

The use of activated carbon for the recovery of gold and silver from gold-plant solutions

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SYNOPSIS

When activated carbon is used for the recovery of gold and silver from Witwatersrand gold-plant solutions, severe fouling of the carbon by calcium carbonate is experienced. Also, difficulty is encountered in the retention of the adsorbed silver on the carbon because it is displaced by gold.

The acidification of plant pregnant solutions before they are contacted with carbon was therefore investigated as a means of overcoming these shortcomings. The results from batch laboratory experiments on the effect of pH on gold adsorption from plant solutions and from synthetic solutions of high ionic strength indicated reaction rate optima in the region of pH 5 and below pH 1. The effect of pH on the equilibrium capacity constant for gold adsorption onto activated carbon was also studied, using both a plant solution and a synthetic solution of high ionic strength. In the case of the plant solution, the results suggested only a marginal change in carbon capacity for gold in the pH range 12 to 6, with significant increases in capacity at lower pH values. In the case of the synthetic solution of high ionic strength, the capacity constant was found to increase steadily as the pH was lowered from 12 to 1. It was also found that the gold adsorption capacity of the carbon was significantly better for the synthetic solution. No precipitation of gold from the pregnant solution (gold content approximately 6 g/t) was noted as the pH was decreased to values as low as 1. However, about 25 per cent of the 0,6 g/t silver content was found to have precipitated when a pH value of 3,0 was attained. Further substantial precipitation of silver took place as the pH was lowered further.

The investigation was extended by the passing of suitably acidified gold-plant solutions through one or more columns containing activated carbon. Preliminary results showed that the particle size of the carbon had a significant effect on the rate of gold adsorption. No displacement of adsorbed silver by gold was observed to take place at an influent pH of 5. In a typical continuous 'merry-go-round' operation involving three columns in which gold was eluted from the lead column every 48 hours, effluent values averaging 0,001 g/t gold could be consistently achieved under simulated plant-operating conditions. The results were obtained at relatively high velocities of influent solution, resulting in very little hold-up of gold in the carbon-recovery circuit.

More than 99,9 per cent of the gold and more than 99,8 per cent of the silver was recovered in the adsorption circuit, while the elution data indicated an average elution recovery of 99,8 per cent of the adsorbed gold and 98,2 per cent of the adsorbed silver. Elution of the carbon was carried out at 91°C. This involved pretreatment of the carbon with a sodium cyanide solution, followed by elution with deionized water. At a loading flowrate of 66 bed volumes per hour, the indicated take-up of metals on the carbon in the lead column was as follows: 53 kg/t gold, 6 kg/t silver, 57 kg/t copper, 14 kg/t nickel, and 1 kg/t zinc. Only a trace of cobalt was adsorbed. At an elution rate of 1,7 bed volumes per hour, the lead column was found to be completely stripped in under 5 hours, with concentrations of gold in the eluate reaching 6 to 7 g/l.

Besides the excellent adsorption and elution results obtained when acidified pregnant solution was used, no fouling of the carbon was indicated, and the pressure drop across the three columns was considered to be well within practical limits. When compared with conventional zinc precipitation, the carbon process would appear to have considerable economic merit, with strong indications that significant savings would be possible both in capital and operating costs. Further pilot-plant experiments, preferably on a gold plant, would be required before a meaningful cost comparison could be made with the existing process.

SAMEVATTING

Wanneer geaktiveerde koolstof gebruik word vir die herwinning van goud- en silwerwaardes uit Witwatersrand goudaanlegoplossings word besoedeling van die koolstof deur kalsiumkarbonaat ondervind. Verder is dit moeilik om geadsorbeerde silwer op die koolstof te behou weens die verplasing daarvan deur goud.

Die aansuring van dragtige aanlegoplossings voordat dit in aanraking met koolstof kom, is ondersoek as 'n moontlikheid om hierdie tekortkoming te oorkom. Gegewens van lotgewys laboratorium eksperimente op die effek van pH op goud adsorpsie van aanlegoplossings en sintetiese oplossings met 'n hoë ionsterkte het gedui op reaksietempo optima in die omgewing van pH 5 en onder pH 1. Die invloed van pH op die ewewigskapasiteitskonstante vir die adsorpsie van goud op geaktiveerde koolstof, was ook ondersoek met beide aanlegoplossings en sintetiese oplossings van hoë ionsterkte. In die geval van die aanlegoplossing was daar volgens die resultate slegs 'n geringe verandering in die goud kapasiteit van die koolstof in die pH gebied 12 tot 6, met betekenisvolle toenames by laer pH waardes. In die geval van die sintetiese oplossing met hoë ionsterkte is gevind dat die kapasiteitskonstante voortdurend toeneem terwyl die pH verlaag word van 12 na 1. Dit is ook gevind dat die adsorpsiekapasiteit van koolstof vir goud betekenisvol beter is vir die sintetiese oplossing. Geen presipitering van goud uit die dragtige oplossing is opgemerk wanneer die pH tot selfs 1 verlaag is nie. Dit is egter gevind dat 25 persent van die silwer reeds neergeslaan het wanneer 'n pH van 3,0 bereik is. Met verdere verlaging van die pH het aansienlike verdere presipitering van silwer plaasgevind.

Verdere ondersoek was beperk tot die deurloping van geskikte aangesuurde goudaanlegoplossings deur een of meer kolomme wat geaktiveerde koolstof bevat. Voorlopige resultate het getoon dat die deeltjiegrootte van die koolstof 'n betekenisvolle uitwerking op die tempo van goudadsorpsie het. Geen verplasing van geadsorbeerde silwer deur goud is waargeneem by 'n invloed pH van 5 nie. In 'n tipiese ononderbroke 'mallemeule' opset met drie kolomme, en waarin goud elke 48 uur van die eerste kolom ge-elueer is, kon gemiddelde goudwaardes van 0,001 g/t bereik word onder gesimuleerde aanleg werktoestande. Die gegewens is by relatief hoë invloed oplossingstempo verkry met geringe ophou van goud in die koolstof herwinningssbaan.

Meer as 99,9 persent van die goud en meer as 99,8 persent van die silwer is herwin in die adsorpsiebaan, terwyl 'n gemiddelde elueringsherwinning van 99,8 persent van die geadsorbeerde goud en 98,2 van die geadsorbeerde silwer deur die elueringsgegewens aangedui is. Eluering van die koolstof is by 91°C uitgevoer. Dit sluit vooraf

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behandeling van die koolstof met natriumsianiedoplossing in, gevolg deur eluering met gedeioniseerde water. By 'n ladingsvloeiempo van 66 bedvolumes per uur is die volgende aanduiding verkry vir opname van metale op die koolstof in die eerstekolom:- 53 kg/t goud, 6 kg/t silwer, 57 kg/t koper, 14 kg/t nikkel, 1 kg/t sink. Slegs spore van kobalt het geadsorbeer. Met 'n elueringstempo van 1,7 bedvolumes per uur is dit gevind dat die eerstekolom volledig gestroop kan word in minder as 5 uur. Goud konsentrasies in die eluaat het 6 tot 7 g/l bereik.

Behalwe vir die uitstekende adsorpsie en elueringsdata wat verkry is met aangesuurde dragtige oplossings, was daar geen aanduiding van besoedeling van die koolstof solank die drukval tussen die drie kolomme binne praktiese perke gehou is nie. Wanneer die proses met konvensionele sinkpresipitering vergelyk word, blyk dit dat die koolstof-proses aansienlike ekonomiese voordele inhou, met sterk aanduidings van moontlike betekenisvolle besparings beide in kapitaal en bedryfskoste. Verdere proefnemings op toetsaanleg skaal, verkieslik op 'n goudaanleg, is nodig voordat 'n betekenisvolle kostevergelyking met die bestaande proses gemaak kan word.

Introduction

The zinc-cementation process for the recovery of gold and silver from cyanide solutions was introduced on the Witwatersrand in 1890¹. With the addition of lead salts and the use of zinc dust rather than shavings, and with de-aeration of solutions, the process is one of great efficiency considering the low gold tenor of the solutions involved. Like cyanidation, cementation is a complex heterogeneous redox process. Zinc is dissolved at the anodic areas of a surface, and the electrons released serve to reduce the aurous ions at the cathodic areas.

It is generally accepted that cementation is sensitive to alkalinity and to the concentration of free cyanide in solution. Moreover, many of the more common constituents of gold-cyanidation solutions influence the cementation reaction. For example, sodium sulphide and the cyanide complexes of copper, arsenic, and antimony significantly decrease the recovery of gold when they are present in concentrations of more than 10^{-5} M. The extent of the decrease in gold recovery increases progressively with concentration until cementation ceases altogether.

The Merrill-Crowe process as currently practised in South Africa requires very careful control in order to yield barren solutions analysing less than 0,01 g/t gold. It is, at the same time, a relatively labour-intensive operation.

Activated carbon was introduced in about 1880 as a means of recovering gold from solution. It was a strong competitor for zinc precipitation during the early years of the cyanidation process. However, it rapidly lost ground as the technology of zinc cementation improved and because of certain limitations associated with its use, which are discussed below.

An important characteristic of activated carbon is its ability to function with unimpaired efficiency in foul cyanide solutions. It has been used for the recovery of residual gold from extremely dilute barren solutions and from the effluent from slimes dams. Carbon-in-pulp^{2, 3} has been used to adsorb gold direct from cyanidation pulps, thus obviating any filtration stage.

The lack of a suitable means of stripping adsorbed gold from loaded carbon presented a serious disadvantage to the carbon process. In relatively recent times, processes have been developed that allow the carbon to be re-used. The gold is eluted with alkaline solutions of sodium sulphide and sodium sulphite⁴, a boiling solution of sodium cyanide and sodium hydroxide⁵, deionized water⁶, or organic solvents⁷, and the gold is then recovered from solution by electrolysis.

Investigations carried out at the Anglo American Research Laboratories (AARL) into the use of activated carbon for the recovery of gold from gold-plant effluents

have resulted in the introduction of several important innovations in this field of gold technology. More efficient means of gold elution⁶ and gold electrowinning⁸, together with a relatively inexpensive method of thermal regeneration of the carbon, have all been demonstrated at pilot-plant level⁹. These developments in the recovery of gold from both solutions and pulps have undoubtedly made the use of activated carbon technically and economically more attractive. It was thus only a logical development to include the treatment of gold pregnant solutions as well as effluent solutions within the scope of the investigational work at these laboratories.

Materials

Test solutions

The adsorption of gold onto carbon from both synthetic and plant solutions was studied. Clarified pregnant solution obtained from the gold plant at Western Deep Levels Gold Mine was stored at the Laboratory in two 3,3 m³ rubber-lined tanks. The composition of one such bulk solution, together with the effect of storage on its stability, is presented in Table I.

In view of the important role played by the ionic strength of the adsorption medium¹⁰, two synthetic gold-bearing solutions, one of high ionic strength and the

TABLE I
COMPOSITION AND STABILITY OF GOLD-PLANT PREGNANT SOLUTIONS

Constituent	Concentration of solution as received (pH 10,6) g/t	Concentration of solution after storage for 1 month in sealed container (pH 9,1) g/t
Au	5,4	5,4
Ag	0,69	0,70
Cu	7	7
Ni	2	2
Co	< 1	< 1
Fe	1	< 1
Zn	15	3
Pb	< 1	< 1
Hg	0,01	0,01
Al	< 1	< 1
Ca	590	590
Ba	3	< 1
Mg	ND	< 1
Na	310	310
K	45	45
Si	20	12
CNS ⁻	90	100
S ₂ O ₃ ⁼	4	< 1
SO ₄ ⁼	1680	1660
Cl ⁻	240	250
NO ₃ ⁻	ND	190
As	ND	< 1
Free CN ⁻	92	19
Total CN ⁻	94	27
Suspended solids	5	ND

ND=Not determined.

other of low, having gold contents similar to the plant solution were also prepared. The synthetic solution of low ionic strength was made up from deionized water and CP-grade potassium aurocyanide, while the synthetic solution of high ionic strength was similarly prepared except that 1000 g/t calcium as calcium chloride was added to the solution.

Activated carbon

Type G210 and type G215 granular coconut-shell carbons supplied by Le Carbone (Pty) S.A. Ltd were used. Equilibrium capacity constants for gold were measured at pH 10 in standard borate buffer (see below). The values for the two grades of carbon were found to be 35 and 39 mg of gold per gram of carbon respectively.

Methods

Equilibrium capacity constants

The determination of equilibrium capacity constants for gold adsorption onto activated carbon (type G210) at various pH levels was carried out as previously described¹⁰. The capacity constants were subsequently calculated on the assumption that the mechanism of gold adsorption was adequately described by the Freundlich equation over the entire pH range investigated. Any adjustment of solution pH was made with sulphuric acid. Prior to tests on the adsorption, samples of activated carbon were equilibrated at the desired pH level and then dried at 110 °C before use. The equilibration of the carbon samples was carried out in a closed circuit, the solution being circulated by means of a pump. The addition of the necessary amounts of sulphuric acid (10 per cent solution) was controlled by means of a titrimeter. This equilibration procedure was found to be necessary in order to prevent any upward drift in pH values following the addition of carbon to the test solutions.

Reaction rates

The effect of pH on the rate of gold adsorption from three different test solutions, all of which contained 6.2 g/t gold (see above), was compared. Gold adsorption as a function of time was monitored by the addition of 1 g of the equilibrated carbon (type G210) to 1 litre of test solution at the desired pH level while the solution was stirred constantly with the aid of a magnetic stirrer. Test samples of 5 ml each were withdrawn at frequent specified intervals (15, 30, 45, 60, 90, 130, 150, 180, 240, and 300 minutes), and the gold content was determined by atomic-absorption spectrophotometry.

Gold adsorption

Following acidification if required, gold-plant solution was pumped through a stainless-steel heat-exchange spiral immersed in a waterbath at 20 °C. The spiral was in series with three adsorption columns containing granular activated carbon (type G215). The influent solution was pumped at a constant flowrate using an MPL monopump metering pump. Unless otherwise specified, each column (16 mm internal diameter by 100 cm long) was packed with 38 g of a screened fraction of oven-dried granular activated carbon that had previously been equilibrated at the desired pH level. Flow through the columns was always in a downward direction. The effluent from each column was continuously monitored by means of an LKB Minirac fraction col-

lector. Effluent from the first column was sampled every 45 minutes, samples of 20 ml being taken. Samples were taken every 30 minutes from columns 2 and 3 respectively. Gold values in the effluent solutions were analysed by solvent extraction followed by atomic-absorption spectrophotometry. A 10 ml aliquot was taken in the case of the first column, and the gold values were reported to two decimal figures; a composite 400 ml three-hour aliquot was taken from each of columns 2 and 3 respectively, and the gold values were reported to four decimal figures (± 0.0005 g/t sensitivity).

A typical 'merry-go-round' operation was conducted, in which the lead column was taken off-line every 48 hours and eluted (see below) while an additional column containing virgin carbon was added in the last position. The initial loading of gold onto the lead column was subsequently calculated by measurement of the areas under the adsorption curves.

Gold elution

Gold-loaded carbon from the adsorption columns was transferred to a water-jacketed stainless-steel elution column (16 mm internal diameter by 75 cm long). Excess solution was allowed to drain from the column while the temperature of the column was raised to 91 °C. Unless otherwise specified, the carbon was then pretreated with one bed volume of a reagent containing 10 per cent sodium cyanide and 1 per cent sodium hydroxide, which was pumped into the column through a stainless-steel heat-exchange spiral also maintained at 91 °C. In the first continuous adsorption operation (see below), the pretreatment reagent was pumped at 2.83 bed volumes per hour. The pretreated carbon was allowed to 'soak' for 15 minutes, and the gold was eluted at 1.71 bed volumes per hour using deionized water⁵. In the second continuous adsorption experiment, the carbon was pretreated with only half a bed volume of the reagent of 10 per cent sodium cyanide and 1 per cent sodium hydroxide, and was eluted as before except that the 15-minute 'soaking' period was omitted. Eluate solutions containing relatively high concentrations of gold and silver were analysed by fire assay, while lower concentrations were analysed by solvent extraction followed by atomic-absorption spectrophotometry (reported to two decimal figures).

Results

Stability of gold-plant solutions

From the analytical data presented in Table I, it can be seen that the gold-plant solutions under study are not completely stable with respect to storage time. While no precipitation of gold or silver was indicated, the decrease in zinc, barium, total cyanide, and free cyanide, together with a drop in pH values, does indicate a certain degree of instability. The polymerization of free cyanide, together with the oxidation of cyanides to cyanates, may explain to some degree the reasons for such instability.

Because of the possible precipitation of aurous cyanide after the solution has been acidified, the precipitation of gold and silver from a plant solution was initially investigated as a function of pH. This was done by the addition of sulphuric acid to lower the pH of the test

solution to various levels between pH 1 and pH 3. The test samples were then allowed to stand for 24 hours before being filtered, and were analysed for gold and silver some 48 hours later. The results presented in Table II indicate no precipitation of gold even at a pH value as low as 1,0, but as much as 82 per cent of the contained silver was precipitated. The nature of the silver precipitate was not investigated, although it was most likely to be silver cyanide. At pH levels below approximately 4, the precipitation of a small amount of a pink slime was observed. Further analyses on an air-dried sample of the precipitate indicated the presence of 18 per cent copper, 8 per cent iron, 2,6 per cent silver, 1,1 per cent cobalt, 0,9 per cent nickel, and 26,3 per cent water. Examination of an X-ray diffractogram of the material

showed that the precipitate was largely copper ferrocyanide, $\text{Cu}_2\text{Fe}(\text{CN})_6$.

Adsorption of gold onto carbon at conventional pH levels

Preliminary experiments were carried out in which both clarified pregnant solutions and partially clarified plant effluents were fed to a carbon column. This invariably resulted in excessive fouling of the carbon with calcium carbonate. The findings were similar in pilot-plant operations⁹. This carbonate fouling, besides adversely affecting the adsorption of gold, resulted in eventual choking of the carbon bed and necessitated frequent removal of the carbonate by treatment with dilute hydrochloric acid. The build-up of calcium carbonate was found to be erratic in that sometimes little or no carbon fouling occurred. Furthermore, fouling appeared to be most troublesome with fresh, rather than aged, plant solutions. These latter observations indicated that calcium fouling was most sensitive to the pH level of these solutions as the relatively small decrease in pH observed on storage (Table I) was sufficient to allay any fouling problem. Obviously, while the concentrations of both calcium and carbon dioxide play a significant role in this fouling mechanism, the judicious lowering of pH to between 8 and 9 (thus shifting the carbonate equilibrium to the bicarbonate side) would appear to overcome the problem to a large degree. Such a pH adjustment may have considerable merit if excessively alkaline plant solutions or pulps are to be treated with carbon, e.g. in a conventional carbon-in-pulp operation.

Apart from the problem of fouling by calcium carbon-

TABLE II
SOLUTION STABILITY OF GOLD AND SILVER IN CLARIFIED GOLD-PLANT SOLUTION

Solution pH	Acid addition ml H_2SO_4 /l	Solution analysis*	
		g/t Au	g/t Ag
9,8	as received	5,26	0,55
3,0	0,29	5,52	0,42
2,8	0,33	5,57	0,35
2,6	0,37	5,50	0,23
2,4	0,59	5,44	0,13
2,2	0,81	5,57	0,09
2,0	1,18	5,40	0,09
1,8	2,06	5,46	0,09
1,6	2,87	5,38	0,09
1,4	4,42	5,57	0,10
1,2	5,08	5,61	0,10
1,0	11,11	5,44	0,10

*Gold and silver determined by atomic-absorption spectrophotometry after solvent extraction.

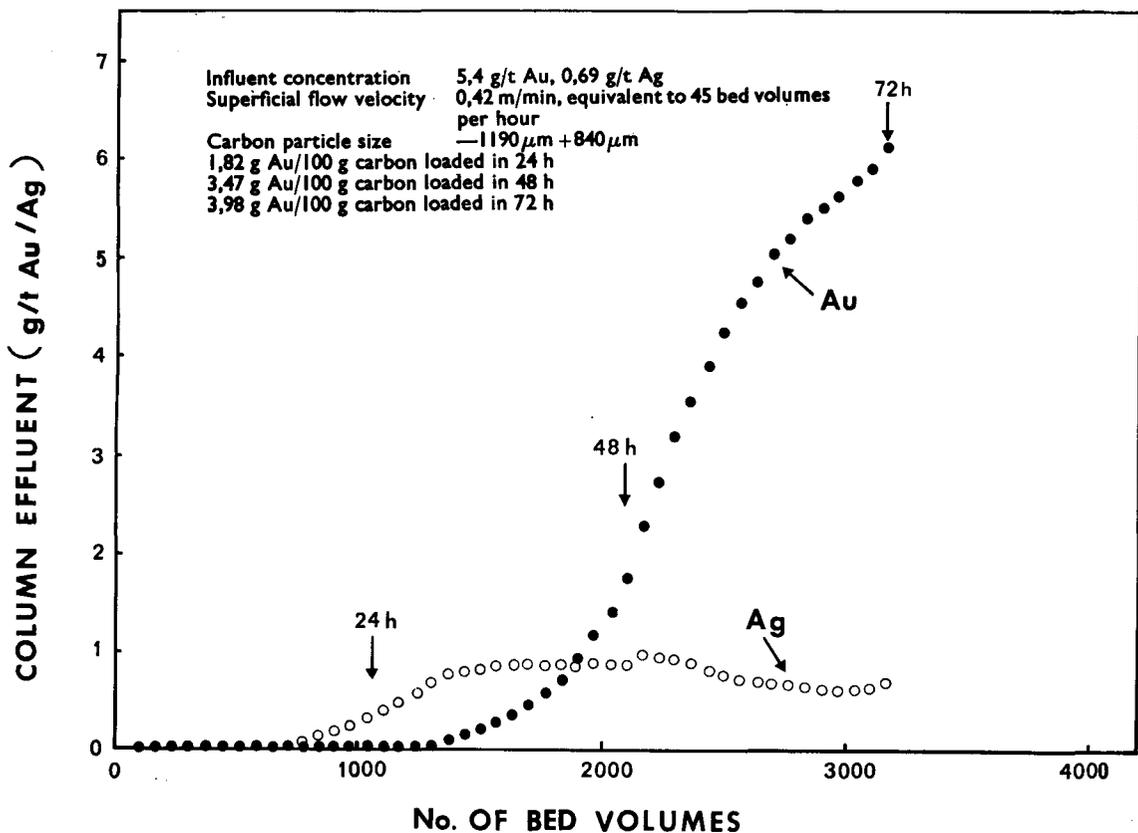


Fig. 1—The adsorption of gold and silver from a plant solution at pH 9,8

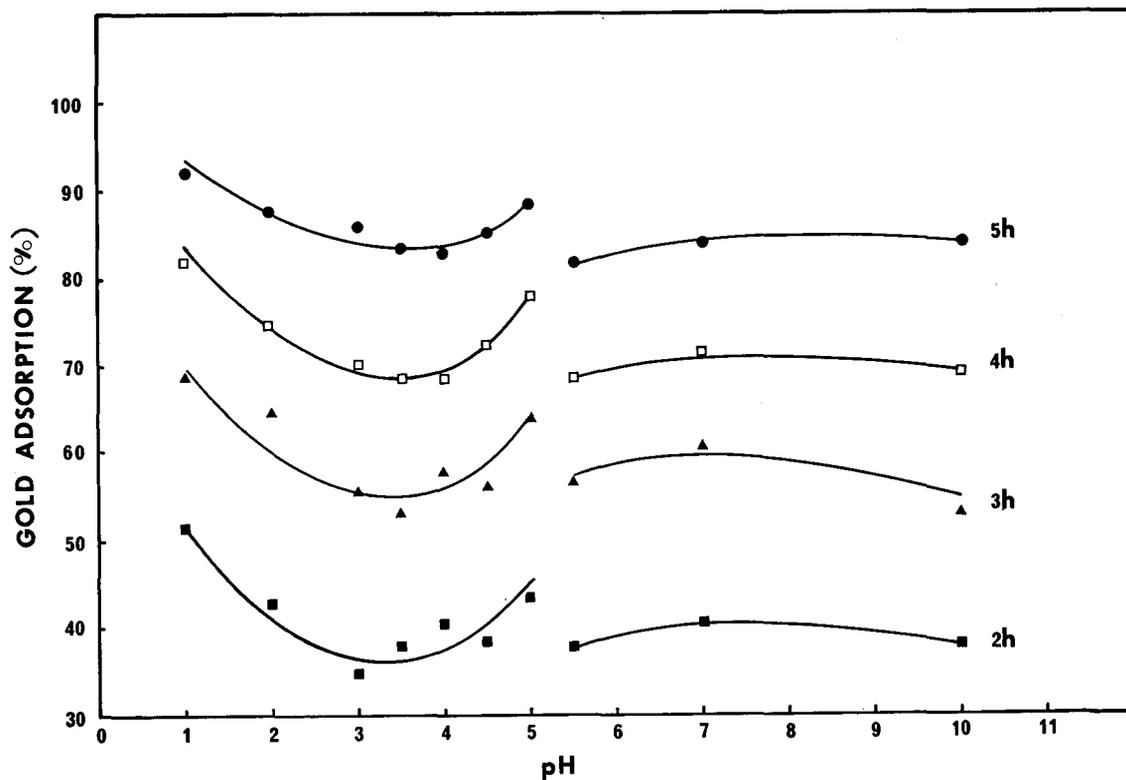


Fig. 2—The effect of pH on the rate of gold adsorption from a plant solution

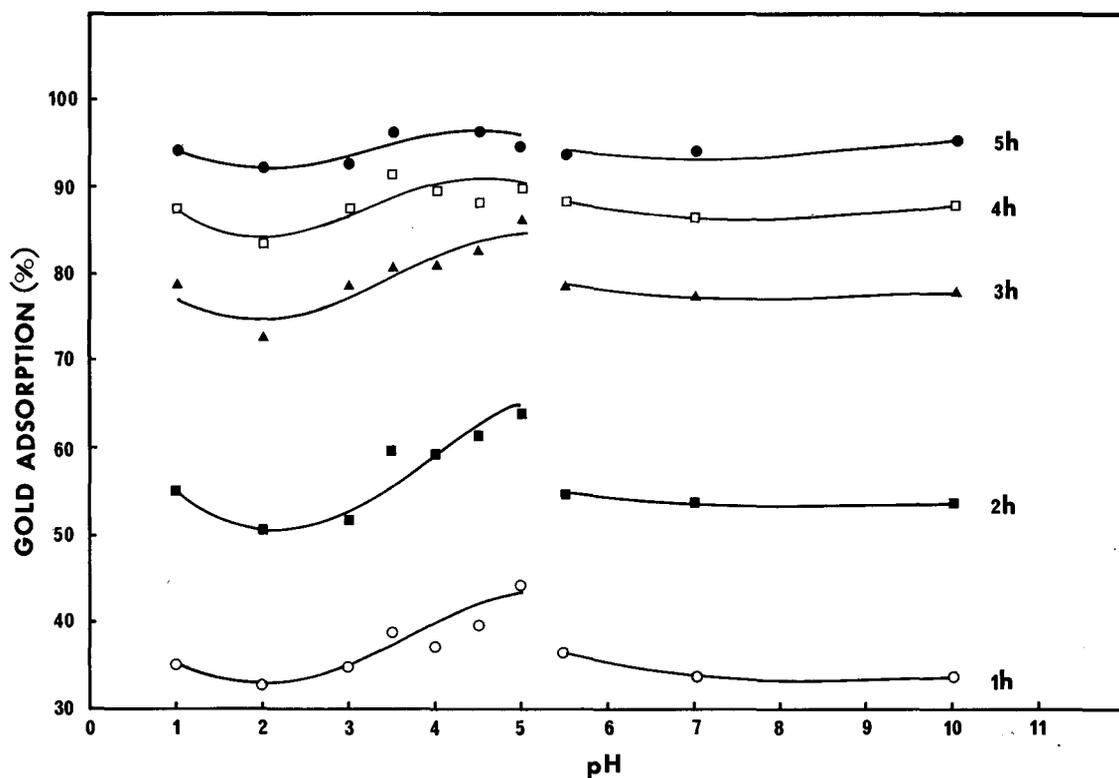


Fig. 3—The effect of pH on the rate of gold adsorption from a synthetic solution of high ionic strength

ate, the displacement of silver by influent gold values in a column operation presents problems in a merry-go-round system for the treatment of clarified pregnant solutions. Fig. 1 illustrates a typical breakthrough curve obtained when an 'aged' pregnant plant solution with a pH value of 9,8 was pumped through a column containing activated carbon. In this instance, fouling of the carbon by calcium carbonate was not observed. The early breakthrough of silver ahead of gold, together with the fact that the tenor of the silver in the effluent was higher than that in the influent, strongly suggests such a displacement mechanism. This displacement of silver, occurring at an average carbon loading of approximately 1 per cent gold in this instance, would result in a serious build-up of silver in a merry-go-round circuit, necessitating a more complex cycle of adsorption and elution if excessive losses of silver are to be avoided.

These two effects (i.e. the fouling of carbon with calcium carbonate and possible high silver losses) associated with the use of carbon at the pH levels occurring in a conventional plant were considered to be a sufficient inducement for further investigations to be conducted on the adsorption of gold at lower pH levels.

Effect of pH on the kinetics of gold adsorption

Adsorption data concerning the effect of pH on the rate of gold adsorption from the three test solutions studied are presented graphically in Figs. 2 to 4.

In the case of both the plant solution and the synthetic solution of high ionic strength, there are similarities in the rate of gold adsorption at various pH levels, although the adsorption is significantly better for the synthetic solution. In both cases, an optimum at pH 5 is indicated,

together with a marked fall-off in the rate of gold adsorption above pH 5 (Figs. 2 and 3). However, gold adsorption from the synthetic solution of low ionic strength displays a very different kinetic picture (Fig. 4). In this instance, pH can be seen to have a far bigger effect on adsorption rates especially at high pH levels, with optima being indicated at pH levels of approximately 4 and below 1 respectively.

The reasons for the discrepancies noted between the rates of gold adsorption from the plant solutions and those from synthetic solutions are at this stage not easily defined. Both thiosulphate and thiocyanate anions were, however, shown to have a very detrimental effect on the rates of gold adsorption when added individually to a synthetic solution at the approximate concentration levels found in the plant solution (Table I). While the addition of 100 g/t thiocyanate as sodium thiocyanate was found to have a most detrimental effect at high pH levels, the presence of only 4 g/t thiosulphate added as sodium thiosulphate was found to have the most adverse effect on adsorption rates at low pH levels.

Effect of pH on equilibrium capacity constants

Capacity constants illustrating gold adsorption as a function of pH are presented graphically in Fig. 5. The data also allow comparison of gold adsorption from both a plant solution and a synthetic solution of high ionic strength. In the case of the plant solution, a very gradual increase in carbon capacity can be seen as the pH is decreased from 12 to 6. At lower pH levels, a sharp increase in capacity constant is indicated, with an optimum at approximately pH 2 to 2,5. The subsequent decline in gold capacity at still lower pH levels probably

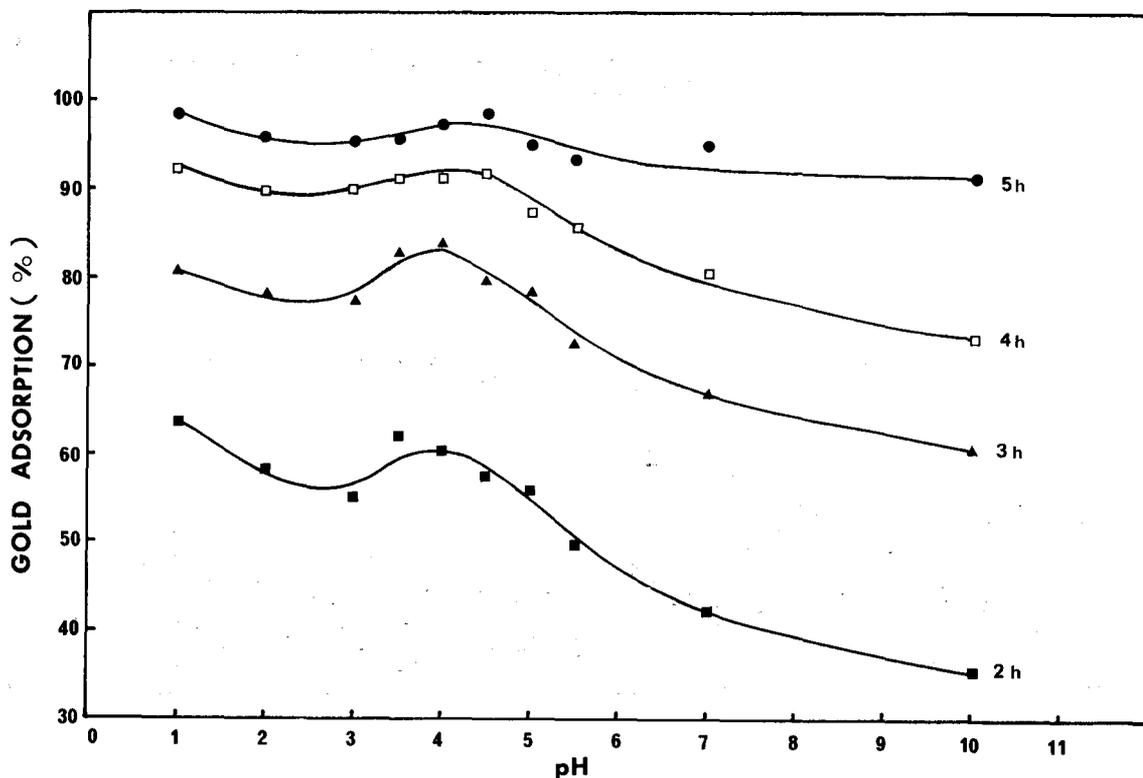


Fig. 4—The effect of pH on the rate of gold adsorption from a synthetic solution of low ionic strength

corresponds to the formation of aurous cyanide. The formation (and possible precipitation) of aurous cyanide would presumably interfere with any anionic adsorption mechanism.

The effect of pH on gold adsorption from the synthetic solution can immediately be seen to be similar to that from the plant solution. However, the capacity constants are generally very much better for synthetic than for plant solutions. Again, while the reasons for such differences are not easily explained, it was shown that the

addition of both thiosulphate and thiocyanate to synthetic solutions had very detrimental effects on gold capacity constants. The addition of 100 g/t thiocyanate to a synthetic solution of high ionic strength at pH 5.0 was shown to reduce the capacity constant from 58 to 40 mg of gold per gram of carbon. Likewise, the addition of only 6 g/t thiosulphate reduced the capacity constant to 38 mg of gold per gram of carbon.

The effect of pH on the Freundlich constant¹⁰, n , was also calculated from the above equilibrium adsorption

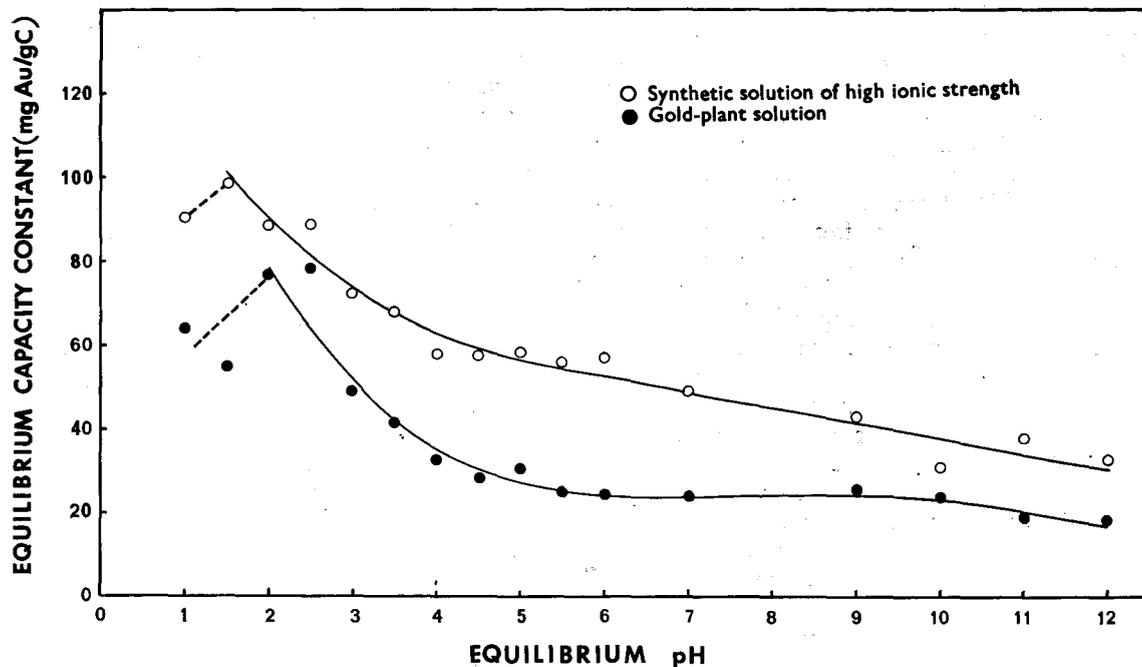


Fig. 5—The effect of pH on the Freundlich equilibrium capacity constant for gold adsorption onto activated carbon

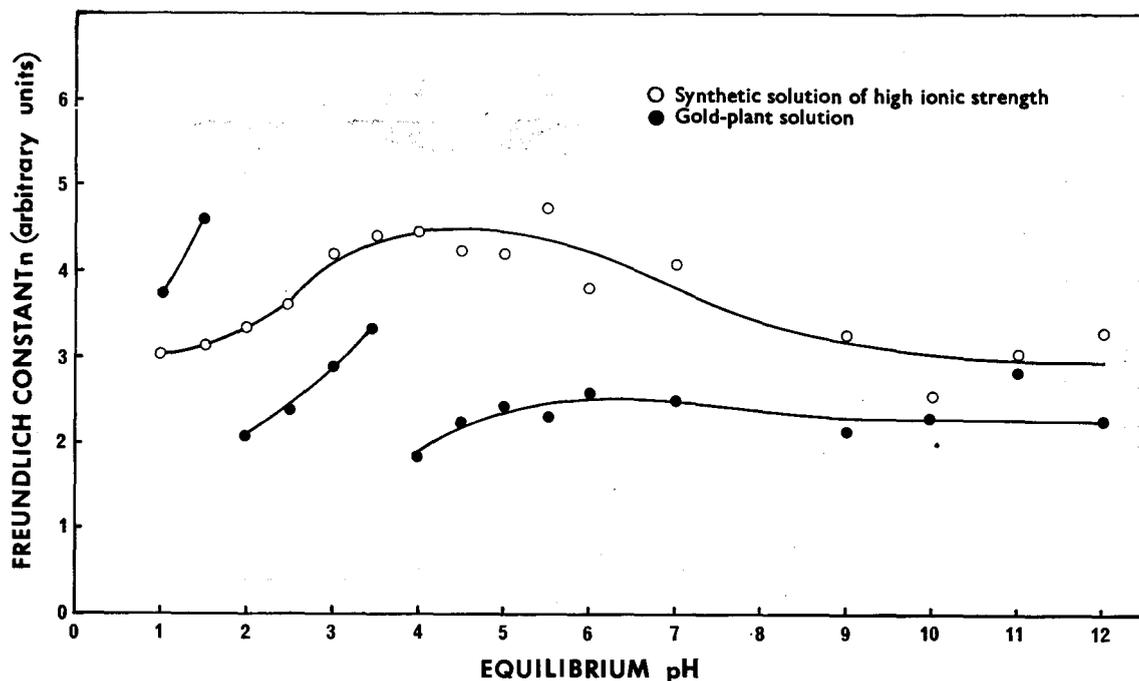


Fig. 6—The effect of pH on the Freundlich constant n

data (Fig. 6). While the behaviour of the plant solution is significantly different from that of the synthetic solution, indicating poorer gold adsorption, the breaks in continuity at pH levels below 4 and 2 are again evident. The optimum values of n were obtained when the synthetic solution was used at pH 4 to 5.

Gold adsorption at pH 5

Preliminary experiments were carried out in which acidified plant solutions at pH 2,5 were pumped through individual columns containing activated carbon. Acidification to this level entailed the addition of approximately 550 g/t sulphuric acid to the original plant solution. It was demonstrated that significantly higher gold loadings on carbon could be achieved at this influent pH. Loadings approaching 10 g of gold per 100 g of carbon were obtained when plant solution acidified to pH 2,5 was used. This compared with only 4 to 5 g of gold per 100 g of carbon achieved with a conventional plant solution (pH 10,2). It was also shown that higher influent flow-rates could be used beneficially after acidification to pH 2,5. Furthermore, no displacement of silver by adsorbed gold values occurred at pH 2,5, although a significant amount of silver, together with copper ferrocyanide, was precipitated under such pH conditions (Table II). This precipitation resulted in a minor amount of carbon fouling, which increased the pressure drop across the carbon bed. The carbon fouling also presented operational problems when in-line acidification was carried out. In view of this latter problem, together with the earlier findings suggesting adsorption reaction rate optima in the region of pH 5 (see reaction rate data), further investigations were confined to the treatment of

acidified plant solutions in this particular pH region. Acidification of plant solution to pH 5 entailed the addition of only 220 g/t sulphuric acid. While no precipitation of copper ferrocyanide or silver was observed at this pH level, a small amount of a white precipitate identified as zinc ferrocyanide was noted. Fig. 7 illustrates a typical partial breakthrough curve for gold and silver values, which was obtained when an acidified plant solution at pH 5 and containing 6,2 g/t gold was pumped through a single column as previously described. The sympathetic breakthrough of both gold and silver under such conditions can be compared with the premature displacement of silver that was observed when a non-acidified plant solution was used. (Fig. 1).

In view of the possible large hold-up of bullion in an envisaged carbon circuit, the parameters most likely to influence such a situation were also briefly considered. Fig. 8 illustrates the effect of the particle size of the carbon on the adsorption of gold when suitably acidified plant solution was pumped through individual columns containing two different screen fractions of type G215 carbon. The beneficial use of the finer fraction of carbon (that between 1190 and 840 μm) is most evident. In this instance, influent flowrates were maintained at approximately 45 bed volumes per hour while influent was pumped continuously for 72 hours. Even at such relatively high flow velocities, no excessive pressure drop across the carbon bed was observed in either instance (less than 20 kPa per metre of carbon bed). Testwork using a fraction between 840 and 297 μm of a similar grade of carbon, while indicating even better gold adsorption, showed a pressure drop of about 100 kPa per

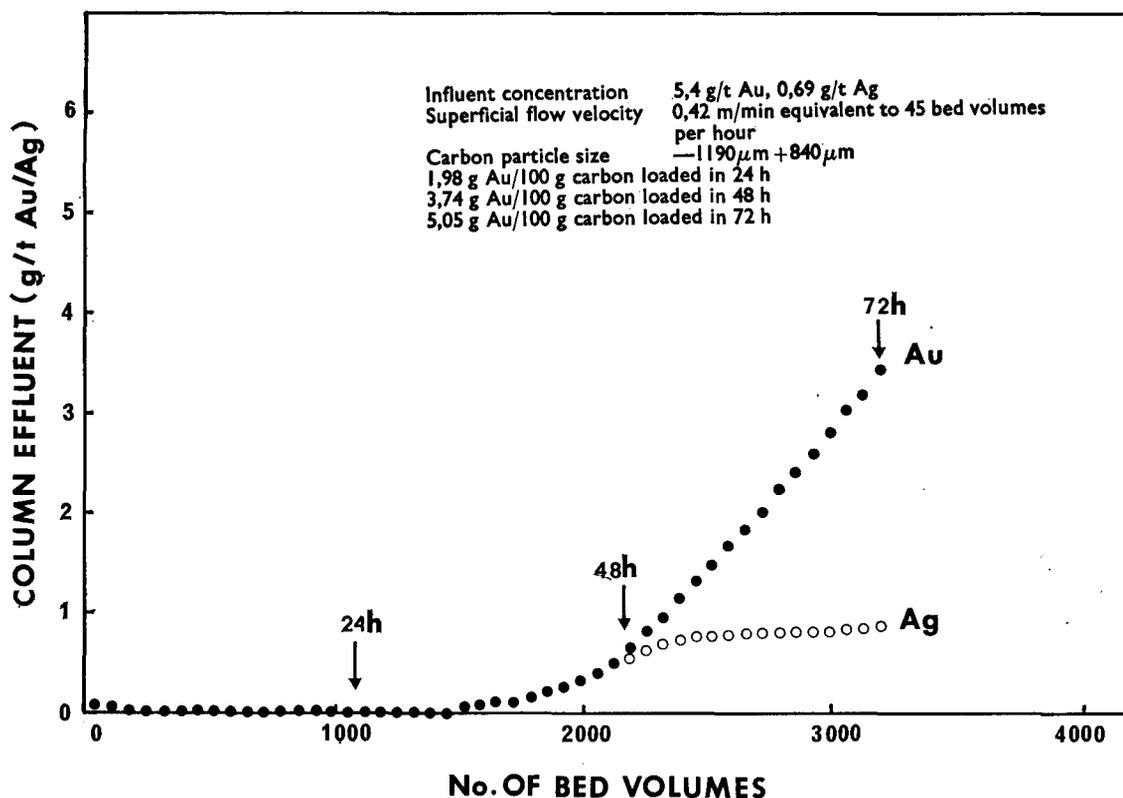


Fig. 7.—The adsorption of gold and silver from an acidified plant solution at pH 5,0

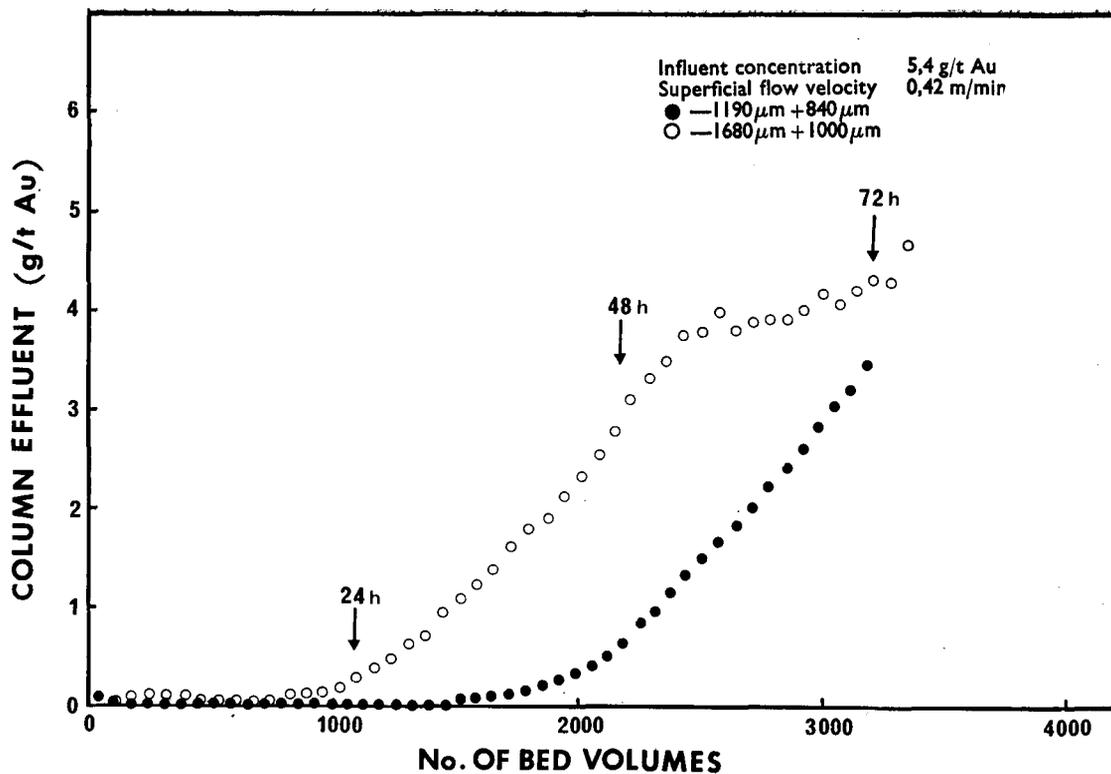


Fig. 8—The effect of carbon particle size on gold adsorption

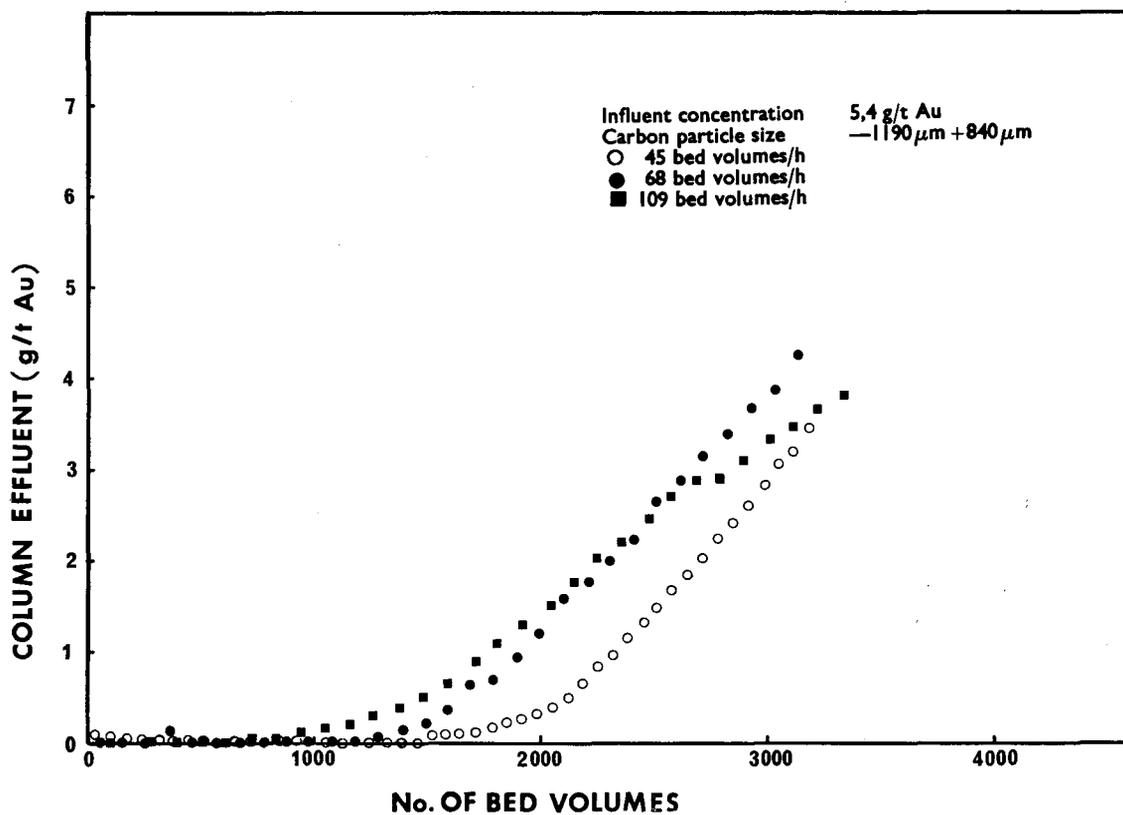


Fig. 9—The effect of influent flowrates on gold adsorption

metre of carbon bed across the carbon bed. This was considered to be excessive from the point of view of any possible scale-up in the size of the operation. Further testwork was thus confined to the use of a narrow size range (between 1190 and 840 μm) of type G215 carbon. The choice of a relatively narrow range of particle sizes of carbon has considerable operational advantages when related to packed-bed column operation. This is because it results in lower packing densities, and consequently lower pressure drops. The bulk density of the above selected carbon fraction was approximately 0,33 g/cm^3 , which can be compared with packing densities of up to 0,5 g/cm^3 for carbon of a similar grade but wider particle-size range.

The effect of influent flowrates on gold adsorption was also investigated in the present context. As can be expected, the use of relatively high influent flowrates will minimize any hold-up of bullion in the carbon-adsorption circuit. Fig. 9 illustrates the effect of pumping suitably acidified plant solution through individual columns containing activated carbon. Superficial influent flow velocities varying from 0,42 to 1,05 m/min were employed. From the results presented, it is most evident that only small differences in the gold breakthrough curves resulted when flowrates were increased from 45 to 109 bed volumes per hour. These observations suggest that the rates of gold adsorption must be extremely high and the adsorption reaction zone very narrow. In the case where the influent was pumped at 109 bed volumes per hour, a loading of 4,16 g of gold per 100 g of carbon in 24 hours was noted. It was also observed that little, if any, displacement of silver by influent gold values occurred under the prescribed conditions.

Displacement of adsorbed metal values

Gold-plant solution having a pH of 9,3 and containing 5,4 g/t gold was pumped through a column at a superficial flow velocity of 0,42 m/min for 24 hours. Thereafter the entire column was carefully cut into sections and individual sections were analysed. A similar operation was carried out using the same gold-plant solution acidified to pH 4,5. Figs. 10 and 11 illustrate the values of adsorbed metal obtained at the two different pH levels. In the case of the conventional plant solution (Fig. 10), the displacement sequence gold-silver-nickel-copper was clearly evident, while the concentrations of calcium built up to nearly 1 per cent at the top of the column. Conversely, adsorption carried out under acid conditions (Fig. 11) indicated no such displacement sequence, although a major amount of copper was adsorbed at the top of the column. This adsorbed copper complex, which was thought to be $\text{Cu}(\text{CN})_2^{-1}$, may explain to a large degree the disparity between acidified plant solutions and synthetic solutions under similar pH conditions (see above).

It has been suggested¹¹ that the increase in copper adsorption is related to the negative charge on the corresponding anionic complex. Thus, at conventional pH levels, where the $\text{Cu}(\text{CN})_4^{3-}$ complex predominates, the adsorption of copper is poor and the copper is easily displaced by more strongly adsorbed metal species (see above). Conversely, at lower pH levels, decomposition of the above complex, yielding initially $\text{Cu}(\text{CN})_3^{2-}$ and subsequently $\text{Cu}(\text{CN})_2^{-1}$, results in a substantial increase in copper adsorption owing to the lower anionic charge on the copper complex. Furthermore, the observed precipitation of copper as a pink ferrocyanide complex at pH

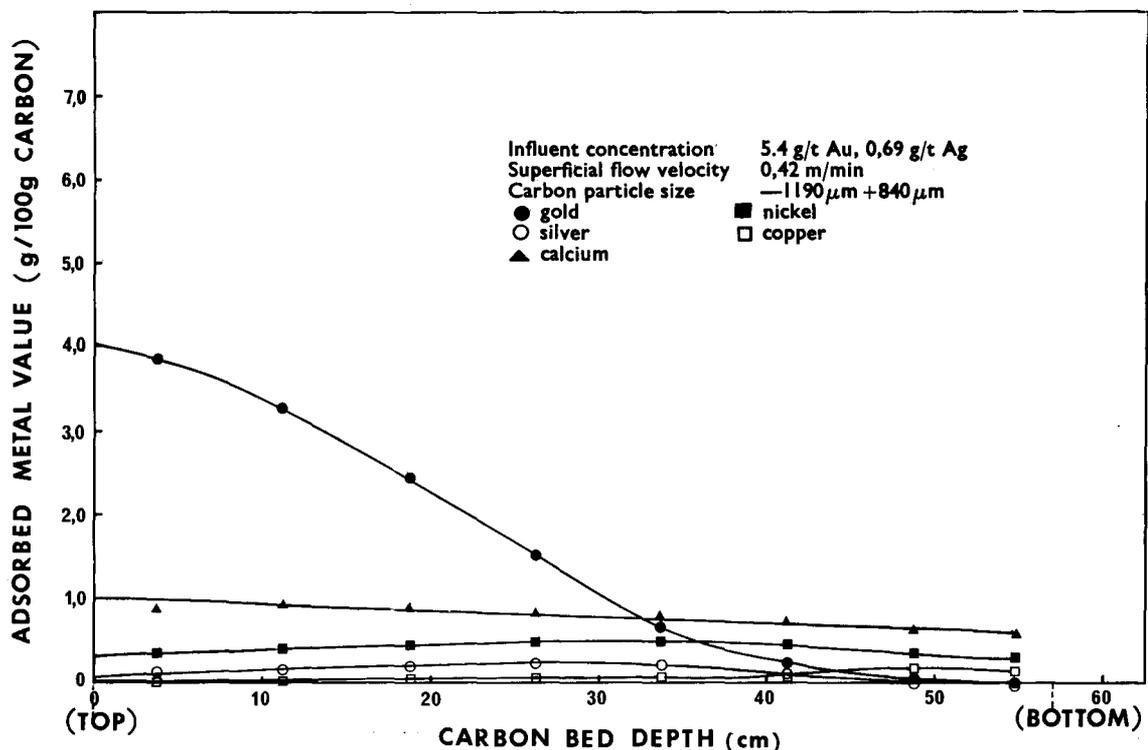


Fig. 10—The adsorption of metal values from a plant solution at pH 9,3

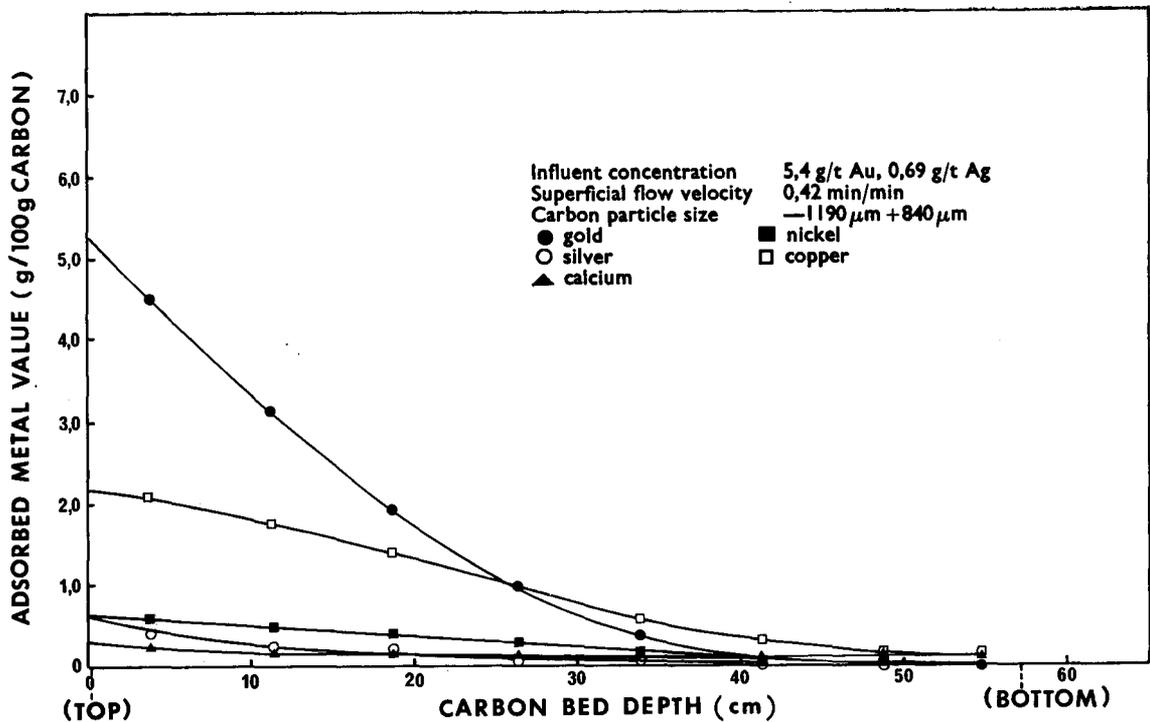


Fig. 11—The adsorption of metal values from an acidified plant solution at pH 4,5

TABLE III

OPERATION OF A 'MERRY-GO-ROUND' ACTIVATED-CARBON ADSORPTION CIRCUIT AT AN INFLUENT FLOWRATE OF 45 BED VOLUMES PER HOUR
(Superficial flow velocity = 0,42 m/min)

Column sequence	Total number of bed volumes passed/operational time, h	Effluent from second column (daily average concentrations)		Effluent from last column (daily average concentrations)	
		g/t Au	g/t Ag	g/t Au	g/t Ag
A — B — C	1059/0-24	0,0018	< 0,001	0,0022	< 0,002
A — B — C	2117/24-48	0,0008	0,006	0,0008	< 0,001
B — C — D	3176/48-72	0,0013	< 0,001	0,0007	< 0,001
B — C — D	4234/72-96	0,0033	0,010	0,0040	< 0,001
C — D — E	5293/96-120	0,0010	< 0,001	0,0010	< 0,001
C — D — E	6351/120-144	0,0014	0,022	0,0019	< 0,001
Average effluent values for 6 days		0,0016	< 0,006	0,0018	< 0,001

levels below 4 may explain the discontinuities observed in gold adsorption rates and capacity constant data under such acidic conditions. Likewise, the discontinuities observed at pH 1 to 2 may coincide with the formation of aurous cyanide. Both of these aspects are well illustrated in Figs. 5 and 6.

Continuous gold adsorption at an influent flowrate of 45 bed volumes per hour

Acidified gold-plant solution at pH 5,0 containing 5,4 g/t gold was pumped at a flowrate of 45 bed volumes per hour through a simulated merry-go-round circuit for a period of 6 days (continuous pumping was suspended temporarily after 96 hours owing to a weekend shut-down). A summary of the results is presented in Table III, while the elution data for column B are shown in Table IV. Gold-adsorption data for the first column of the merry-go-round circuit are presented graphically in Fig. 12.

With regard to gold adsorption, average values of gold in the effluent over the 6 days of 0,0016 g/t and 0,0018 g/t

from columns 2 and 3 respectively are most noteworthy. Such values also indicated that column C was in fact doing little or no work with respect to gold adsorption. A gold loading of 3,2 g per 100 g of carbon was indicated on the lead column (column A) using the adsorption data presented in Table III. However, elution data indicated progressive gold loadings of 3,3, 3,6, and 3,7 g per 100 g of carbon on columns A, B, and C respectively as these were brought into the lead position.

Fig. 13 illustrates a typical elution profile of gold and silver values from columns of loaded carbon. It shows that virtually complete gold elution was effected in 6 to 7 bed volumes (elution data taken from column C). Analyses of samples of the eluted carbon indicated that 99,9 per cent of the gold and 99,8 per cent of the silver was eluted under the specified conditions. The elution data also indicated the adsorption of considerable concentrations of copper (3,1 to 3,9 g per 100 g of carbon), zinc (1 to 1,3 g per 100 g of carbon), and nickel (0,9 to 1,1 g per 100 g of carbon). The elution of rela-

TABLE IV
ELUTION OF LOADED CARBON FOLLOWING A 48h ADSORPTION CYCLE AT 45 BED VOLUMES PER HOUR
ELUTION OF COLUMN B

Constituents	No. of bed volumes of eluate (1 bed volume = 166,6 ml)										Total mass mg	Carbon loading* g/110g C
	0,523	1,402	2,251	3,100	3,953	4,811	5,677	6,522	7,367	8,25		
Au (g/t)	348	894	4980	5196	2046	488	51	5,80	0,77	0,25	1374	3,62
Au (mg)	21,23	91,64	493,02	514,40	203,58	44,80	5,15	0,57	0,08	0,02		
Ag (g/t)	77	735	312	6	0	0	0,28	0,16	0,12	0,07		
Ag (mg)	4,70	75,34	30,89	0,59	0,00	0,00	0,03	0,02	0,01	0,01		
Cu (g/t)	5100	11200	200	3	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Cu (mg)	311,1	1148,0	19,89	0,3	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Co (g/t)	3	2	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Co (mg)	0,2	0,2	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Ni (g/t)	870	2660	860	19	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Ni (mg)	53,1	272,7	85,1	1,9	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Fe (g/t)	22	44	6	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Fe (mg)	1,3	4,5	0,6	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Zn (g/t)	1160	3940	95	1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Zn (mg)	70,8	403,9	9,4	0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1		
Ca (g/t)	720	200	21	10	9	7	7	7	9	7		
Ca (mg)	43,9	20,5	2,1	1,0	0,9	0,7	0,7	0,7	0,9	0,7		
SiO ₂ (g/t)	35	22	320	210	120	90	95	75	80	75		
SiO ₂ (mg)	2,1	2,3	31,7	20,8	11,9	9,0	9,6	7,4	7,9	7,7		
SiO ₃ (g/t)	ND	1200	<0,1	25	0,7	4,5	1,3	3,1	5,4	ND		
CNS ⁻ (g/t)	ND	470	90	10	5,0	4,8	2,8	1,2	0,3	0,7		

ELUTION RECOVERY (COLUMN B)

Element	Carbon loading g/t		Eluted carbon g/t	Recovery %
	36200	2900		
Gold			54	99,9
Silver			81	97,2

*On the assumption of complete elution except for Au, Ag, and SiO₂

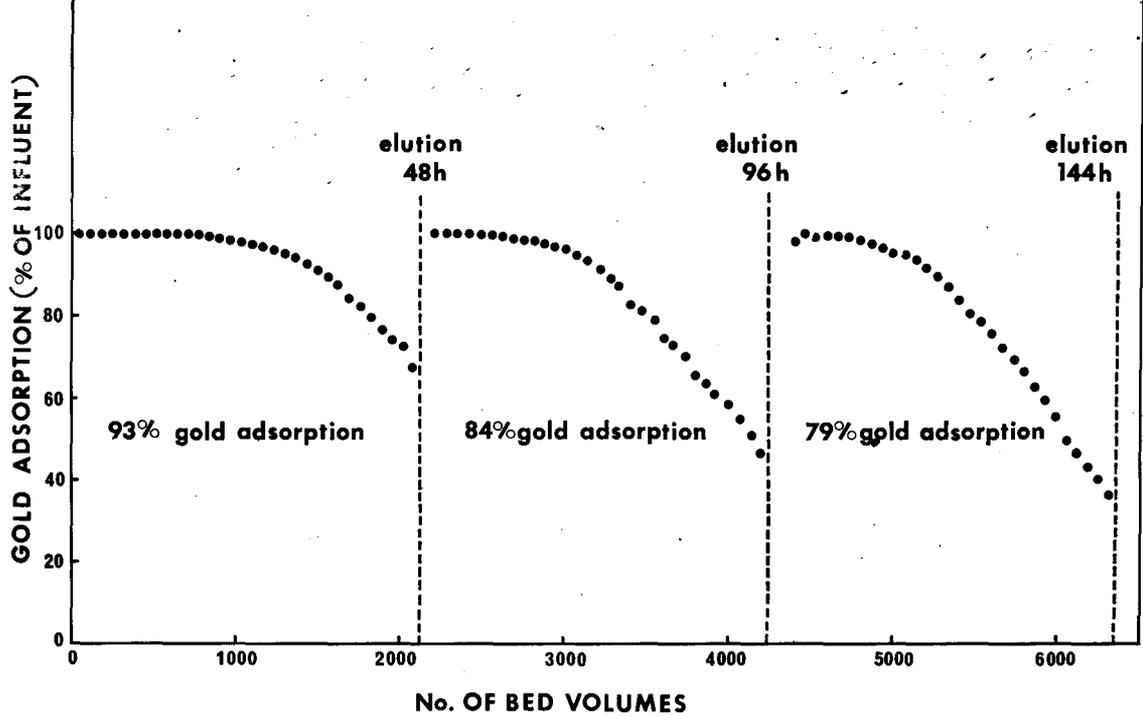


Fig. 12—The adsorption of gold in the first column of a merry-go-round circuit operating at 45 bed volumes per hour

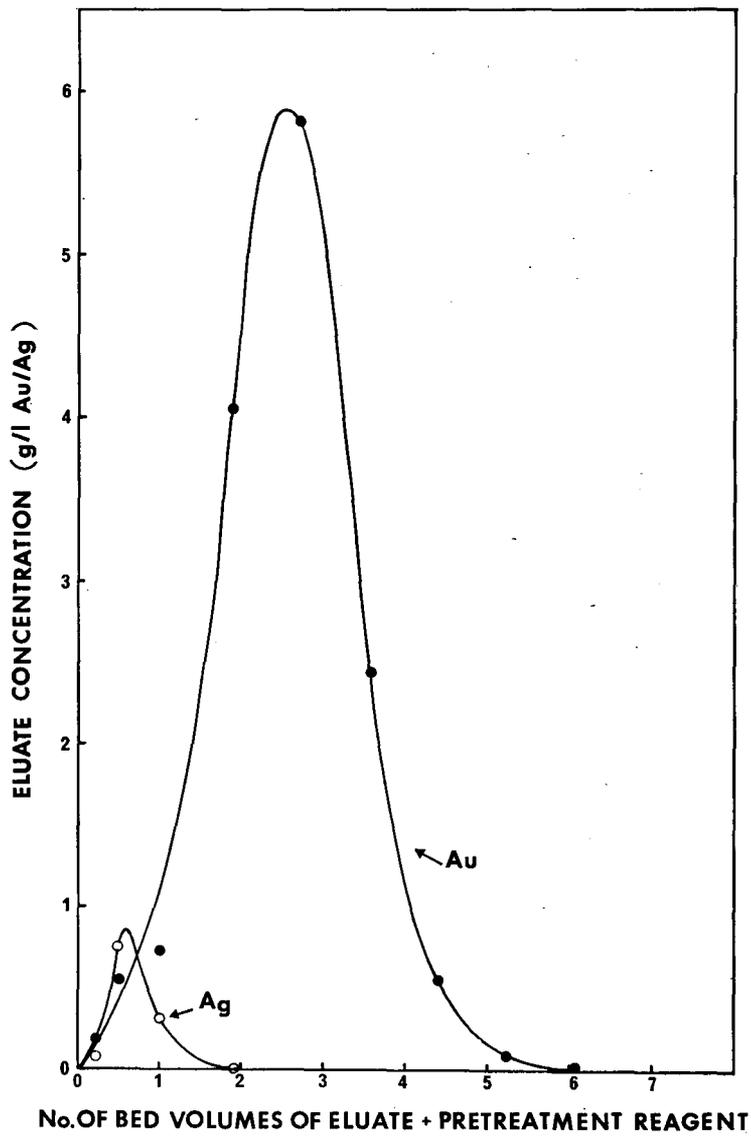


Fig. 13—The elution of gold and silver from loaded carbon using deionized water as an eluant

tively high concentrations of thiocyanate and thio-sulphate complexes, together with low concentrations of iron and cobalt, are also noteworthy.

The increase in the pH of column effluent from an initial influent value of 5,0 to a final effluent value of approximately 6,0 was an interesting observation. The effluent from the first column was also found to have a pH of approximately 6,0, implying that the rise in pH occurred where the adsorption of gold was greatest. Ion exchange, or replacement of basic groups on the carbon surface by aurocyanide anions, is strongly suggested.

Continuous gold adsorption at an influent flowrate of 66 bed volumes per hour

In order to achieve even higher gold loadings on the lead column and at the same time to make more effective use of the last column, influent flowrates were increased from 45 to 66 bed volumes per hour and the previous operation (see above) continued. Also, in this operation the influent pH was lowered to a value of 4,3

because of the significant rise in pH observed on the lead column.

From the summary of the resulting adsorption data presented in Table V, average gold effluent values over the 6 days of operation of 0,0008 g/t again indicated a gold adsorption efficiency of more than 99,9 per cent. Likewise, the adsorption of silver was also exceptionally good (more than 99,9 per cent). The adsorption of gold in the first column of the circuit is graphically presented in Fig. 14, and typical elution data from column F are presented in Table VI. While average gold recoveries of 99,7 per cent and silver recoveries of 99,6 per cent were achieved in the present operation, carbon loadings approaching the following were also obtained: 53 kg/t gold, 6 kg/t silver, 57 kg/t copper, 14 kg/t nickel, and 1 kg/t zinc.

Again, the elution of considerable quantities of thio-sulphate and thiocyanate complexes together with small amounts of mercury (0,002 g per 100 g of carbon loading)

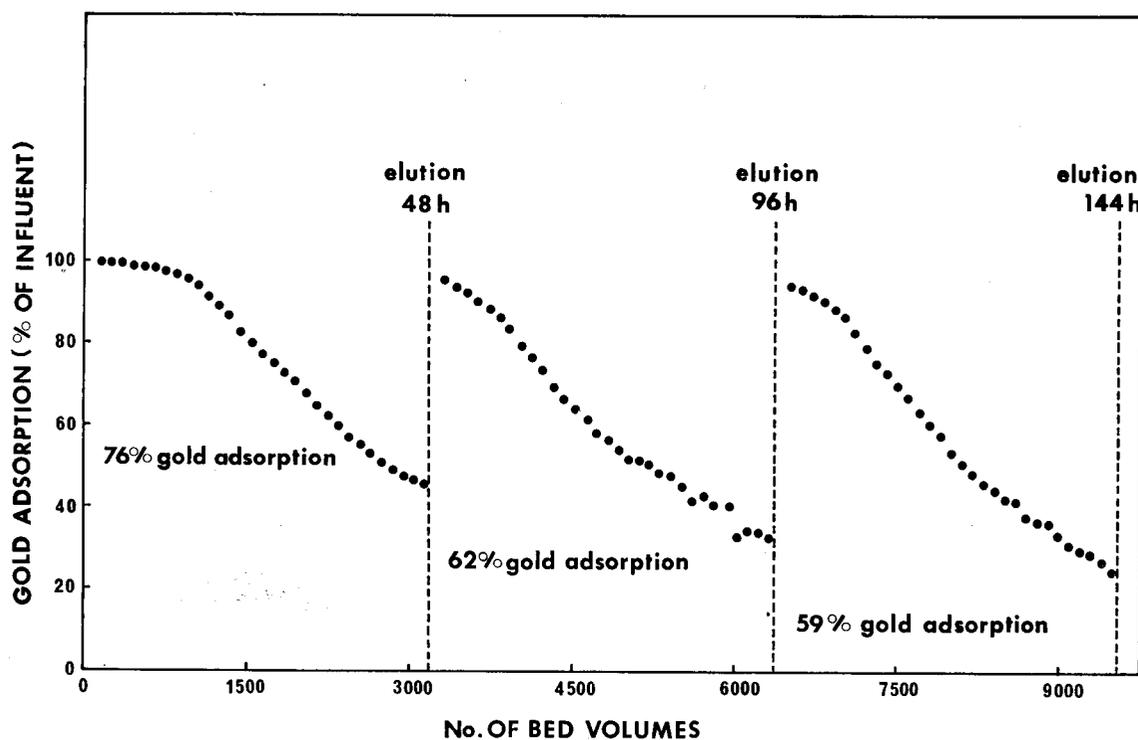


Fig. 14—The adsorption of gold in the first column of a merry-go-round circuit operating at 66 bed volumes per hour

TABLE V

THE OPERATION OF A MERRY-GO-ROUND ACTIVATED-CARBON ADSORPTION CIRCUIT AT AN INFLUENT FLOWRATE OF 66 BED VOLUMES PER HOUR

(Superficial flow velocity = 0,64 m/min)

Column sequence	Total number of bed volumes passed/operational time, h	Effluent from second column (daily average concentration)		Effluent from last column (daily average concentration)	
		g/t Au	g/t Ag	g/t Au	g/t Ag
D—E—F	1590/0-24	0,0020	< 0,001	0,0015	< 0,001
D—E—F	3180/24-48	0,0220	0,014	0,0005	< 0,001
E—F—G	4770/48-72	0,0024	0,005	0,0005	< 0,001
E—F—G	6360/72-96	0,0709	0,032	0,0005	< 0,001
F—G—H	7950/96-120	0,0034	0,002	0,0008	< 0,001
Average effluent values for 6 days		0,0279	0,016	0,0008	< 0,001

TABLE VI
THE ELUTION OF LOADED CARBON FOLLOWING A 48h ADSORPTION CYCLE AT 66 BED VOLUMES PER HOUR
ELUTION OF COLUMN D

Constituents	No. of bed volumes of eluate (1 bed volume = 166,6 ml)										Total mass mg	Carbon loading* g/100g C
	0,600	1,483	2,341	3,199	4,095	4,953	5,811	6,669	7,591			
Au (g/t)	308	1701	7134	6147	2415	764	194	33	5,70	1877	4,94	
Ag (mg)	21,56	175,20	713,40	614,70	252,37	76,40	19,40	3,30	0,61	19,40	0,12	
Ag (g/t)	79	1598	1104	64	69	10	17	0,12	0,10	297	0,78	
Ag (mg)	5,53	164,59	110,40	6,40	7,21	1,00	1,70	0,01	<1	2221	5,84	
Cu (g/t)	1800	20200	130	11	2	1	1	1	<0,1	694	1,83	
Cu (mg)	126,0	2080,6	13,0	1,1	0,2	0,1	0,1	0,1	<0,1	3	0,01	
Ni (g/t)	1900	5300	150	1	<1	<1	<1	<1	<1	45	0,12	
Ni (mg)	133,0	545,9	15,0	0,1	<0,1	<0,1	<0,1	<0,1	<0,1	37	0,10	
Fe (g/t)	12	20	1	<1	<1	<1	<1	<1	<1	89	> 0,23	
Fe (mg)	0,8	2,1	0,1	<0,1	<0,1	<0,1	<0,1	<0,1	<0,1	0,60	0,002	
Zn (g/t)	9	420	10	1	<1	<1	<1	<1	<1			
Zn (mg)	0,6	43,3	1,0	0,1	<0,1	<0,1	<0,1	<0,1	<0,1			
Ca (g/t)	340	110	10	2	2	2	2	4	5			
Ca (mg)	23,8	10,7	1,0	0,2	0,2	0,2	0,2	0,4	0,5			
SiO ₂ (g/t)	120	350	110	70	70	75	50	45	50			
SiO ₂ (mg)	8,4	34,0	11,0	7,0	7,0	7,5	5,0	4,5	5,4			
Hg (g/t)	0,43	5,46	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	0,02			
Hg (mg)	0,030	0,001	<0,001	<0,001	<0,001	<0,001	<0,001	0,003	0,002			
S ₂ O ₃ ²⁻ (g/t)	560	<1	33	28	17	24	13	6,2	8,9			
CNS ⁻ (g/t)	4650	4720	22	7,2	8,1	5,3	3,1	4,3	2,1			

ELUTION RECOVERY (COLUMN D)			
Element	Carbon loading (g/t)	Eluted carbon (g/t)	Recovery (%)
Gold	49400	40	99,9
Silver	7800	33	99,6

*On the assumption of complete elution except for Au, Ag, and SiO₂

is noteworthy. When these carbon loadings are compared with earlier loadings (see above), the marked decrease in zinc concentration (from 13 kg/t to 1 kg/t) would suggest that only zinc has been replaced on the carbon surface to any significant degree by other adsorbed metal species.

Carbon fouling

It had been established previously⁹ (in experiments similar to those described above) that little or no build-up of metal values or silica on activated carbon results from the repeated use of the carbon in treating conventional plant solutions. However, there remains the possibility of incurring a build-up of calcium sulphate in the present instance. Calcium analyses of the eluted carbon samples are presented in Table VII. These, however, suggest that while a little fouling by calcium sulphate may take place when the pH of the influent solution is 5,0, little or no fouling takes place when the influent pH is lowered to 4,3. This marginal lowering of the influent pH from 5,0 to 4,3, resulting in a considerable decrease in the calcium content of the eluted carbon, may correspond to the formation of soluble calcium bisulphate, rather than the more insoluble calcium sulphate. This small build-up of calcium can be significant and would require careful monitoring in any future investigation.

TABLE VII

THE DETERMINATION OF CALCIUM ON SAMPLES OF ELUTED CARBON

Column sample	Influent pH	Calcium content, g/t
Original carbon equilibrated at pH 5,0		500
A	5,0	4180
B	5,0	4200
C	5,0	4580
D	4,3	1450
E	4,3	1630
F	4,3	2370

Discussion

The results presented indicate that the effect of pH on the rate of gold adsorption and on the capacity of activated carbon to adsorb gold is certainly more complex than originally expected. The similarity between the plant solution and the synthetic solution of high ionic strength may have been anticipated, but the rate optima displayed at pH 5 and below 1 are difficult to explain in terms of a single adsorption mechanism. Likewise, the capacity constant optima are difficult to explain, especially when it is seen that those pH values at which exceptionally high capacity constants were obtained (in the region of pH 3,0 to 3,5) correspond to the pH levels at which exceptionally low rates of gold adsorption were observed. The differences in reaction rates displayed by the plant solution and the synthetic solution of high ionic strength are also noteworthy. The reasons for such a disparity are at this stage only speculative, and further investigations in this direction would appear to be warranted. The increased adsorption of copper as a competing anion at a lower pH level may to some degree explain certain of these observed differences.

The present investigation has demonstrated that significant improvements can be made in the use of activated carbon for the recovery of gold and silver from

gold-plant solutions (containing relatively low concentrations of copper). First, the carbon fouling that was observed both at high pH (due to calcium carbonate) and at low pH (due to copper ferrocyanide slime) is not evident when plant solutions are acidified to pH values between 4 and 5. This aspect, besides increasing the effectiveness of carbon with respect to gold adsorption, has significant operational advantages. Second, significant savings are effected in the sulphuric acid required to acidify to between pH 4 and 5 (and later the lime required to neutralize effluent to pH 8 or higher), when compared with acidification to lower pH values. Acidification to pH 5,3 was found to require the addition of 0,220 kg/t of sulphuric acid (0,55 cent per cubic metre of solution at a sulphuric acid cost of R25 per ton), while adjustment to pH 2,5 required 0,575 kg/t sulphuric acid (1,44 cents per cubic metre of solution). Such costs could be roughly doubled when the subsequent neutralization costs are included. These cost savings resulting from operation at pH 4 to 5 could be made without the sacrifice of gold-adsorption rates. Third, the efficient recovery of silver when adsorption takes place at pH 4 to 5 is a distinct advantage. The recovery of silver at current prices is worth approximately 10 cents per ton of ore treated, and it is therefore important for the silver to be recovered as completely as possible.

When compared with conventional zinc precipitation, the carbon process operated at pH 4 to 5 would appear to have considerable economic merit. If the gold in average plant effluents could be reduced from between 0,01 and 0,02 g/t (conventional circuit) to 0,001 g/t, a saving of 8 to 16 cents per ton of ore treated would result if the gold price is taken as R5000 per kilogram. This alone would correspond to between R16 000 and R32 000 per month on a mine treating 200 000 tons per month. The major operating costs in a carbon circuit of the type described would involve respectively the acidification and neutralization of the plant solutions before and after they were contacted with carbon. This cost is not likely to exceed 2 cents per ton of ore treated. Furthermore, both the lower capital investment for a carbon plant and the lower operating costs would appear to favour such an operation above conventional zinc precipitation. A preliminary costing exercise carried out at the AARL indicated a capital saving of approximately R380 000 for a mine treating 264 000 tons per month, while operating costs were reduced by R210 000 per annum.

From a practical point of view, the present findings indicate a very simple process for the recovery and electrowinning of gold from acidified gold-plant pregnant solutions. Whereas the adsorption of gold from alkaline solutions entails relatively slow adsorption kinetics, resulting in low carbon loadings and longer adsorption cycles, together with calcium carbonate fouling of the carbon, the reverse is true when adsorption is carried out at pH 4 to 5. Not only will very little hold-up of gold occur in such a process, but far more use is made of very much less carbon in a smaller carbon circuit.

Further investigations related to the re-use of the carbon in a continuous merry-go-round circuit, together with more exhaustive modelling exercises, would be required before an economically meaningful case could

be made for the use of carbon rather than zinc for recovering gold in an existing gold plant.

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