements

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References


Asian mining

The Asian Mining International Exhibition and Conference that were to have been held in November 1984, as announced in our issue of August 1983, has been rescheduled to take place in Manila, Philippines, from 13th to 16th February, 1985.

The Institution of Mining and Metallurgy, together with the Chamber of Mines of the Philippines, is organizing the Conference, which will be a forum for the discussion of mining projects and developments in Asia, and of opportunities for investment in mining within the region.

The organizing committee will invite noted authors to present papers, and welcomes additional submissions on technical and operational aspects of mining, treatment, and exploration, and broader topics such as resource investment and safety. Abstracts (200 to 300 words) of papers for consideration and Conference enquiries should be addressed to The Secretary, Institution of Mining and Metallurgy, 44 Portland Place, London WIN 4BR, United Kingdom.

Enquiries about the Exhibition should be made to Industrial Trade Fairs International Ltd, Radcliffe House, Blenheim Court, Solihull, West Midlands B91 2BG, United Kingdom. Tel.: 021-705-6707; telex: 337073.