

The absorption of gold cyanide onto activated carbon. III. Factors influencing the rate of loading and the equilibrium capacity

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SYNOPSIS

The results are reported of experiments on the influence of a number of variables on the rate of loading of gold cyanide onto activated carbon and the equilibrium capacity of the carbon. These variables include the concentrations of gold and free cyanide in solution, the pH value and ionic strength of the solution, the concentration of organic compounds in the solution, the temperature, the particle size of the carbon, and the mixing efficiency. The experiments were carried out under approximately steady-state conditions to simulate the conditions in a countercurrent carbon-in-pulp absorption plant.

In addition, the results are reported of experiments to establish whether the absorption of gold cyanide onto activated carbon is a reversible process.

SAMEVATTING

Daar word verslag gedoen oor die resultate van eksperimente in verband met die invloed van 'n aantal veranderlikes op die laaitempo van goudsianied op geaktiveerde koolstof en die ewewigskapasiteit van die koolstof. Hierdie veranderlikes sluit in die konsentrasie van goud en vry sianied in oplossing, die pH-waarde en ioonsterkte van die oplossing, die konsentrasie van organiese verbindings in die oplossing, die temperatuur, die partikelgrootte van die koolstof en die mengdoeltreffendheid. Die eksperimente is in min of meer bestendige toestande uitgevoer om die toestande in 'n teenstroom-koolstof-in-pulpabsorpsieaanleg na te boots.

Verder word daar verslag gedoen oor die resultate van eksperimente om vas te stel of die absorpsie van goudsianied op geaktiveerde koolstof 'n omkeerbare proses is.

Introduction

The extraction of gold from cyanided pulps by the carbon-in-pulp (CIP) process is currently attracting great interest in gold-producing countries. Considerable effort has gone into the development of various aspects of the process in South Africa¹⁻⁶, and a number of plants are operating or are under construction in this country.

Perhaps the most important aspect of the process is the absorption since it determines not only the amount of soluble gold lost in the residues from a plant, but also the lock-up of gold in the plant and the quantity of carbon reporting for elution and reactivation each day. Unlike simple ion-exchange processes, the rate of extraction of gold cyanide by activated carbon is relatively slow, and it therefore becomes a most important factor in determining the optimum operating conditions of a CIP absorption section.

The first paper⁶ in this series describes kinetic studies of the extraction of gold cyanide by carbon in the laboratory and on CIP pilot plants. The second paper⁷ shows how kinetic models are used to model and optimize CIP absorption with respect to parameters such as the carbon concentration in each stage and the number of stages required to produce a certain value in the barren solution.

These models are of great value in the optimization of the performance on any particular CIP plant. However, if differences in the rate of extraction from one CIP plant to another are to be rationalized, the various parameters

that influence the rate of extraction must be examined in detail and their relative importance in the rate expression assessed. This aspect is considered in this paper, as is the effect on the rate of extraction of variables such as the concentrations of gold, free cyanide, and organic solvents in solution; the pH value, ionic strength, and temperature of the solution; the particle size of the carbon; and the mixing efficiency. In addition, the effect of these variables on the equilibrium loading of gold cyanide on carbon is examined.

Experimental Method

The experiments were carried out in a 500 ml glass cell filled with clarified gold cyanide solution (Fig. 1). The carbon was isolated in the cell in a cone-shaped tube with an opening protected by a porous-glass frit, and the solution in the cell was stirred with a magnetic bar. The carbon and the magnetic bar were separated so that there would be no attrition of the carbon particles. A peristaltic pump circulated the solution through the cell, then through the sample compartment of a Beckman Acta CIII ultraviolet spectrophotometer, and finally back through the carbon bed into the glass cell.

Before carbon was introduced into the circuit, the wavelength of the spectrophotometer was adjusted to 239,2 nm (which corresponds to one of the absorption maxima of the gold cyanide ion), and the absorption was measured. After the carbon had been introduced to the circuit, the absorbance due to the gold cyanide ion decreased (as a result of the extraction of gold by the carbon), and sufficient gold cyanide was added from an external source (by use of a digital burette) to restore the original absorbance level. A kinetic profile of the reaction could be obtained from a plot of the amount of gold injected from the external source versus time. The

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SA ISSN 0038-223X/\$3.00 + 0.00.

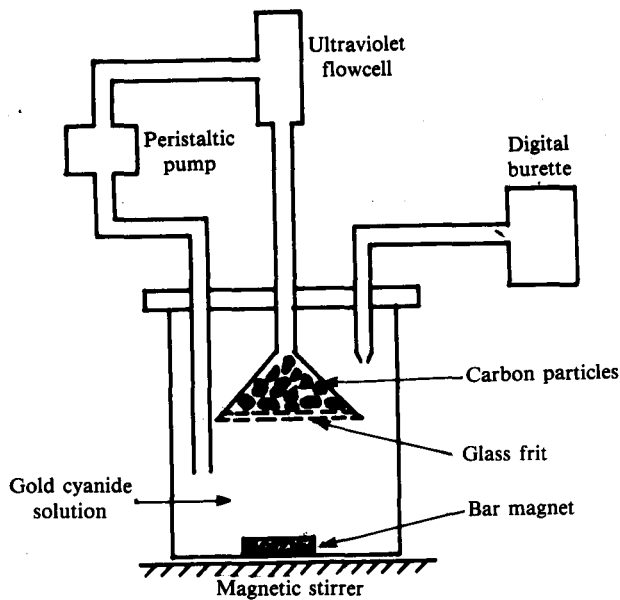


Fig. 1—Apparatus for the measurement of gold loading onto activated carbon under steady-state conditions in solution

solution in the cell was sampled periodically between the start of the reaction and equilibrium, and analysed for gold (by atomic-absorption spectroscopy), to ensure that the gold in solution, as determined by ultraviolet absorption, remained in a steady-state condition. For the equilibrium data, the reaction was continued until the ultraviolet absorption remained steady for several hours. This technique is similar to that used previously in a study of the rate of uranium extraction by ion-exchange resins⁸.

In those experiments which were designed to test the effect of agitation on the rate of the reaction, the carbon and the gold cyanide solution were mixed freely in a cell with baffles, and this was stirred by an impeller driven by a Heidolph RZR50 variable-speed motor. The solution was delivered to the spectrophotometer flowcell with the peristaltic pump via a glass frit to ensure that no small particles of carbon entered the flowcell.

The ultraviolet absorbance of the gold cyanide ion is sufficiently sensitive for gold to be detected accurately at concentrations of more than 5 p.p.m. For experiments in more dilute solutions, a gold isotope and radioactive counting equipment were used for the continuous detection of gold in solution. A sample of gold cyanide (AuCN) was irradiated by the Isotope Production Unit of the Atomic Energy Board (now the Atomic Energy Corporation of South Africa Limited) before being dissolved in potassium cyanide solution to give the desired concentration of gold in solution. The gold isotope (Au¹⁹⁸), has a half-life of only 2,7 days, but it was not necessary to correct for radioactive decay since only the initial rate of loading (about 30 minutes) was measured in the isotope experiments. In other respects, the experimental procedure was the same as that described above. Solution was pumped from the reactor cell through a flowcell located over a caesium iodide crystal, and back to the reactor cell. The radioactive impulse was transmitted via a

photomultiplier to a Nuclear Enterprises Limited model SR5 scaler-ratemeter. As the count rate decreased because of absorption of the Au¹⁹⁸ isotope by the activated carbon, sufficient labelled gold cyanide was added from an external source to restore the original count rate. This technique permitted the concentration of gold in solution to be estimated at levels as low as 0,01 p.p.m. and to be monitored accurately at concentrations of 0,1 p.p.m. and higher. For both procedures, the concentration of gold in the external source was 500 times greater than that in the reactor cell.

In certain of the experiments, the monitoring of the reaction by ultraviolet spectroscopy was not convenient. For example, in the experiments designed to quantify the effect of organic compounds in solution on the loading rate of gold cyanide onto activated carbon, the organic compounds interfered with the ultraviolet absorption spectrum of gold cyanide. Secondly, in the experiments designed to quantify the effect of pulp density on the rate of gold loading, clear solution could not be delivered continuously to the flowcell of the spectrophotometer. In these two instances, therefore, the rates of reaction were measured in batch tests in the stirred, baffled cell described above. The initial concentration of gold in solution was 20 mg/l, and samples were taken every 5 minutes for 1 hour after the addition of carbon. The samples were analysed for gold by atomic-absorption spectrophotometry so that the course of the reaction could be monitored.

The solutions were prepared by dissolution of either potassium aurocyanide or irradiated gold cyanide (both supplied by Johnson Matthey Limited) in water from a Millipore purification system. Metsorb 101 activated carbon, supplied by Chemviron, was used throughout. Unless stated otherwise, the carbon was screened to a size fraction between 0,84 and 0,50 mm for all the experiments.

Results and Discussion

The results were treated with a rate equation in which it is assumed that the rate is proportional to the concentration of gold in solution but independent of the concentration of gold on the carbon, as found for the initial stages of loading when the reaction is far from equilibrium. Under these conditions,

$$\frac{d[Au]_c}{dt} = k[Au]_s, \quad \dots \dots \dots (1)$$

where $[Au]_c$ and $[Au]_s$ are the concentrations of gold (p.p.m.) on the carbon and in the solution, and k is a rate constant.

In the experimental procedure used here, the rate is given by

$$\frac{d[Au]_c}{dt} = \frac{VC}{M_c t} \quad \text{mg} \cdot \text{kg}^{-1} \cdot \text{h}^{-1}, \quad \dots \dots \dots (2)$$

where V is the volume (litre) of concentrated gold solution added from the external source in time t (h), C is the concentration of gold in the external source ($\text{mg} \cdot \text{l}^{-1}$), and M_c is the mass of carbon (kg) in the reactor cell. The values of k obtained by this procedure were determined from the loading results over the first 30 minutes of extraction. During that period, the rate as defined in

equation (2) was always approximately constant.

For the batch-extraction tests, the rate results were analysed by use of the integrated form of equation (1) combined with a mass balance of gold in the reaction, i.e.

$$\ln \frac{[Au]_s^0}{[Au]_s} = \frac{kM_c t}{M_s}, \dots \dots \dots (3)$$

where $[Au]_s^0$ and $[Au]_s$ are the concentrations of gold in solution at time zero and t respectively, M_c is the mass of carbon, and M_s the mass (or volume) of solution.

Effect of Mixing Efficiency

The concentration of gold in solution was varied from 0,1 to 100 p.p.m., and the rate of extraction was measured under controlled conditions of pH, ionic strength, and mixing efficiency. For concentrations of gold in solution of 1 p.p.m. or less, the isotope method was used for the continuous monitoring of gold in solution; for higher concentrations, the ultraviolet-spectroscopy method was used. The experiments were carried out at four stirring speeds and also under variable conditions of pH and ionic strength in an attempt to establish the relative contributions from film- and particle-diffusion control.

Attention is drawn to several features of the results, which are illustrated in Figs. 2 and 3.

- (i) At gold concentrations of 1 p.p.m. or less, the value of k was approximately independent of the pH value and ionic strength of the solution. Moreover, in that concentration range, the rate of extraction was strongly dependent on the stirring speed and the value of k remained constant for all gold concentrations. These facts are consistent with a reaction mechanism in which control by film diffusion predominates.
- (ii) Vermeulen⁹ has shown that, under conditions of control by particle diffusion, the rate of extraction should be virtually independent of the concentration of ions in solution. This is confirmed by recent studies⁸ on the rate of extraction of uranium with a strong-base resin. The value of k should therefore decrease with an increase in the contribution from a reaction that is controlled by particle diffusion. On the basis of this argument, the results shown indicate that control by particle diffusion is significant at gold concentrations of 10 p.p.m. and more in a solution of low ionic strength, and at a gold concentration of 100 p.p.m. in a well-mixed solution of higher ionic strength (0,11 M).
- (iii) In general, the contribution from control by particle diffusion increases with the stirring speed and concentration of gold in solution. Moreover, since ionic strength and pH can influence the rate of extraction only when it is controlled by particle diffusion, one might expect these parameters to have the greatest influence on the rate at high stirring speeds and high concentrations of gold in solution. This, too, is borne out by the results, which indicate that, in well-mixed solutions containing 100 p.p.m. of gold, there is a four-fold decrease in the rate when the acidity and the ionic strength are reduced. This decrease is

due to the contribution from slow intraparticle diffusion in the solution of low acid and low ionic strengths.

The most important practical implication of these results is that mixing is an important parameter in CIP design. Generally, the ionic strength of a plant solution lies between the two extremes tested, and it can therefore be predicted that film diffusion will control the rate of extraction at gold concentrations in solution of at least

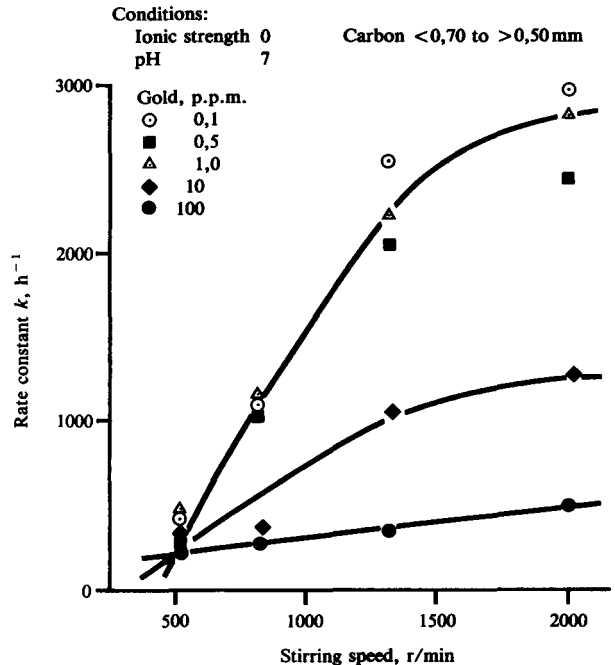


Fig. 2— The influence of impeller velocity in a baffled reaction vessel on the rate of extraction of gold cyanide by Metsorb 101 activated carbon

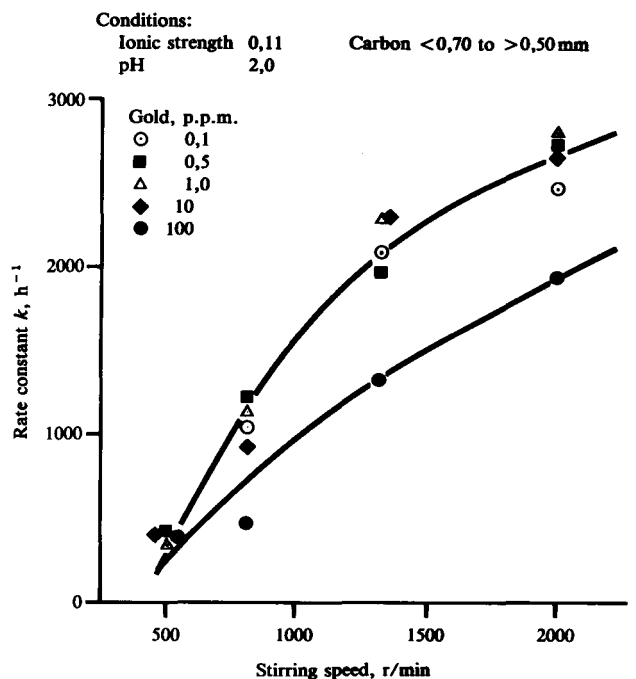


Fig. 3— The influence of impeller velocity in a baffled reaction vessel on the rate of extraction of gold cyanide by Metsorb 101 activated carbon

1 p.p.m., and perhaps even at concentrations as high as 10 p.p.m. In most CIP operations, the concentration of gold in solution is substantially lower than 1 p.p.m. in all but the first absorption stage. The rate of gold extraction under these conditions is therefore a sensitive function of the mixing efficiency in the absorption tank.

Effect of Interruptions in the Absorption

The interruption test is a convenient method of distinguishing between control by film diffusion and that by particle diffusion. In this experiment, the carbon is separated from the gold cyanide solution for several hours, so interrupting the absorption process. If the process is controlled by particle diffusion, the period of interruption allows time for the gold on the carbon to distribute itself evenly throughout the carbon matrix, i.e. the high concentration of gold at the carbon surface diffuses slowly into the interior of the carbon particle. The rate of extraction immediately after the interruption should therefore be faster than it was before the interruption. If, on the other hand, the extraction process is controlled by film diffusion, the gold on the carbon is always distributed evenly over the entire carbon matrix, and interruption of the process has no effect on the rate of extraction.

Experiments were carried out in which gold cyanide was loaded onto carbon from a solution containing 30 p.p.m. of gold with an ionic strength of 0,2 M. The absorption was carried out at a pH value of 2 and at a normal plant pH value of about 11. In each instance, the absorption process was interrupted twice. On the first occasion the gold loading on the carbon had reached about 50 per cent, and on the second occasion about 80 per cent, of its equilibrium value.

The results (Fig. 4) show that in both instances the rate was noticeably faster after the second interruption. This suggests that control by particle diffusion is significantly close to equilibrium. However, the rate of

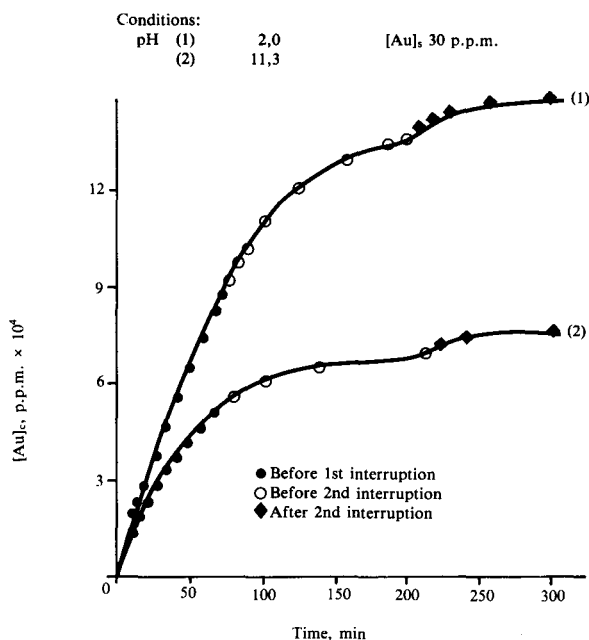


Fig. 4—Effect of interruptions in the absorption process on the rate of gold extraction

extraction from acid solution was unchanged after the first interruption, which suggests that control by film diffusion is dominant at loadings of up to 50 per cent of the equilibrium value.

Effect of pH

The pH value of a solution containing 30 p.p.m. of gold as gold cyanide was varied from 1,5 to 11,3, and the rate of loading and the equilibrium loading on activated carbon were measured. The results (Table I) indicate that the pH value of solution has a marked effect on equilibrium loading, especially at values below 7. This agrees with the observations of McDougall *et al.*². The rate also increases slightly in more acid solutions, indicating that there is a contribution from control by particle diffusion at the higher pH values at 30 p.p.m. of gold in solution

Effect of Ionic Strength

The rate of extraction and equilibrium loading were determined from solutions of variable ionic strength containing 30 p.p.m. of gold. The results (Table II) indicate that the loading rate and equilibrium loading capacity increase with increasing ionic strength. The effect on the loading capacity is much greater than that on the loading rate, as was observed with varying acidity.

Effect of Temperature and Free Cyanide

The rate of loading and the equilibrium loading were measured at various temperatures between 20 and 80°C and several concentrations of free cyanide between 0 and 1300 p.p.m. In all the tests, the ionic strength was adjusted to 0,1 M with sodium chloride.

The results are given in Table III, from which a number of interesting features emerge. Perhaps of greatest

Table I

EFFECT OF pH ON RATE OF LOADING AND EQUILIBRIUM CAPACITY

Conditions:
Ionic strength 0,2 M

pH value	k h^{-1}	Capacity p.p.m.
11,3	3 010	75 000
9,1	3 000	86 000
7,1	3 660	92 000
4,2	3 900	122 000
3,1	4 420	143 000
1,5	4 880	216 000

TABLE II

EFFECT OF IONIC STRENGTH ON RATE OF LOADING AND EQUILIBRIUM LOADING CAPACITY

Conditions
pH 6,5

Ionic strength M	k h^{-1}	Capacity p.p.m.
0,005	3 150	56 000
0,010	3 690	60 000
0,020	3 480	63 000
0,050	3 902	73 000
0,100	3 310	84 000
1,000	4 150	113 000

significance is the fact that the equilibrium loading is exothermic in nature. This feature was pointed out by Dixon *et al.*¹⁰ and McDougall *et al.*², and forms the basis of the high-temperature elution procedure adopted on most CIP plants today. The increase in loading rate with temperature is fairly small, in common with most diffusion-controlled processes, and an Arrhenius plot of the rate results is given in Fig. 5. The best straight line through the points yields a value of 2,6 kcal·mol⁻¹ for the activation energy, which agrees with the value obtained by Dixon *et al.*¹⁰.

An increase in the concentration of free cyanide depresses the rate of loading and the equilibrium capacity, and this feature is also utilized in the elution of gold from activated carbons.

TABLE III

EFFECT OF TEMPERATURE AND SODIUM CYANIDE CONCENTRATION ON THE LOADING

Conditions:

Gold in solution 25 p.p.m.
pH 10,4 to 10,8

Temperature °C	Free cyanide p.p.m.	<i>k</i> h ⁻¹	Capacity p.p.m.
20	0	3 400	73 000
25	130	3 390	62 000
24	260	2 620	57 000
23	1 300	2 950	59 000
44	0	4 190	48 000
43	130	4 070	47 000
42	260	3 150	42 000
43	1 300	3 010	33 000
62	0	4 900	35 000
62	130	4 920	29 000
62	260	3 900	29 000
62	1 300	4 060	26 000
81,5	260	5 330	20 000

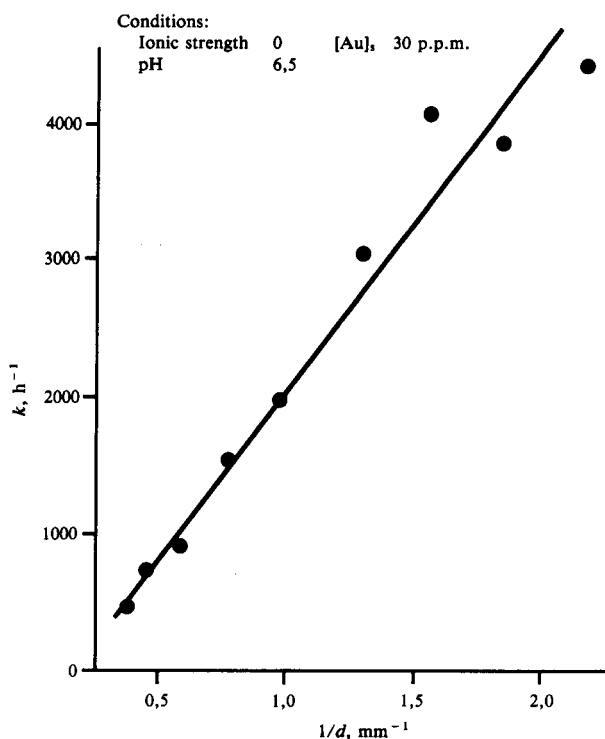


Fig. 6—Effect of mean carbon-particle diameter on the rate of gold extraction

Effect of Particle Size

A sample of activated carbon was screened to various size fractions in the range 0,42 to 2,38 mm, and the initial extraction rate of gold cyanide was measured as a function of particle size. (It should be noted that the particle size has no influence on the ultimate loading capacity.) The results are characterized by an inverse dependence of the rate on mean particle diameter (Fig. 6). This is generally believed to be indicative of a reaction that is controlled by film diffusion, an inverse squared dependence pointing to control by particle diffusion.

Effect of Pulp Density

The effect of pulp density was examined in the stirred, baffled cell in batch-extraction tests. In each test, 0,5 g of activated carbon was contacted with 500 ml of solution to which different quantities of dry and chemically inert solids from a Witwatersrand gold mine had been added. The results (Table IV) indicate that the concentration of inert solids in a pulp has a marked effect on

TABLE IV

EFFECT OF PULP DENSITY ON RATE OF LOADING

Conditions:

Ionic strength 0 Carbon particle size <0,70 to >0,50 mm
pH value 7 Stirring speed 1250 r/min

Solids content in pulp (m/m)	<i>k</i> h ⁻¹
0	2 070
10	1 860
20	1 480
30	1 250
50	1 190

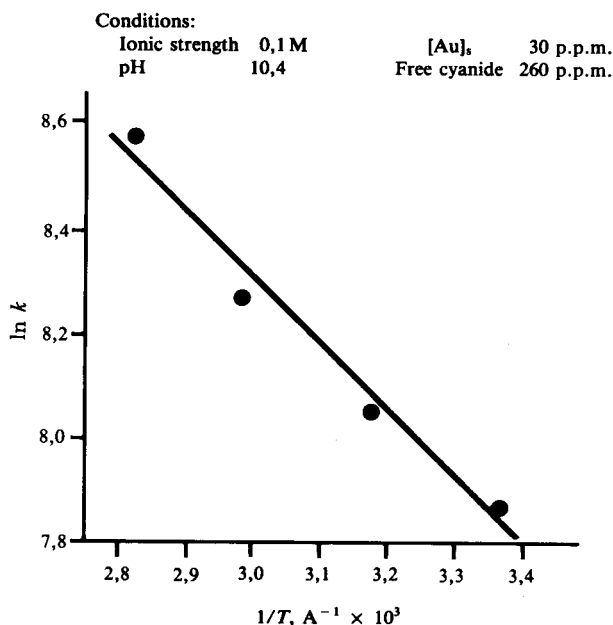


Fig. 5—Effect of temperature on the rate of gold extraction

TABLE V
EFFECT OF ORGANIC SOLVENTS ON LOADING RATE

Conditions		Rate constant, k , for different solvents, h^{-1}					
Ionic strength	≈ 0	pH	7				
Stirring speed	1250 r/min	Carbon	< 0,70 to 70,50 mm				
Solvent concentration % (m/m)	Solids concentration % (m/m)	Rate constant, k , for different solvents, h^{-1}					
		Heptane	Benzene	Acetone	Acetonitrile	Ethanol	Methanol
0	0	2 070	2 070	2 070	2 070	2 070	2 070
0,005	0	1 479	1 169				
0,02	0	896	1 023				
0,05	0	136	317				
0,05	50	850	980				
0,5	0			461	840	1 140	1 095
1,0	0			286	384	852	1 245
2,0	0			174	245	327	1 086
2,0	50			578	662	757	968

TABLE VI

EFFECT OF ORGANIC SOLVENTS ON EQUILIBRIUM LOADING

Conditions:

Ionic strength 0 Au in soln at equilibrium 30 mg/l
pH 7

Solvent	Solvent concentration (% m/m)	Equilibrium capacity p.p.m.
Nil	0	41 400
Ethanol	0,5	40 200
Ethanol	1,0	30 950
Ethanol	2,0	32 300
Acetone	2,0	34 400
Acetonitrile	2,0	26 680

the rate of gold extraction by carbon. It is not certain whether this is due to a decrease in mixing efficiency with increasing concentration of solids, or whether it is due to physical 'blinding' of the carbon surface by slimes in the pulp.

Effect of Organic Solvents

It has been demonstrated that polar solvents such as ethanol, acetone, and acetonitrile markedly improve the elution of gold from activated carbon^{11,12}, and mixtures of ethanol and water are used as the eluant on a few plants in the U.S.A. It has also been observed on operating CIP plants and pilot plants that solvents such as kerosene, which is insoluble in water, have an adverse effect on the loading of gold cyanide onto carbon. To quantify these effects, solutions and pulps containing gold cyanide were spiked with various solvents, and the rate of loading and the equilibrium loading capacity were measured in batch tests in a stirred cell. The range of solvents included four polar compounds, which are soluble in water, an aliphatic compound (heptane), which is insoluble in water, and an aromatic compound (benzene), which is insoluble in water. The rate data are shown in Table V and the equilibrium results in Table VI. From these it can be seen that organic solvents have a major influence on the rate of reaction, but far less effect on the equilibrium loading. In fact, the effect on the equilibrium loading may be even less than that portrayed in Table VI since it was difficult to measure the equilibrium load-

ing in some cases because the loading rates were very slow.

It is significant that the influence of the organic solvents on the rate of loading is substantially reduced in the presence of 50 per cent solids, indicating that a portion of the organic solvent is adsorbed by the inert solids, thereby reducing the effective concentration in the solution or on the carbon.

One possible mechanism of carbon 'poisoning' that affects the rate of loading but not the loading capacity could be the absorption of a film of the solvent onto the superficial surface of the carbon granule (which thereby creates a barrier to mass transfer) without significant penetration of the solvent into the pores of the granule. This has been identified as the probable mechanism in the poisoning of carbon by species such as hematite and organic compounds that are insoluble in water^{3,5}, and seems the most likely mechanism of poisoning by heptane and benzene. This mechanism predicts that the rate of elution would be similarly affected adversely by slow mass transfer across the organic film. This is clearly not the case with water-soluble solvents (acetone, acetonitrile, ethanol, and methanol). The explanation of the unusual loading and stripping characteristics in the presence of low concentrations of these compounds is more likely to be associated with solvation of the gold cyanide ion by these solvents than by interaction between the solvent and the carbon.

Effect of Competition from Copper Cyanide

A number of base metals are usually leached with gold in cyanide solution, notably copper, nickel, cobalt, iron, and zinc. However, with the exception of copper, and to a lesser extent nickel, the cyanide complexes of these metals are not loaded well onto activated carbon, and their presence in solution has little effect on the extraction efficiency of gold. Copper is particularly interesting: the loading of its cyanide complexes onto carbon is greatly influenced by the chemical conditions in the solution. Under certain conditions, it is loaded more strongly than gold and actually 'squeezes' gold cyanide off the carbon; under other conditions, it is not loaded at all.

The two most important parameters affecting the

TABLE VII

EFFECT OF CYANIDE CONCENTRATION AND pH VALUE ON THE LOADING OF GOLD AND COPPER

Conditions:

Gold in solution 9,2 p.p.m.

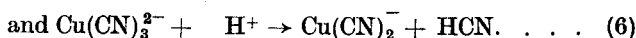
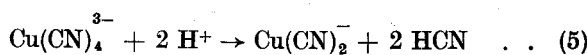
Copper in solution p.p.m.	NaCN added p.p.m.	pH value	Gold on carbon p.p.m.	Copper on carbon p.p.m.
0	0	10,5	44 000	0
0	0	5,0	67 400	0
0	300	10,5	34 500	0
0	300	5,0	60 000	0
80	300	10,5	33 460	600
80	300	5,0	19 800	50 900

loading of copper are the concentration of free cyanide in solution and the pH value of the solution. The effect of pH on the loading of copper and gold onto carbon from cyanide solution is shown in Table VII. These results were obtained for a number of solutions that contained about 10 p.p.m. of gold (as gold cyanide) and various quantities of copper or cyanide ions, or both. Each solution was pumped through a bed of carbon until equilibrium was reached, at which point the concentration of gold and copper in the solution emerging from the column was the same as that entering the column. The loaded carbon was then analysed for gold and carbon.

The results show, firstly, that the loading of gold is improved when the pH value or the concentration of free cyanide ions in solution is decreased; secondly, that copper is loaded very well from a cyanide solution at a pH value of 5, whereas very little copper is loaded at a pH value of 10,5, an effect that was observed by Davidson *et al.*¹³. Moreover, the high copper loading at a pH value of 5 is, to a certain extent, at the expense of gold loading, which decreases by some 40 per cent.

In an examination of the effect of free-cyanide concentration on copper loading, several solutions containing 10 p.p.m. of gold and 25 p.p.m. of copper (as copper sulphate) were prepared. Various quantities of sodium cyanide were added to the solutions so that the ratios of cyanide to copper ranged from 1 : 1 to 10 : 1. These synthetic solutions were then pumped continuously through a bed of carbon until equilibrium was reached. In one series of experiments, the pH value was held at 6,0; in a second series, it was adjusted to about 10. The results (Fig. 7) indicate that the maximum absorption of copper occurs at a ratio of cyanide to copper of 2 : 1. Moreover, under these conditions, the loading of gold cyanide passed through a minimum, confirming that the two complexes compete for absorption sites on the carbon. At higher ratios of cyanide to copper, the copper loading decreased rapidly, indicating that the $\text{Cu}(\text{CN})^-$ complex was loaded well, whereas the $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ species did not load appreciably, as has been suggested by Davidson *et al.*¹³. The same trends were observed at pH 10 as at pH 6, although the copper loading was much lower at the higher pH value. The effect of pH on copper loading is, in all probability, associated with the concentration of free cyanide since any decrease in pH value enhances the following reactions and has the same effect on the distribution of copper cyanide

species as a reduction in the concentration of free cyanide:



An interesting practical example of the profound influence that the chemical composition of a solution can have on copper loading is provided by the operating results from two South African plants that recover gold with activated carbon (Table VIII).

Since copper follows gold through elution and electro-winning in a normal CIP plant, high concentrations of copper cause problems not only in the absorption but also in the downstream unit operations. Plant B, for example, is currently producing bullion that has a gold content of about 2 per cent and a copper content of more than 95 per cent. The results presented here indicate that increases in the pH value and the free-cyanide concentration in the feed solution to plant B would alleviate, if not eradicate, the problems being encountered with copper.

TABLE VIII

THE LOADING OF COPPER ONTO ACTIVATED CARBON AT TWO OPERATING GOLD PLANTS IN SOUTH AFRICA

Plant	pH value of solution	Free cyanide p.p.m.	Copper in solution p.p.m.	Copper on carbon p.p.m.
A	10	300	150	300
B	7	≈ 0	2	30 000

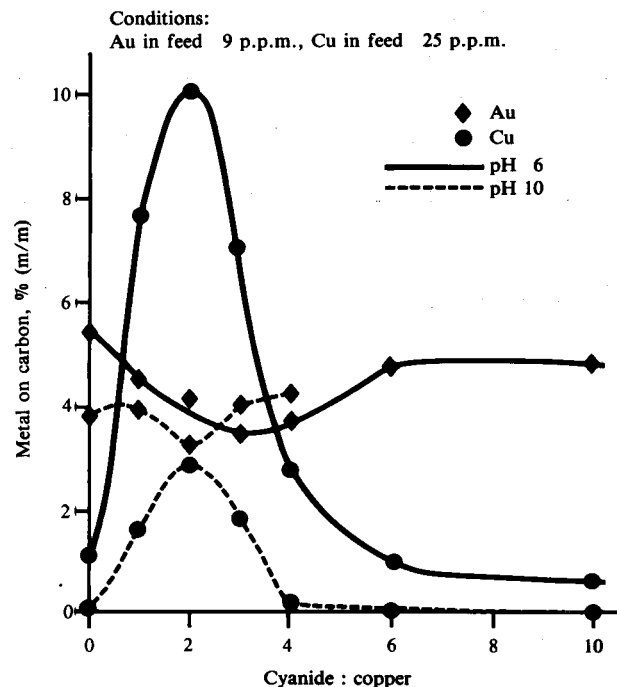


Fig. 7—Effect of the ratio of cyanide to copper on the relative equilibrium loading capacities of copper cyanide and gold cyanide

Reversibility of the Absorption of Gold

The initial rate of loading of gold cyanide onto activated carbon is fast and, as shown earlier, is generally controlled by film diffusion under the conditions prevailing on CIP plants. However, the rate of approach to equilibrium is extremely slow as demonstrated by McDougal *et al.*², and is undoubtedly controlled by particle diffusion. This very slow approach to equilibrium is probably associated with physical, rather than chemical, phenomena, i.e. the initial rapid loading could be associated with gold absorption in the large macropores of the carbon (which comprise a small percentage of the total carbon surface), whereas the slow approach to equilibrium could be associated with slow diffusion of gold cyanide into the micropores. As the cross-sectional area of micropores approaches the cross-sectional area of the gold cyanide ion, intraparticle resistance to mass transfer becomes infinite.

To establish whether the loading of gold cyanide onto carbon is an irreversible process, a sample of activated carbon was taken from the first stage of a CIP pilot plant and isolated in a basket in the fifth stage. The basket consisted of a 20-mesh screen (supported on a stainless-steel frame) that permitted a free flow of pulp through the interior of the basket but prevented the carbon in the basket from mixing with carbon in the fifth stage. The interior of the basket was agitated by an air sparge. The basket was left in the fifth stage for several hours, and samples of carbon were withdrawn periodically from the basket and analysed for gold.

The results (Table IX) indicate that the absorption of gold cyanide onto activated carbon is not an irreversible process. An analysis of these results showed that the concentration of gold on the carbon decreases almost linearly with time, but that the rate of desorption is extremely slow, with a half-life of about 48 hours. One implication of this in CIP practice is that, if a well-loaded particle of carbon breaks up and passes through the 20-mesh peripheral screens with the pulp, not much gold will be desorbed from the particle before the pulp (which has an average residence time of about 1 hour per stage) passes out of the last stage of the CIP plant. The gold associated with attrited carbon particles should therefore

TABLE IX

THE DESORPTION OF GOLD CYANIDE FROM ACTIVATED CARBON IN A CYANIDE PULP THAT HAD BEEN DEPLETED OF GOLD

Time h	Gold in solution p.p.m.	Gold on the carbon p.p.m.
0	0,033	4 276
1	0,033	4 200
2	0,033	4 146
3	0,033	4 120
4	0,033	3 948
5	0,033	3 946
6	0,033	3 819
7	0,033	3 825
8	0,033	3 740
9	0,033	3 746
10	0,033	3 620
11	0,033	3 514
12	0,033	3 276
16	0,021	3 440
32	0,021	2 764

be detectable from an increase in the amount of undissolved gold in the solid residues from CIP as compared with the amount in the solid feed to CIP. The fact that such an increase appears never to have been detected in practice¹⁴ indicates that the fracture of 'well-loaded' carbon in the absorption stages is not a serious problem in CIP.

Tests designed to substantiate these findings were carried out in the laboratory. Large particles of carbon (larger than 2,2 mm) were loaded with gold from cyanide solution, and were then treated under various conditions with small particles of carbon (smaller than 0,84 mm) that contained no gold. After a time, the large and small particles, having been separated by screening, were analysed for gold to establish whether the gold that had been absorbed on the large particles had been desorbed and re-absorbed onto the small particles. The results are presented in Table X.

Under the first set of conditions (particles in intimate contact), the small and large particles were mixed intimately by being rolled in a plastic bottle, and the effect of the cyanide concentration on the transfer of gold was examined.

The results indicate that, irrespective of cyanide concentration, equilibrium was reached in less than 24 hours, with an approximately equal distribution of gold between the small and the large particles. However, the concentration of gold in solution apparently increased with time and with cyanide in solution. In this regard, it is interesting to note that gold was transferred from the large to the small particles even when the carbon particles had been mixed in distilled water that contained no cyanide. Moreover, this migration occurred despite the fact that the concentration of gold in solution after 24 hours was almost zero (less than 0,1 p.p.m.). This suggests that, when there is intimate contact between particles, $Au(CN)_2^-$ is transferred across the thin film separating the particles without diffusion into the bulk of the solution. This effect, known as contact ion exchange, has been observed¹⁵ with ion-exchange resins.

The results obtained under the second set of conditions provide evidence of such an effect. In these tests, the small and large particles were separated by a glass frit, and, even in the presence of 0,5 per cent cyanide in solution, equilibrium had not been reached after a period of 7 days. In the absence of free cyanide, only 3 per cent of the gold had migrated to the small particles after 7 days. It is therefore evident that a fairly rapid rate of migration depends on intimate contact between particles.

These experiments provide further substantial evidence that the loading of gold onto activated carbon is a reversible process.

Conclusions

It was shown that the most important parameter governing the rate of extraction of gold is the mixing efficiency or the hydrodynamic conditions within a CIP contactor. This stems directly from the fact that, under most of the conditions used in CIP, film diffusion predominates in limiting the rate of extraction of gold cyanide. Therefore, features such as design of contactor,

TABLE X
THE MIGRATION OF GOLD FROM LARGE TO SMALL PARTICLES OF CARBON UNDER VARIOUS CONDITIONS

Solution	Conditions	Gold in solution and on carbon, p.p.m.								
		t = 0			t = 24 h			t = 168 h		
		[Au] _c		[Au] _s	[Au] _c		[Au] _s	[Au] _c		[Au] _s
		> 2 mm	< 0,8 mm		> 2 mm	< 0,8 mm		> 2 mm	< 0,8 mm	
Water NaCN, 0,1 % NaCN, 0,5 %	Particles in intimate contact	34 700	0	0	16 660	15 160	~ 0	19 000	14 780	~ 0
		34 700	0	0	16 710	15 040	1,55	13 730	15 410	1,65
		34 700	0	0	14 220	17 020	3,85	15 750	14 470	4,35
Water NaCN, 0,5 %	Particles separated by a glass frit	20 000	0	n.d.	n.d.	n.d.	n.d.	18 260	680	n.d.
		20 000	0	n.d.	n.d.	n.d.	n.d.	12 400	7 100	n.d.

n.d. = not determine

choice of agitator, and pulp density are very important in CIP absorption.

Another parameter that has a significant effect on the rate of extraction is the mean particle size of the carbon granules. The fact that the rate increases linearly with the reciprocal of the particle size points to the possible use of smaller carbon granules in the future, especially in view of the rapid improvements that are taking place in the area of carbon screening³. For example, a decrease in carbon particle size from between 6 and 16 mesh to between 14 and 20 mesh (and this would certainly be feasible from a screening point of view) would permit the flowrate of pulp to a plant to be increased by 50 to 100 per cent with no loss in extraction efficiency.

The third factor that has a major influence on the rate is the presence of compounds that poison the carbon. Recent studies^{3,5,8} have identified a number of such poisons, which may comprise either organic species (flotation reagents, lubricating oils, kerosene, other solvents) or inorganic species (calcium carbonate, hematite). The presence of poisons in a CIP plant can be identified by a low extraction efficiency in the first few stages and, as the poison becomes absorbed on the carbon, a gradually increasing extraction efficiency towards the latter stages of the plant. Since these poisons affect the rate of loading far more than the loading capacity, their influence can be counteracted to a certain extent simply by an increase in the concentration of carbon in those stages where the extraction efficiency is poor.

Finally, the results presented here show that the ionic strength and pH of a solution have very little effect on the rate of extraction under conditions that favour control by film diffusion.

A number of factors influence the equilibrium loading capacity of gold cyanide on activated carbon. These factors have the greatest effect on CIP performance where the loading of gold is allowed to approach the equilibrium value. As the loading in any stage approaches its equilibrium value, the rate of extraction decreases and therefore any factor that influences the equilibrium loading has a bearing on plant performance under these conditions. The work presented here shows that the most important variables affecting the equilibrium loading are the ionic strength, pH value, and temperature of solution, whereas carbon poisoning has less effect. Under certain circumstances, the absorption of copper cyanide complexes onto carbon can have a significant effect on gold absorption, and experience with various CIP operations has shown that high concentrations of nickel cyanide can also reduce the equilibrium loading of gold cyanide on activated carbon.

Acknowledgements

This paper is published by permission of the Council for Mineral Technology. The excellent technical assistance of Mrs O. Wellington and Mrs M. Conradie is gratefully acknowledged.

References

- LAXEN, P. A., BECKER, G. S. M., and RUBIN, R. Developments in the application of carbon-in-pulp for gold recovery from South African ores. *J. S. Afr. Inst. Min. Metall.*, vol. 79, no. 11. 1979. pp. 315-326.
- MCDUGALL, G. J., HANCOCK, R. D., NICOL, M. J., WELLINGTON, O. L., and COPPERTHWAIT, R. G. The mechanism of the absorption of gold cyanide onto activated carbon. *J. S. Afr. Inst. Min. Metall.*, vol. 80, no. 11. 1980. pp. 344-356.
- LAXEN, P. A., FLEMING, C. A., HOLTUM, D. A., and RUBIN, R. A review of pilot-plant testwork conducted on the carbon-in-pulp process for the recovery of gold. *Proceedings 12th C.M.M.I. Congress*. Glen, H. W. (ed.). Johannesburg, The South African Institute of Mining and Metallurgy, 1982. vol. 2, pp. 551-561.
- FLEMING, C. A., and NICOL, M. J. Alternative processes to filtration: carbon-in-pulp and resin-in-pulp in the metallurgical industry. *Proc. Hydrometallurgy 81 Symposium*. London, The Society of Chemical Industry, 1981. Paper C2, pp. 1-16.
- FLEMING, C. A. Recent developments in carbon-in-pulp technology in South Africa. *Hydrometallurgy. Research, Development and Plant Practice*. K. Osseo-Asare and J. D. Muller (eds.). Proc. 3rd International Symposium on Hydrometallurgy. (112th Annual AIME meeting, Atlanta, Georgia, Mar. 1983) pp. 839-858.
- NICOL, M. J., FLEMING, C. A., and CROMBERG, G. The absorption of gold cyanide onto activated carbon. I. The kinetics of absorption from pulps. *J. S. Afr. Inst. Min. Metall.*, vol. 84, no. 2. 1984. pp. 50-54.
- NICOL, M. J., FLEMING, C. A., and CROMBERG, G. The absorption of gold cyanide onto activated carbon. II. Application of the kinetic model to multistage absorption circuits. *J. S. Afr. Inst. Min. Metall.*, vol. 84, no. 3. 1984. pp. 70-78.
- FLEMING, C. A., and NICOL, M. J. A comparative study of kinetic models for the extraction of uranium by strong-base anion-exchange resins. *J. S. Afr. Inst. Min. Metall.*, vol. 80, no. 2, 1980. pp. 70-78.
- VERMEULEN, T. Theory for irreversible and constant pattern solid diffusion. *Ind. Engng Chem.*, vol. 45. 1953. pp. 1664-1670.
- DIXON, S., CHO, E. H., and PITT, C. H. The interaction between gold cyanide, silver cyanide, and high surface area charcoal. *A.I. Ch. E. Symp. Series*, vol. 74, no. 173. 1978. pp. 75-83.
- DAVIDSON, R. J., and VERONESE, V. Metal recovery. *S. Afr. Patent 78/5463*. 26th Sep., 1978. 10 pp.
- HEINEN, H. J., PETERSON, D. G., and LINDSTROM, R. E. Desorption of gold from activated carbon. *U.S. Patent 4,208,378*. 17th Jun., 1980.
- DAVIDSON, R. J., VERONESE, V., and NKOSI, M. V. The use of activated carbon for the recovery of gold and silver from gold-plant solutions. *J. S. Afr. Inst. Min. Metall.*, vol. 79, no. 10. 1979. pp. 281-297.
- LAXEN, P. A. Randburg, Council for Mineral Technology, private communication. Nov. 1980.
- BUNZYL, K., and SCHULTZ, W. Kinetics of differentially small conversions in contact isotopic and contact ion exchange. *Anal. Chem.*, vol. 54. 1982. pp. 272-277.