The mechanism of gold adsorption on activated charcoal

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SYNOPSIS

The adsorption of gold onto activated charcoal is most dependent on the concentration and character of the 'spectator' cations present in the adsorption medium. In the presence of calcium ions, gold is adsorbed as the calcium aurocyanide complex. The degree to which the aurocyanide complexes are adsorbed follows the series Ca> Mg> H> Li> Na> K, calcium aurocyanide being the most stable complex and potassium aurocyanide the least firmly bound. If a loaded charcoal, where the gold is present as the calcium complex, is treated initially with either sodium carbonate or potassium carbonate solutions, the gold can subsequently be eluted from the charcoal with hot deionized water as either the sodium or the potassium complex respectively. The elution of gold with deionized water appears to be most attractive practically and economically, and has several potential applications in the recovery of gold from dilute solutions.

SAMEVATTING

Die adsorpsie van goud op geaktiveerde houtskool hang in 'n groot mate af van die konsentrasie en aard van die „toeskouerkatione" wat in die adsorpsiemiddel aanwesig is. In die aanwesigheid van kalsium-ione word goud as die kalsiumgoudsianiedkomplekse geadsorbeer, volg die serie Ca> Mg> H> Li> Na> K. Die kalsiumgoud-sianied is die mees stabiele kompleks terwyl kalsiumgoudsianied die minste stabiel is. As 'n belaste houtskool, waar die goud as die kalsiumkompleks teenwoordig is, aanvanklik met natriumkarbonaat- of kaliumkarbonaat-oplossings behandel word, kan die goud later met warm gedeioniseerde water as onderskeidelik die natrium- of die kaliumkompleks uit die houtskool gewas word. Die uitwassing van goud met gedeioniseerde water lyk prakties en ekonomies baie belowend en het verskeie moontlike gebruike by die herwinning van goud uit verdunde oplossings.

INTRODUCTION

Activated carbon has been used in purification schemes for centuries because of its remarkable adsorption properties. While these properties are certainly related to the porous nature of the carbon, the detailed mechanism of adsorption remains rather speculative at the present time. In the case of non-electrolytes, physical or 'specific' adsorption[1] takes place at the solid-liquid interface, whereas with electrolytes a chemical or 'non-specific' adsorption takes place in the electrical double-layer surrounding each carbon surface.

It has been proposed[1] that active carbon behaves like a gas (oxygen) electrode in which irreversibly fixed molecular oxygen reacts with the surface of the carbon to form a surface complex or functional group that is sufficiently active to cause the oxidation of water as follows:

$$C_xO + H_2O \longrightarrow C_x^{2+} + 2OH^-.$$
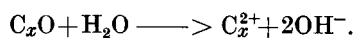
The presence of such charged sites on the carbon surface, together with the nature of the surrounding electrical double-layer, does explain, at least qualitatively, many of the

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observed influences affecting the adsorption of certain charged ions. The present study is confined to some of the factors influencing the adsorption of gold onto activated charcoal as the aurocyanide anion. The motivation behind such a fundamental study is threefold: (a) as a means of optimizing the conditions of gold recovery in actual practice, (b) to assess quantitatively the selection of charcoals suitable for gold recovery, and (c) to provide a means of assessing the activity of regenerated charcoals. A literature survey of the above requirements revealed very little relevant information.

It has been amply demonstrated that, even on a commercial scale, activated charcoal is a most efficient and selective scavenger for gold from gold-plant effluents, the major problem to date being the recovery of the gold from the loaded charcoal to allow re-use of the latter. Methods involving expensive and hazardous reagents such as sodium sulphide/sodium sulphite/sodium hydroxide[2], boiling sodium cyanide/sodium hydroxide[3], pressure leaching at 150°C with sodium cyanide/sodium hydroxide[4], and anhydrous ammonia[5], have all been used but have not yet proved to be attractive. This has perhaps inhibited the wider use of activated charcoal as a means

for the economic concentration of gold from dilute cyanide solutions.

The present investigation has demonstrated the critical role played by both the character and concentration of the 'spectator' cations in effecting gold adsorption and, consequently, the feasibility of using hot deionized water as an efficient eluant in the recovery of gold from activated charcoal.

EXPERIMENTAL METHOD

Type G210 granulated coconut-shell charcoal (0,5 to 2 mm) supplied by Le Carbone SA (Pty) Ltd was used throughout the present investigation. All other chemicals used were of C.P. grade.

Gold Adsorption

The gold capacity of activated charcoal was evaluated as follows. A given weight of the air-dry charcoal was shaken with 100 ml of an approximately 100 p.p.m. solution of potassium aurocyanide for 17 hours under ambient conditions, the slurry was filtered through Whatman No. 540 filter paper, and the filtrate was analysed for gold.

The degree of gold adsorption occurring at equilibrium was measured using the empirical Freundlich Isotherm. The curve obtained by plotting the amount of solute adsorbed per unit mass of adsorbent against residual solute
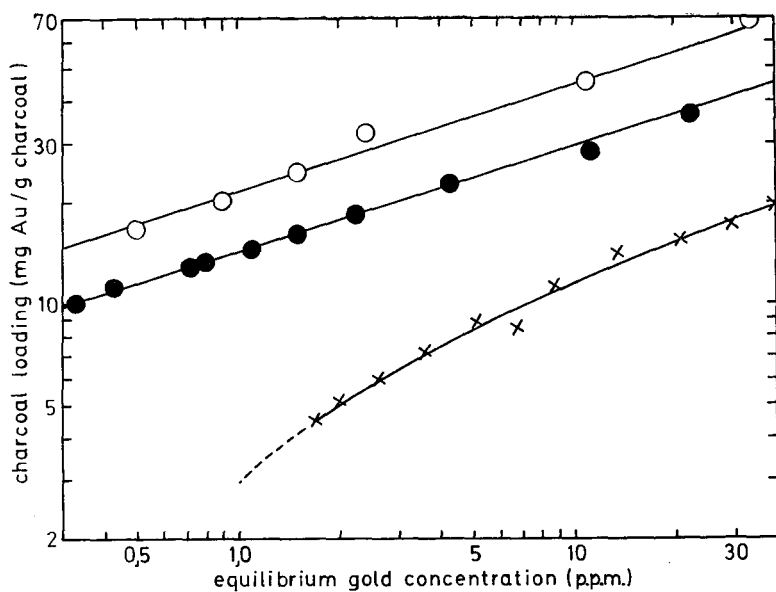
Fig. I—The effect of ionic strength on the adsorption of gold at pH 10 (○ 0,2M boric acid/0,2M potassium chloride/sodium hydroxide buffer solution, ● municipal tap water, ✕ deionized water)

the charcoal, deionized water was pumped through the column, and the subsequent eluate fractions were analysed. A high-quality deionized water was used in the present study (conductivity ca 1500 μS/m, Na 0,5 p.p.m., K 0,2 p.p.m., Ca 0,15 p.p.m., Mg 0,01 p.p.m.).

FACTORS AFFECTING GOLD ADSORPTION

Effect of Ionic Strength on Gold Adsorption

Early attempts using tap water, and finally deionized water, to reproduce adsorption isotherms under conditions of constant pH and temperature proved futile. Good reproducibility was, however, achieved in a strong 0,2 M boric acid/0,2 M potassium chloride/ sodium hydroxide buffer solution (pH 10,0). Fig. 1 illustrates a wide divergence of capacity constants, k, although the n values remain virtually constant at 3,2. A progressive increase in k values from 5 mg/g with deionized water to 22 mg/g in the standard boric buffer solution suggested that the ionic strength of the adsorption medium played some important role in the adsorption
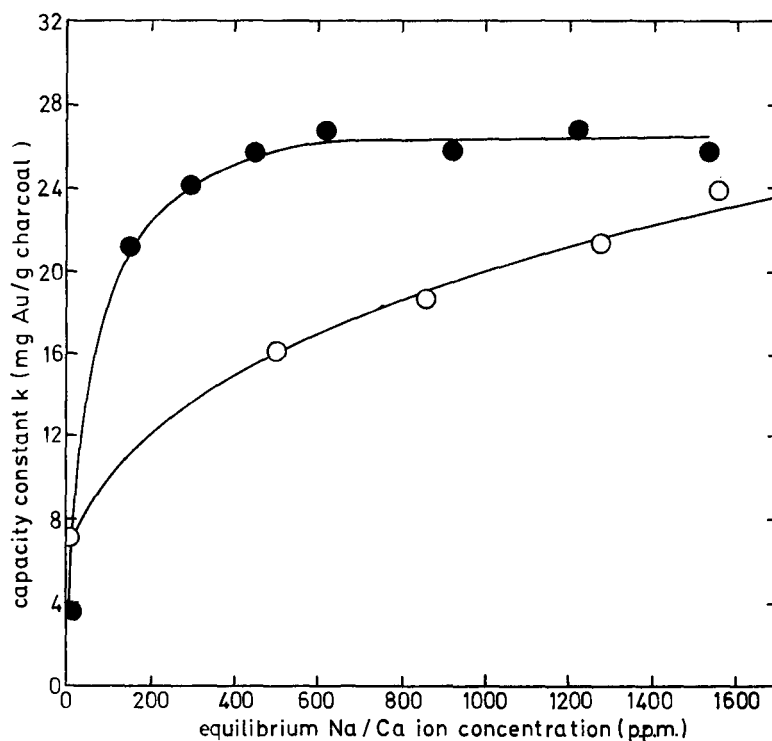
concentration at a given temperature results in an isotherm equilibrium curve (the mass of the adsorbent is assumed to be proportional to its surface area). By the Freundlich isotherm relationship,

$$\frac{X}{M} = kc^{1/n},$$

where X=mass of solute adsorbed or removed from solution,
M=mass of adsorbent,
c=concentration of solute remaining in solution, and

k,n are constants, k being a measure of the fundamental effectiveness of the adsorbent, and n a measure of the change in rate of effectiveness with relative dosage.

The Freundlich equation was found to describe the mechanics of gold adsorption on activated charcoal more accurately than the more theoretical Langmuir equation.

Reaction Rates

Data on adsorption reaction rates were obtained from a given weight of air-dried charcoal that had been shaken with 100 ml of an approximately 100 p.p.m. solution of potassium aurocyanide for a given time interval before filtration and analysis. The pH of the adsorption medium was adjusted by the addition of 0,1N sodium hydroxide or

0,1N hydrochloric acid as required.
Gold Elution

15 g of air-dried loaded charcoal (ca 0,5 % Au) was placed in an oil-jacketed chromatography column (0,9 cm internal diameter by 40 cm) in series with an LKB 17000 Minirac fraction collector. After wetting back

Fig. 2—The effect of sodium and calcium ions on the adsorption of gold at pH 7,2 (● Ca^{2+} added as calcium chloride ○ Na^{+} added as sodium chloride)

mechanism. The mechanism was thought to involve stabilizing the charge on the relatively large aurocyanide anion by means of a complementary small cation, indicating the important role played by 'spectator' cations comprising the charged electrical double-layer surrounding charcoal surfaces.

Fig. 2 shows the effect of an increase in the ionic strength of the adsorption medium with sodium and calcium ions, respectively. A very marked increase in the capacity constant, k, of the charcoal can be observed in each instance, although the addition of calcium ions has a far greater effect than the addition of sodium ions. This very large difference in k produced by the presence of sodium and calcium ions cannot be explained in terms of ionic strength alone, and it is considered that the adsorbed calcium aurocyanide complex is, in addition, more stable than the sodium aurocyanide complex.

The influence of excessive additions of calcium ions to the adsorption medium likewise had a noticeable effect on both reaction rates and on adsorption isotherms when compared with the effects produced by the addition of sodium ions. Figs. 3 and 4 illustrate the reaction rates for gold adsorption at various pH levels (3 to 11) obtained in the presence of excess sodium and calcium ions respectively. It can be seen that the addition of 1000 p.p.m. of calcium ions has a greater influence on the kinetics of gold adsorption than does the presence of 2000 p.p.m. of sodium ions.

Fig. 5 illustrates the equilibrium adsorption isotherms obtained at pH 10 for gold solutions in various ionic media in contact with activated charcoal. Both the capacity constant, k, and the slope ($n=3,2$) for the isotherm carried out in the presence of excess sodium ions (graph O in Fig. 5) were typical of solutions containing only sodium and potassium cations. Results were easily reproducible, and the adsorption of gold was found to obey the Freundlich equation between equilibrium concentrations 0,01 to 100 p.p.m. of gold. Conversely, gold
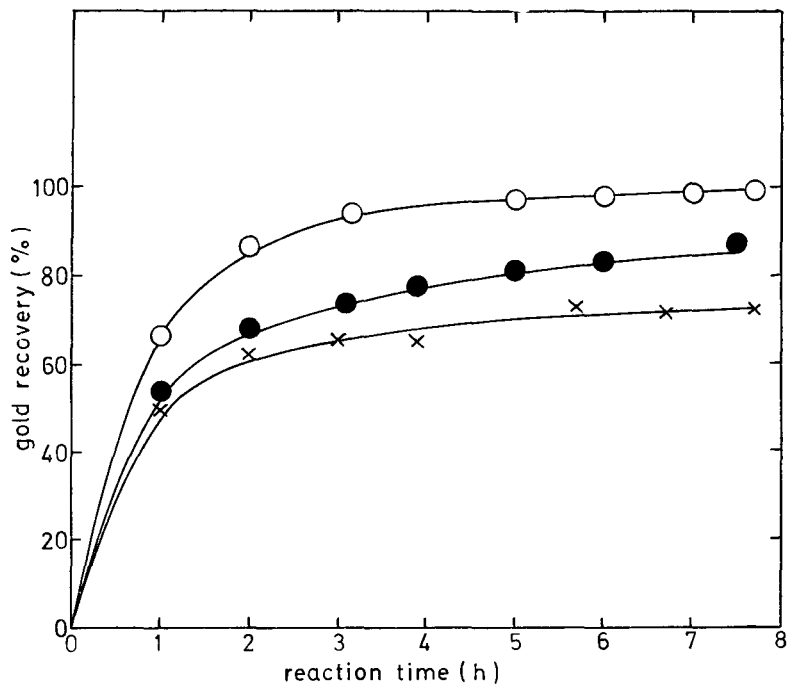

Fig. 3—The effect of pH on reaction rates in the presence of 2000 p.p.m. of sodium added as sodium chloride
(O pH 3,3, ● pH 7,4, × pH 11,3)
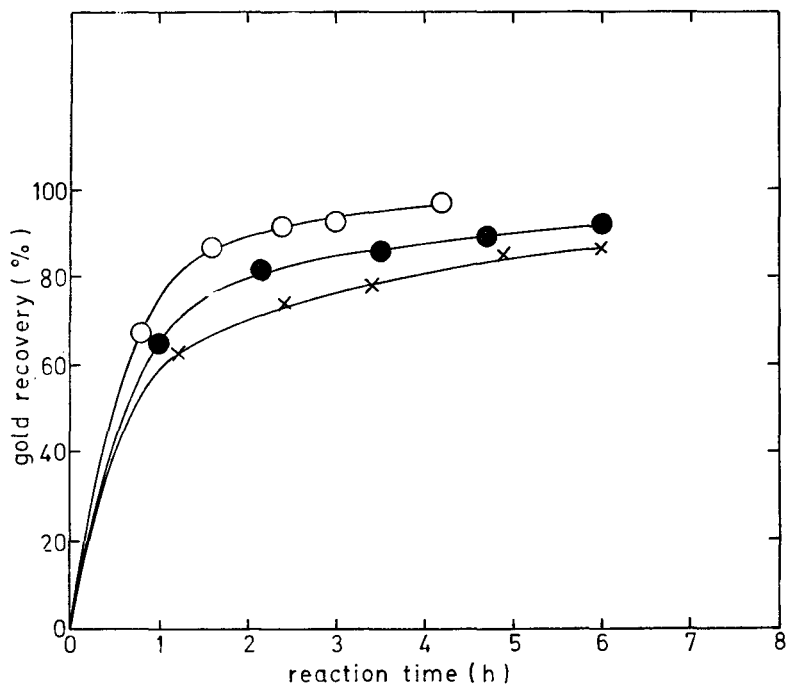

Fig. 4—The effect of pH on reaction rates in the presence of 1000 p.p.m. of calcium added as calcium chloride
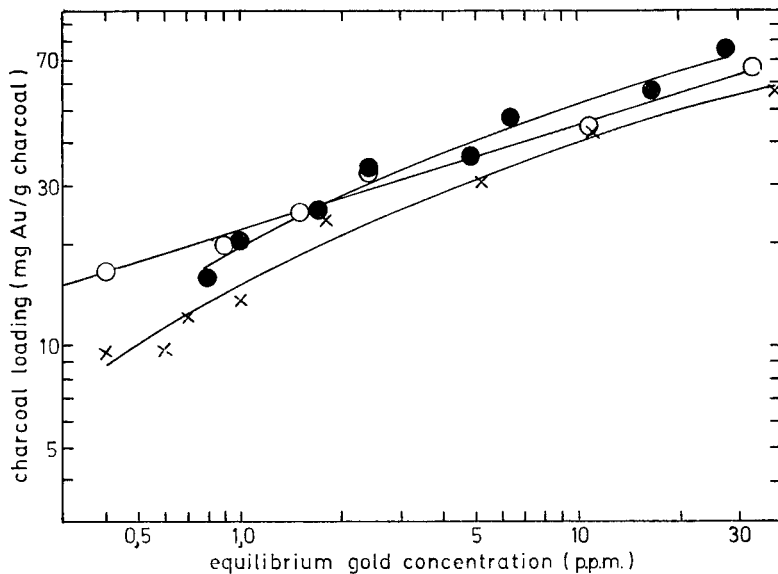(O pH 3,1, ● pH 7,2, × pH 10,6)

Fig. 5—The effect of the ionic media on the adsorption of gold at pH 10
(O 0,2M boric acid/0,2M potassium chloride/sodium hydroxide buffer solution,
● 1000 p.p.m. Ca²⁺ added as calcium chloride,
× gold-plant effluent)

adsorption carried out in the presence of excess calcium ions (graphs ● and × in Fig. 5) yielded poor reproducibility, the isotherm resulting in a different value for n ($n \approx 2$) and not displaying a linear log-log relationship. The similarity between the isotherm obtained in the presence of 1000 p.p.m. of calcium ions and that obtained with gold-plant effluent to which potassium aurocyanide had been added should be noted.

Effect of pH on Gold Adsorption

Because both hydrogen and hydroxide ions tend to be adsorbed fairly strongly by activated carbons, the adsorption of other ions is influenced to a considerable extent by the pH of the solution medium. Fig. 6 shows the effect of pH on the adsorption capacity of activated charcoal for gold in the presence of 2000 p.p.m. of sodium ions added as sodium chloride. The pH was adjusted by the addition of either sodium hydroxide or hydrochloric acid to the system. An increase in the capacity constant, k, from 18 mg/g at pH 10 to 44 mg/g at pH 4 should be noted. This observed decrease in k at higher pH values can be expected if it is considered that both the hydroxide and aurocyanide anions are competing for active adsorption sites on the char-

coal surface. Likewise, the reaction rates of gold adsorption were found to increase considerably when the pH of the adsorption medium was lowered (Figs. 3 and 4).

Effect of Temperature on Gold Adsorption

Being an exothermic reaction, adsorption tends to increase with decreasing temperature. The energy changes accompanying adsorption are usually very small, and thus

small ambient variations in temperature tend not to alter the adsorption process to any significant extent. Studies of equilibrium gold adsorption carried out under isothermal conditions in a strong boric acid/potassium chloride/sodium hydroxide buffer solution at pH 10 as a function of temperature (20 to 30 °C) indicated a linear variation in the capacity constant, k, of only 0,3 mg/g/°C.

Because earlier findings had demonstrated that gold adsorption was most dependent on both the concentration and character of the 'spectator' cations present in the adsorption medium, the use of deionized water was immediately suggested as an eluant for the subsequent recovery of gold from activated charcoal. Studies of equilibrium adsorption carried out under ambient conditions (22 °C) with deionized water yielded a capacity constant, k, of 5 mg/g, which was significantly less than the values observed at higher ionic strengths (Fig. 1), where k was 22 mg/g. This effect when deionized water is used can be expected to be greatly magnified at elevated temperatures. Fig. 7 illustrates the equilibrium isotherm for gold adsorption carried out at 94 °C (refluxed at the boil for 7 hours) with deionized water. A
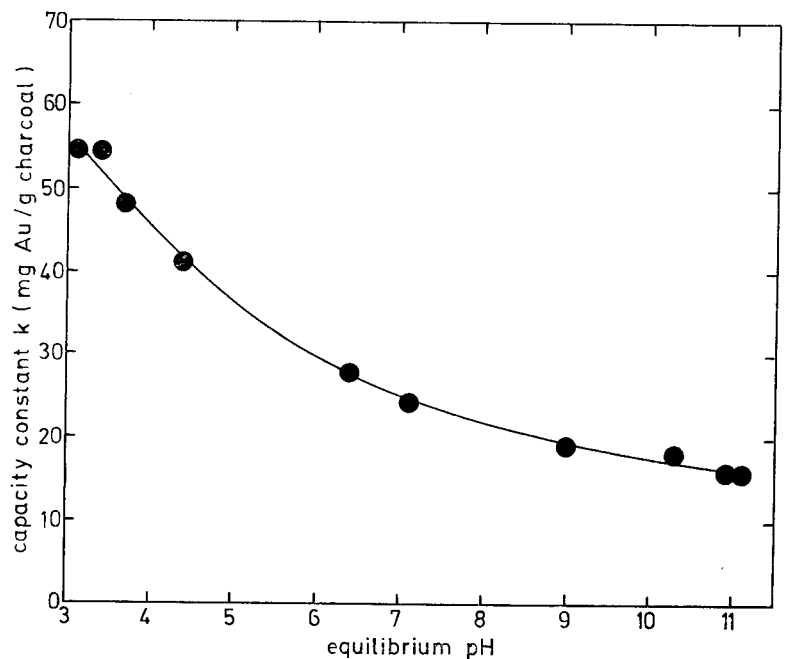

Fig. 6—The effect of pH on the adsorption of gold in the presence of 2000 p.p.m. of sodium

capacity constant, k, of only 0,13 mg/g was obtained. It can also be noted that concentrations of sodium and potassium ions in solution increased progressively to 5 and 40 p.p.m. respectively as larger amounts of charcoal were used. The increase was attributed to the leaching of impurities from the original charcoal (see Table I).

The above findings suggested the use of hot deionized water as an eluant in the recovery of gold from activated charcoal. Further investigation was confined to a demonstration that such a possibility did in fact exist.

ELUTION OF GOLD FROM ACTIVATED CHARCOAL WITH DEIONIZED WATER

Elution from Charcoal Loaded with Potassium Aurocyanide

Activated charcoal was loaded to 0,63 per cent gold by being shaken in a solution of potassium aurocyanide and then being air-dried prior to use. The subsequent elution of the loaded charcoal at a flow velocity of 2,4 cm/min and 90 °C with deionized water as eluant yielded a gold recovery of 43 per cent in 21 bed volumes (Fig. 8).
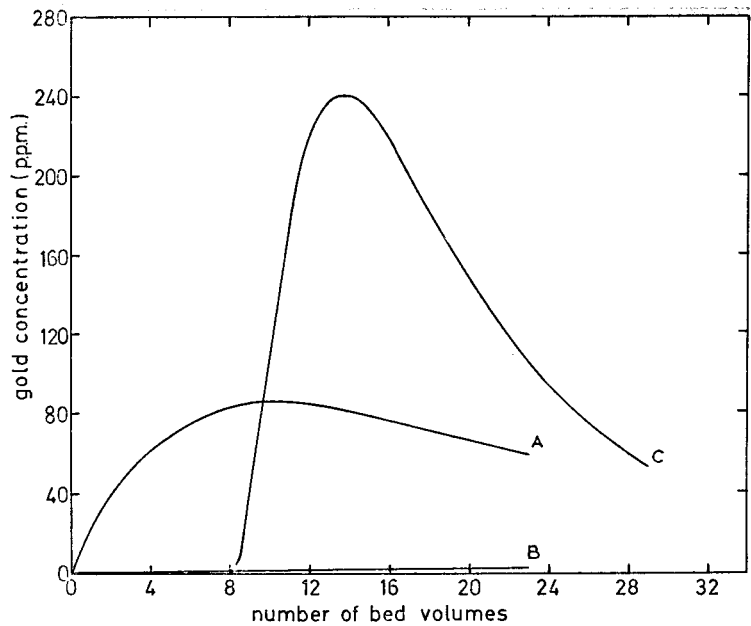
In a similar exercise, the loaded

Fig. 8—The elution of charcoal loaded with potassium aurocyanide (0,63 per cent Au) at 90°C using deionized water
A no carbonate pretreatment
B pretreated with 5 per cent calcium chloride
C pretreated with 10 per cent sodium carbonate)

charcoal was soaked in a 5 per cent calcium chloride solution overnight before being washed and eluted at 90 °C as above. After elution with 22 bed volumes, a recovery of only 1 per cent gold was recorded (Fig. 8).

The same charcoal sample was then treated with 8 bed volumes of a 10 per cent sodium carbonate solution at 50 °C before being eluted with deionized water at 90 °C. A gold recovery of 80 per cent in 21 bed volumes of deionized water was recorded (Fig. 8).

Elution from Charcoal Loaded from Gold-plant Effluent

Activated charcoal was loaded to 0,33 per cent gold from a gold-plant effluent containing ca 0,1 p.p.m. of gold. Table I, which compares the composition of the original charcoal with that of the loaded charcoal, shows that there was a large increase in the calcium content of the loaded charcoal.

The elution of the above loaded charcoal, when only deionized water at 90 °C was used, yielded a gold recovery of only 2 per cent in 8 bed volumes.

Samples of the loaded charcoal were then each pretreated, before elution at 90 °C, with 8 bed volumes of the following reagents at 50 °C with deionized water as before: 10 per cent potassium carbonate, 10 per cent sodium carbonate, 1,5 per cent lithium carbonate (saturated solution), 10 per cent ammonium carbonate, and 10 per cent sodium chloride.
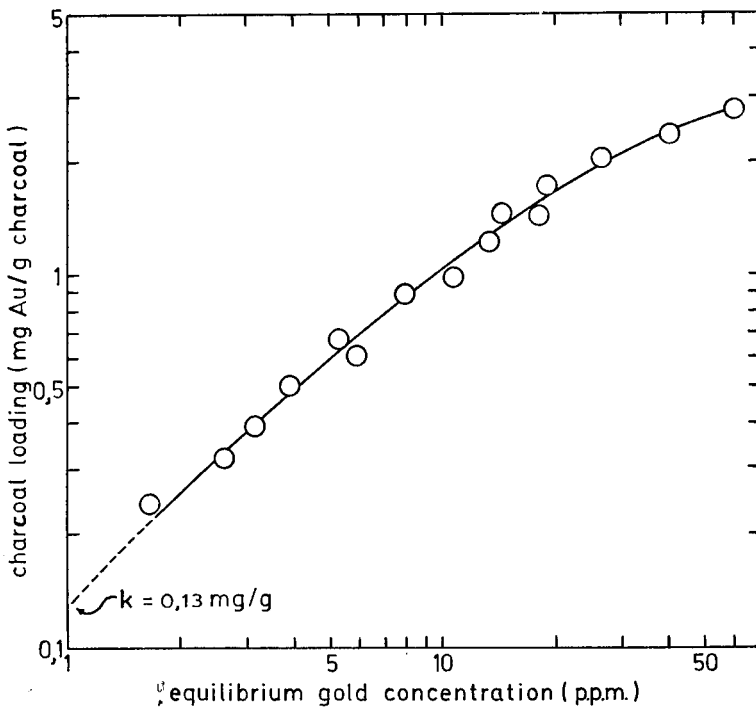
Fig. 7—The equilibrium adsorption isotherm for gold adsorption at 94°C using deionized water

TABLE I

THE COMPOSITION OF ACTIVATED CHARCOAL LOADED TO 0,3 PER CENT GOLD FROM GOLD-PLANT EFFLUENT

Element	Original charcoal p.p.m.	Loaded charcoal p.p.m.	Acid-washed loaded charcoal p.p.m.
Na	18 500	4 500	—
K	10 400	1 900	—
Ca	640	4 800	410
Mg	300	100	—
Au	0	3 300	3 500
Ag	< 10	45	25
Fe	1 500	1 500	1 600
Ni	10	2 500	290
Cu	20	240	170
Co	4	2	—
Zn	120	380	80

The semi-quantitative spectrographic analysis, reported in p.p.m., for the loaded charcoal is as follows:
Sr 30, Bi < 5, Pb 10, Sb < 10, Sn 5, Y < 10, Be < 0,1, Mo < 10, Nb < 1000, La < 100, V 10, Zr 10, Cd < 5, Ti 50, Al 100, Ba < 100, Ge < 5, Si 300, Cr < 50, Mn 10, B 10, As 100

Fig. 9 illustrates the resulting elution patterns, which indicate that only potassium, lithium, and sodium carbonate have any significant effect on the subsequent elution of gold. The gold recovery was 84 per cent in 20 bed volumes of deionized water when 10 per cent potassium carbonate was used.

In a similar exercise, a sample of loaded charcoal was eluted with 4 bed volumes of 5 per cent potassium carbonate at 50 °C, followed by elution with deionized water at 90 °C, the flow velocity being maintained at 0,74 cm/min. The subsequent analysis of the eluate fractions (Table II) indicates the simultaneous elution of gold and silver in the form of their potassium cyanide complexes, together with the elution of nickel and copper. The antipathetic relationship between gold and silver with respect to calcium and magnesium is striking, indicating that gold does not elute as a calcium or magnesium aurocyanide under such conditions.

Effect of Acid Pretreatment on Charcoal Loaded from Gold-plant Effluent

A sample of charcoal loaded from a gold-plant effluent was acid-washed by means of continuous elution overnight with 2,5 per cent (v/v) nitric acid/2,5 per cent (v/v) hydrochloric acid in order to remove the majority of the adsorbed elements (see Table I). No gold was eluted during this process.

The charcoal was then eluted with 4 bed volumes of 5 per cent potassium carbonate at 50 °C, followed by 23 bed volumes of deionized water at 90 °C, a flow velocity of 0,74 cm/min being maintained throughout the elution. A gold recovery of only 47 per cent was recorded, which can be compared with a recovery of 91 per cent achieved in the elution, under similar conditions, of charcoal that had not been washed in acid. A considerably reduced gold recovery can be noted.

A sample of the acid-washed

TABLE II

THE CONTINUOUS ELUTION OF VARIOUS ADSORBED ELEMENTS FROM ACTIVATED CHARCOAL LOADED FROM GOLD-PLANT EFFLUENT

Elution volume ml	K p.p.m.	Na p.p.m.	Ca p.p.m.	Mg p.p.m.	Au p.p.m.	Ag p.p.m.	Fe p.p.m.	Ni p.p.m.	Cu p.p.m.	Co p.p.m.	Zn p.p.m.
19	16 000	200	4,6	0,8	1,3	< 1	5	9	2	< 1	3
39	22 000	41	2,8	0,6	1,5		3	11	1		5
60	24 000	25	2,0	0,6	1,6		2	14	2		5
80	24 000	23	1,8	< 0,5	1,8		2	17	3		5
100	25 000	22	1,8		2,0		2	18	4		5
121	20 000	22	< 0,5		28	—	2	—	—	—	—
141	2 700	5			96	12	< 1	860	35	< 1	5
160	660	5			144	16		200	12		2
179	660	5			185	13		60	6		2
198	510	6			213	9		20	5		1
217	400	6			235	6		11	3		< 1
236	340	6			228	3		7	2		
255	290	6			209	2		4	2		
275	260	7	1,0		192	1		3	2		
293	240	7	1,0		170	1		2	1		
312	220	7	0,8		145	1		2	1		
332	180	7	0,8		121	1		1	1		
349	160	7	0,8		92	< 1		1	1		
370	130	8	1,0		82			1	1		
389	100	8	1,2		65			1	1		
440	108	8	1,2		52			1	1		
423	83	8	1,2		39			1	< 1		
442	73	9	1,6		29			1			
461	57	8	2,4		20			1			
480	41	8	3,6		13,3			1			
498	30	6	6,6		9,1			1			
517	17,6	6	10,0	0,6	7,0			< 1			
536	10,4	5	12,0	0,6	5,8						
555	6,9	5	13,0	0,6	5,1						
575	4,7	5	13,8	0,8	4,8						

NOTE:
1. Fractions of 0 to 100 ml were eluted with 5 per cent K_2CO_3 at 50 °C.
2. Fractions of 100 to 575 ml were eluted with deionized water at 90 °C.
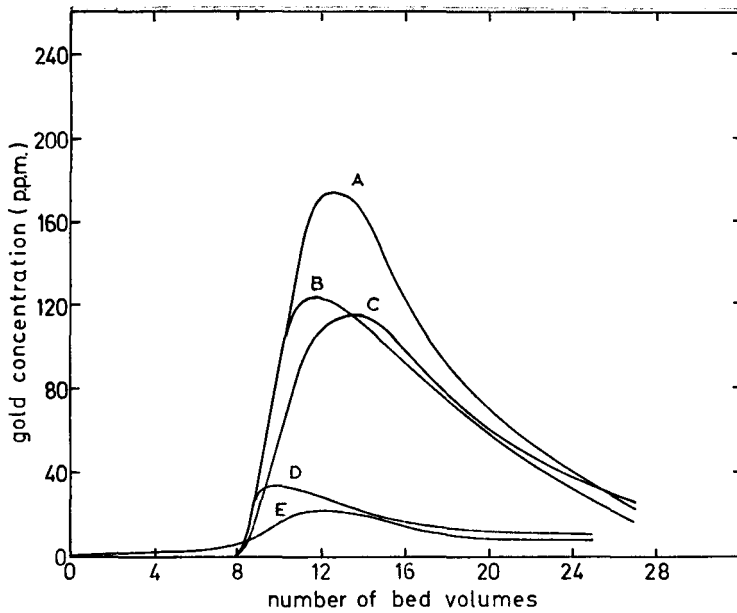3. 25 ml = 1 bed volume.

Fig. 9—The elution of loaded charcoal (0,33 per cent Au) at 90 °C using a carbonate pretreatment at 50 °C
(A pretreatment 10 per cent potassium carbonate, gold recovery 84 per cent
B pretreatment 1,5 per cent lithium carbonate, gold recovery 68 per cent
C pretreatment 10 per cent sodium carbonate, gold recovery 60 per cent
D pretreatment 10 per cent ammonium carbonate, gold recovery 18 per cent
E pretreatment 10 per cent sodium chloride, gold recovery 12 per cent)
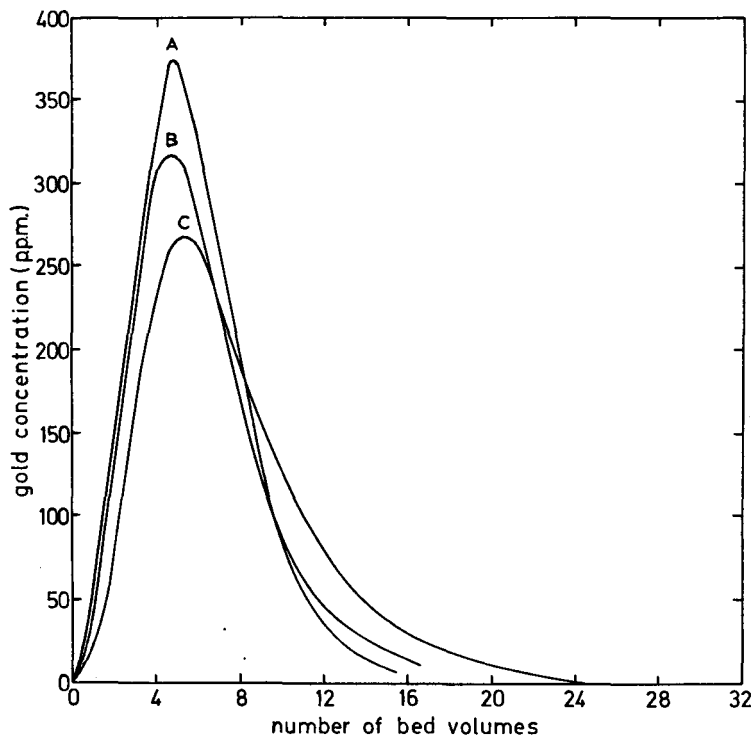

Fig. 10—The effect of flow velocities on the elution of gold at 90 °C using deionizd water
(A eluted at 0,18 cm/min, B eluted at 0,45 cm/min, C eluted at 0,72 cm/min)

charcoal was then eluted as above, save for the pretreatment stage, where a 5 per cent potassium carbonate/3 per cent potassium hydroxide solution was used, instead of the 5 per cent potassium carbonate solution. A subsequent gold recovery of 87 per cent in 16 bed volumes of deionized water was obtained, indicating the important role played by the potassium hydroxide in effecting gold elution under the prescribed conditions.

Optimization of the Carbonate Pretreatment

Initially, the application of 8 bed volumes of 10 per cent potassium carbonate eluted at 50 °C resulted in good gold recoveries from charcoal loaded from gold-plant effluent. During the course of the investigation, the temperatures of pretreatment were raised to 90 °C, and the carbonate treatment was limited to ca $\frac{1}{2}$ bed volume (the dry loaded charcoal was placed in the column before 12 ml of the carbonate solution was pumped in, and then the saturated charcoal was allowed to stand for 2 hours before being eluted with water). Potassium hydroxide was also added to the pretreatment solution with beneficial results.

Table III summarizes the gold recoveries obtained as a function of the potassium carbonate treatment used. Gold recoveries were highest when a 5 per cent potassium carbonate/10 per cent potassium hydroxide solution was used in a continuous elution procedure.

Effect of Flowrates

Fig. 10 illustrates the effect of decreasing the flowrate of the eluant using a 3 per cent potassium carbonate/1 per cent potassium hydroxide pretreatment as indicated in Table III. The sharper elution patterns obtained as flow velocities decreased from 0,74 to 0,20 cm/min suggest that the kinetics of gold desorption are diffusion controlled under the prescribed conditions.

Gold Elution at Higher Temperatures

As is to be expected, the elution of gold from activated charcoal is greatly enhanced at higher temperatures, affording the use of faster flowrates and thus shorter elution times, as well as yielding more-concentrated gold eluates.

Fig. 11 shows the elution of gold

TABLE III

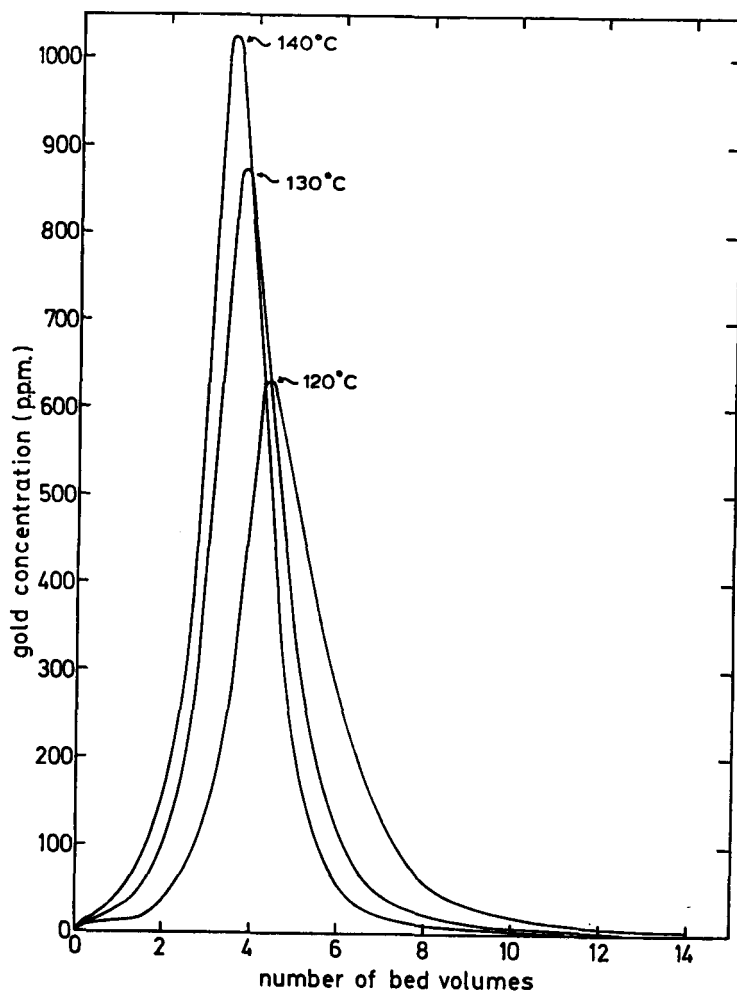| Pretreatment	Flow velocity cm/min	No. of bed volumes (carbonate pretreat-ment)	Temp. of pretreat-ment °C	Temp. of elution °C	Gold recovery
1% K_2CO_3	2,37	4	50	90	70% in 24 bed vol.
5% K_2CO_3	0,74	8	50	90	91% in 19 bed vol.
10% K_2CO_3	2,37	8	50	90	48% in 20 bed vol.
0,5% K_2CO_3+ 0,5% KOH	0,74	ca $\frac{1}{2}$	90	90	35% in 24 bed vol.
1% K_2CO_3+ 1% KOH	0,74	ca $\frac{1}{2}$	90	90	73% in 16 bed vol. 82% in 24 bed vol.
3% K_2CO_3+ 1% KOH	0,74	ca $\frac{1}{2}$	90	90	88% in 16 bed vol. 93% in 24 bed vol.
5% K_2CO_3+ 3% KOH	0,74	ca $\frac{1}{2}$	90	90	96% in 16 bed vol. 98% in 25 bed vol.
5% K_2CO_3+ 3% KOH	0,74	1	90	90	98% in 16 bed vol. 99% in 25 bed vol.
10% K_2CO_3+ 5% KOH	0,74	1	90	90	94% in 7 bed vol. 98% in 12 bed vol. 99% in 24 bed vol.
5% K_2CO_3+ 10% KOH	0,74	1	90	90	94% in 7 bed vol. 99% in 12 bed vol. 100% in 22 bed vol.

Fig. II—The effect of temperature on the elution of gold at a flow velocity of 3,6 cm/min

at 120 to 140 °C carried out at 3 to 4 bar using a 1 bed volume pretreatment of a 10 per cent potassium carbonate/5 per cent potassium hydroxide solution and eluting at a flow velocity of 3,5 cm/min. Elution at 140 °C can be seen to yield a gold recovery of 95 per cent in 10 bed volumes, the complete elution taking 1,9 hours and yielding an eluate averaging 200 p.p.m. of gold. Alternatively, by use of selective elution, a 91 per cent recovery of gold can be obtained in an eluate averaging 500 p.p.m. of gold.

Use of Municipal Water as Eluant

While the present study on elution has been confined to the use of a high-quality deionized water, the presence of relatively high concentrations of potassium in the eluate (Table III) suggest that suitably softened municipal water can be used as eluant. In comparative elution studies carried out at 90 °C with 5 per cent potassium carbonate/3 per cent potassium hydroxide as the pretreatment reagent, the following gold recoveries were recorded after elution with 20 bed volumes of different types of water:

97,3 per cent with deionized water,
97,6 per cent with a 'soft' municipal water (25 p.p.m. of calcium),
96,8 per cent with a 'medium' municipal water (103 p.p.m. of calcium),
81,7 per cent with a 'hard' municipal water (234 p.p.m. of calcium), and
93,1 per cent with a 'hard' municipal water suitably softened by the addition of potassium carbonate.

The above study suggests that medium-soft municipal waters can be satisfactorily used as eluants for the elution of gold from charcoal under the prescribed experimental conditions.

Capacity of Regenerated Charcoals

Studies of equilibrium isothermal gold adsorption on charcoal loaded with potassium aurocyanide and subsequently eluted at 90 °C by the prescribed process indicated no decrease in the capacity constant, k, when tested in a boric acid buffer solution containing 100 p.p.m. of gold as potassium aurocyanide. The regeneration of charcoal loaded from

gold-plant effluent does, however, result in a decrease in the activity of the charcoal due to the presence of organic poisons. A soluble yellow organic fraction was, in fact, observed to elute with the otherwise colourless gold eluate. Infrared analysis of this organic fraction strongly suggested the presence of a saponified lubricating oil or grease. As the activity of such regenerated charcoal will almost surely be a function of the time period of initial loading, together with the elution characteristics of such organic poisons, further investigation is required in this direction.

MECHANISM OF GOLD ADSORPTION

The investigation into the effects of sodium chloride and calcium chloride additions on the subsequent adsorption of gold onto activated charcoal suggested significant differences in the behaviour of the sodium and calcium ions, which were not completely explained in terms of ionic strength alone. While both species considerably aided gold adsorption, calcium additions produced the greatest effects on the charcoal capacity at concentrations well below that of sodium. Likewise, in the presence of an excess of the halide salts, calcium additions resulted in faster reaction rates within the pH range 3 to 11 when compared with sodium. Furthermore, the slopes and shapes of the equilibrium isotherms indicated some difference in the adsorption mechanism when calcium was present as a 'spectator' ion. The formation of a more strongly adsorbed calcium aurocyanide complex would be consistent with these findings.
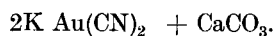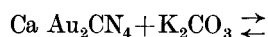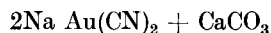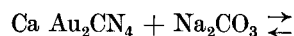
What was most evident, however, was the inability of gold to adsorb in the complete absence of stabilizing cations such as sodium and calcium ions, suggesting the use of deionized water as an eluant for the recovery of gold from loaded charcoal. The adsorption isotherm carried out under reflux had shown this to be a distinct possibility.

Initial attempts to elute gold from charcoal that had been exposed to calcium ions met with no success,

reinforcing the view that the gold was firmly adsorbed as either calcium aurocyanide or hydrogen aurocyanide, depending on the pH of the adsorption medium. Charcoal to which the gold had been added as potassium aurocyanide under neutral pH conditions responded poorly to water elution at 90 °C. A pretreatment with sodium carbonate, however, enhanced the elution significantly. The original adsorption of gold as hydrogen aurocyanide rather than as potassium aurocyanide is suggested, the subsequent addition of sodium carbonate then producing the less firmly adsorbed sodium aurocyanide species:

$$H^+ Au(CN)_2^- + \tfrac{1}{2} Na_2CO_3 \rightleftharpoons$$

$$Na^+ (Au(CN)_2^- + \tfrac{1}{2} H_2CO_3.$$
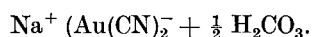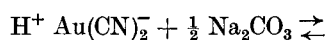
The use of a carbonate pretreatment was then tried on the charcoal loaded from gold-plant effluent that had previously failed to respond to elution with hot deionized water. The good recoveries of gold obtained after such a pretreatment strongly indicated the following reaction mechanism:

$$Ca\ Au_2CN_4 + Na_2CO_3 \rightleftharpoons$$

$$2Na\ Au(CN)_2 + CaCO_3$$

$$Ca\ Au_2CN_4 + K_2CO_3 \rightleftharpoons$$

$$2K\ Au(CN)_2 + CaCO_3.$$

The better recoveries obtained with potassium carbonate imply that potassium aurocyanide is less firmly adsorbed than is sodium aurocyanide.

Further evidence supporting, if not proving, the above mechanism was obtained from the analysis of the eluates for other adsorbed species (Table III). Gold was observed to elute as potassium aurocyanide, being antipathetic to the elution of both calcium and magnesium. Moreover, the analysis of the original loaded charcoal (Table I) strongly suggested the adsorption of gold as the calcium aurocyanide complex.

The acid leaching of loaded charcoal also provided some valuable

information. A potassium carbonate pretreatment followed by water elution yielded a gold recovery of only 47 per cent, indicating either reduction of the loaded gold on the charcoal under such acid conditions (pH approaching 0), or the adsorption of gold as a more firmly held hydrogen aurocyanide complex. That subsequent pretreatment with a potassium carbonate/potassium hydroxide reagent, followed by a water elution, yielded an 89 per cent gold recovery suggests the latter mechanism. While some decomposition of gold to the metallic state (less than 11 per cent) may have taken place, it is nevertheless surprising that total reduction was not effected under such acid conditions.

It thus appears that the degree to which the various cyanide complexes of gold are adsorbed onto surface-active sites (activated charcoal) depends to a very large extent on the character of the complementary cation. Calcium aurocyanide appears to be the most strongly adsorbed complex in the following series:

$$Ca^{2+} > Mg^{2+} > H^+ > Li^+ > Na^+ > K^+.$$
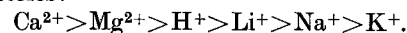
DISCUSSION

The present findings regarding the mechanism of gold adsorption onto surface-active sites immediately emphasizes the important role played by both the calcium cation and the hydroxyl anion. The two species are antipathetic in that high calcium concentrations will favour gold adsorption, while high pH levels will decrease gold adsorption. As such, the findings may have wider ramifications when related to current metallurgical practice where lime is used to maintain pH levels in the cyanidation circuit. The detrimental effect caused by excess calcium[6] may be explained, in part at least, by the adsorption of calcium aurocyanide by gangue materials[7]. As the ionic strength of the adsorption medium has also been shown to play an important role in gold adsorption, the use of foul cyanidation liquors may also be expected to yield poor gold recoveries. The use of sodium hydroxide as a means of maintaining pH levels in the cyanidation circuit is suggested if increased reagent

costs are off-set by higher gold recoveries.

It has been adequately demonstrated that gold can be efficiently eluted from activated charcoal by use of a carbonate pretreatment followed by elution with hot water low in calcium ions. While the efficiency of potassium or sodium carbonate as pretreatment reagents has been shown to be due to the formation of insoluble calcium carbonate, the use of a variety of alkali metal salts producing insoluble calcium compounds may be possible. The use of fluorides, oxalates, and sulphites can be mentioned as examples. On the basis of cost alone, few of these salts can be expected to compete with the use of carbonates. Furthermore, should an excessive build-up occur after repeated use,

calcium carbonate can easily be removed from the charcoal by use of dilute acid.

If the proposed technique is compared with other known methods for the elution of gold from activated charcoal[1-4], it appears that, on the basis of ease of operation, economics, handling of reagents, recovery of gold from pregnant eluate, and overall simplicity, the hot-water process has significant advantages. As the major problem in the elution of gold from activated charcoal has to date been the difficulty involved in the re-use of the charcoal, the development of a simple process using hot water as an eluant immediately enhances the use of activated charcoal as a highly selective ion-exchange medium in the field of gold metallurgy.

ACKNOWLEDGEMENT

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