



The elution of gold from activated carbon at room temperature using sulphide solutions

by M.D. Adams*

Synopsis

One of the main bottle-necks in the carbon-in-pulp process for the recovery of gold is the elution procedure, which typically requires the heating of caustic cyanide eluants to high temperatures for 16 to 24 hours. The present work demonstrates that sodium sulphide solution as an alternative eluant can effect complete elution in about 4 hours at ambient temperatures.

Elution efficiencies of around 100 per cent were obtained in 4 hours with a single pass of eluant containing 0,2 M Na₂S and 0,4 NaOH—about 10 bed-volumes of eluant. The initial rate was slow over the first hour of elution, probably because the activated carbon catalysed the oxidation of sulphide to polysulphide. Elution efficiencies of around 100 per cent were also obtained in less than 4 hours during the batch elution of carbon at liquid-to-solid ratios of about 100. Lower liquid-to-solid ratios resulted in the re-adsorption of gold, probably owing to the oxidation of sulphide to polysulphide, with the resultant formation of gold complexes that were eluted less readily.

Introduction

The carbon-in-pulp (CIP) process is the most widely used method for the recovery of gold in new plants. However, despite the commercial success of the process as a whole, there remains much scope for improvement. One such area is the elution of gold cyanide from loaded carbon. In the Zadra process¹, a hot solution of caustic cyanide (typically comprising about 0,5 per cent NaCN and 1,0 to 2,0 per cent NaOH) is recirculated through an elution column and several electrowinning cells in series. More recent modifications to this process² employ pressurized vessels or steam heat-exchangers to produce the higher column temperatures (about 130°C) required for more efficient elution. Between 16 and 24 hours are typically required before an acceptable degree of elution is attained, and this not only represents a bottleneck in the CIP process, but also involves a large consumption of energy and chemicals (cyanide has been shown to decompose rapidly under these conditions³). It is for these reasons that the recent trend towards low-cyanide elution has arisen.

A popular alternative to the Zadra process was developed by the Anglo American Research Laboratories (AARL)⁴, in which pre-treatment of the carbon with a hot solution of caustic cyanide is followed by elution with hot de-ionized water. However, the total time required for an acceptable degree of elution is similar to that for the Zadra process.

Recent efforts⁵ have been directed towards the development of elution procedures that employ organic solvents such as acetonitrile or ethanol, which have been shown to result in efficient elution in about 8 hours at temperatures between 25 and 70°C. The Micron distillation procedure⁶ involves the refluxing and recycling of hot solvent vapours and condensates through a bed of carbon that acts as a fractionating column. The solvent elution procedures suffer from the disadvantage that the solvent vapours are invariably toxic, and may also represent a fire hazard. The mining community is therefore reluctant to employ these procedures on a large scale.

Early work by Feldtman⁷ and Gross and Scott⁸ indicated the potential of using sodium sulphide for desorbing gold. In 1950, Zadra⁹, in a pilot-plant study, demonstrated the technical and commercial viability of sodium sulphide solutions for the elution of gold at ambient temperatures. He showed the carbon to be eluted efficiently in 4 hours at 25°C, and both the carbon and the eluate were found to be reusable. There are several reasons why this process is not in use today. One is that adsorbed silver and base metals are not eluted, being immobilized as insoluble silver and base-metal sulphides. However, this may not be a great problem, since an equilibrium situation may be reached. The other problem is that the eluted gold is sometimes re-adsorbed onto the carbon, and it is this aspect in particular that this paper addresses.

Experimental Procedure

Approximately 1,1 kg of activated carbon (Le Carbone G210 AS) was screened to a particle size of +1,16–2,07 mm and thoroughly washed with de-ionized water to remove fines and soluble impurities. It was then contacted overnight with 1,44 g of KAu(CN)₂ in approximately 1 litre of de-ionized water to achieve the required gold loading.

Batch Elution Experiments

In each experiment, sulphide eluant was freshly made up by the use of Na₂S·9H₂O. Typically, 5 g of loaded carbon was contacted with the appropriate volume of solution in a round-bottomed magnetically stirred flask with reflux condenser for 48 hours. The solution was sampled periodically and analysed for gold by atomic-absorption spectrophotometry (AAS). The carbon was assayed for gold at the end of the experiment by X-ray fluorescence (XRF) analysis.

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Improved rates of elution were obtained at higher sulphide concentrations and pH values greater than about 13. Higher temperatures increased the initial elution rate, but lowered the overall extraction efficiency, probably because of the deposition of elemental gold on the carbon. Variation of the ionic strength by the addition of NaCl had no effect on the elution, which confirms that the elution mechanism in the case of sulphide is different from that when cyanide or hydroxide is used as the eluant.

It is proposed that the elution of gold by sulphide solutions proceeds by means of an initial step that involves the reaction of polysulphide ions with the adsorbed aurocyanide species, forming AuCN on the carbon and thiocyanate in solution. This step is followed by the formation of poorly adsorbed complexes with sulphide ions, such as AuS₃⁻. The presence of polysulphides, whether generated in situ by the catalytic oxidation effect of activated carbon or by the addition of elemental sulphur, reduces the elution rate and efficiency dramatically. This is probably due to the formation of complexes such as AuS₃⁻ and AuS₂⁻, which have a high adsorption affinity.

Single-pass Elution Experiments

The procedure was identical to that described by Adams and Nicol¹⁰ in a study of the elution of gold from activated carbon using cyanide and hydroxide solutions. Fresh eluant was pumped into a reactor similar to that used for the batch experiments, which contained a fixed mass of carbon and volume of solutions. The eluate was removed by pumping from the top of the solution at the same rate. The eluate fractions were collected and analysed for gold by AAS. In some instances, the UV-VIS spectra of eluate fractions were measured with a Beckman MIV UV-visible spectrophotometer. Unless specified otherwise, the conditions for the elution were as follows:

| | |
|---------------------|----------------------------|
| Temperature | 25 ± 3°C |
| Mass of carbon | 26,7 g (75 ml wet-settled) |
| Flowrate | 200 ml/h |
| [Na ₂ S] | 0,2 M |

Silver-stripping Experiments

A batch of activated carbon was loaded to 1000 g/t of gold and 200 g/t of silver by a method similar to that already described. The carbon then underwent a batch elution by the use of 0,2 M Na₂S at 25°C. After 6 hours, the carbon was filtered off and analysed for silver by XRF analysis.

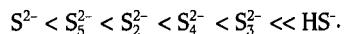
Results and Discussion

Speciation Calculations for Polysulphide Solutions

The relevant reactions and stability constants for sulphides and polysulphides in aqueous solution are listed in Table I. These 'best' values were selected from the most recent literature on the subject¹¹⁻¹³. No stability constants for the S₆²⁻ and higher species were available, and these are therefore not included.

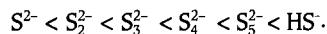
Distribution diagrams for the species were prepared from calculations generated by the HALTAFALL programme¹⁴. The species distribution for a 0,1 M Na₂S solution is shown in Figure 1. The predominant species are H₂S (aq) at pH values below 7 and HS⁻ (aq) at pH values above 7. It is only at pH values greater than 13 that a small fraction of S₂²⁻ (aq) becomes evident.

The situation is somewhat similar in the case of a 0,1 M Na₂S₂ solution, as shown in Figure 2. Small fractions of S_x²⁻ (aq) species become evident only at pH values greater than 13. It is interesting to note that, at pH 14, the fractions of S_x²⁻ species increase in the order



The protonated HS₄⁻, H₂S₄, HS₅⁻, and H₂S₅ species are present to only a negligible extent.

When the solution under consideration contains 0,2 M Na₂S with 0,6 M S, i.e. with a stoichiometry equivalent to Na₂S₄, the S_x²⁻ species begin to play a more predominant role, as shown in Figure 3. Above a pH value of 12, these species are present in significant amounts, with fractions increasing in the order



At a pH value of 14, the S_x²⁻ species constitute about half of the total sulphide species in solution.

Batch Elution with Sulphide Solutions

Effect of Polysulphides at Low Liquid-to-solid Ratios

Zadra⁹ has reported that, during an elution with sodium sulphide, gold was initially re-adsorbed, followed by a slow release of gold from the carbon. No explanation for this behaviour was given. In the present work, batch elution experiments were performed with

- (a) a fresh solution of sodium sulphide made up from Na₂S·9H₂O
- (b) a polysulphide solution of average Na₂S₂ composition, made up with a stoichiometric mixture of Na₂S·9H₂O and elemental sulphur.

Figure 4 shows that a trend similar to that reported by Zadra occurred in the batch elution of 5 g of carbon loaded to 12 800 g/t of gold using 50 ml of solution. The effect was even more enhanced when a polysulphide solution of average 0,1 M Na₂S₂ composition was used.

Table I
Stability constants for polysulphides in aqueous solution

| Soluble species | Reaction | K _n | Ref. |
|-------------------------------|--|-------------------------|------|
| H ₂ S | 2H ⁺ (aq) + S ²⁻ (aq) ⇌ H ₂ S (aq) | 1,23 × 10 ²⁴ | 11 |
| HS ⁻ | H ⁺ (aq) + S ²⁻ (aq) ⇌ HS ⁻ (aq) | 1,25 × 10 ¹⁷ | 12 |
| S ₂ ²⁻ | S ²⁻ (aq) + S ⇌ S ₂ ²⁻ (aq) | 6,92 × 10 ¹ | 13 |
| S ₃ ²⁻ | S ²⁻ (aq) + 2S ⇌ S ₃ ²⁻ (aq) | 1,41 × 10 ³ | 13 |
| S ₄ ²⁻ | S ²⁻ (aq) + 3S ⇌ S ₄ ²⁻ (aq) | 1,38 × 10 ⁴ | 13 |
| S ₅ ²⁻ | S ²⁻ (aq) + 4S ⇌ S ₅ ²⁻ (aq) | 6,61 × 10 ⁴ | 13 |
| HS ₄ ⁻ | H ⁺ (aq) + S ₄ ²⁻ (aq) ⇌ HS ₄ ⁻ (aq) | 2 × 10 ⁶ | 13 |
| H ₂ S ₄ | H ⁺ (aq) + HS ₄ ⁻ (aq) ⇌ H ₂ S ₄ (aq) | 6,31 × 10 ³ | 13 |
| HS ₅ ⁻ | H ⁺ (aq) + S ₅ ²⁻ (aq) ⇌ HS ₅ ⁻ (aq) | 4,57 × 10 ⁵ | 13 |
| H ₂ S ₅ | H ⁺ (aq) + HS ₅ ⁻ (aq) ⇌ H ₂ S ₅ (aq) | 2,88 × 10 ³ | 13 |
| H ₂ O | H ⁺ (aq) + OH ⁻ (aq) ⇌ H ₂ O | 9,9 × 10 ⁻¹⁵ | 13 |

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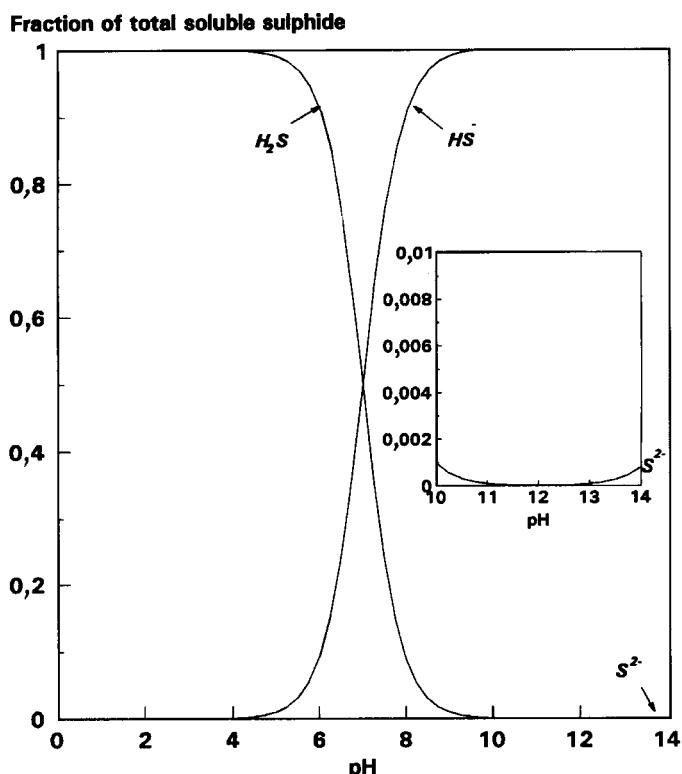


Figure 1—Distribution of sulphide species in the S^{2-} – H_2O system with variation in pH value (0,1 M S^{2-})

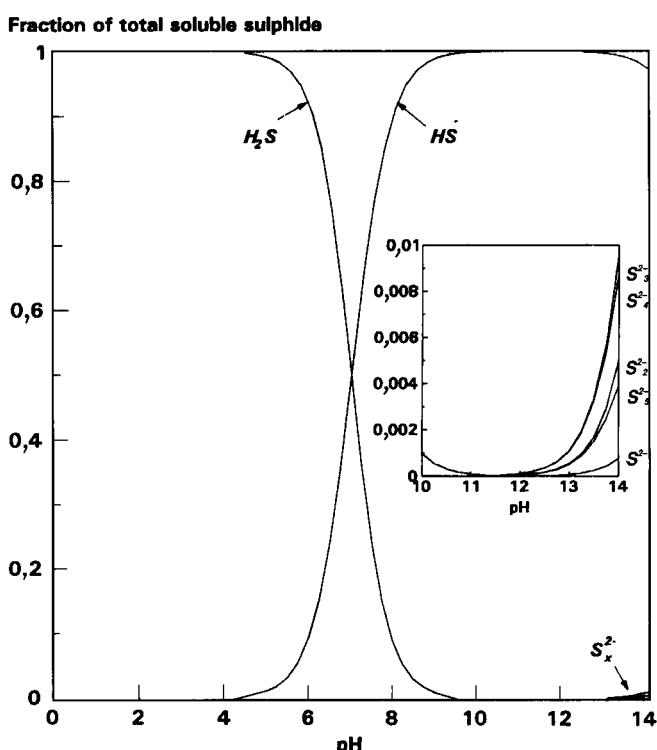


Figure 2—Distribution of polysulphide species in the S – S^{2-} – H_2O system with variation in pH value (0,1 M S_2^{2-})

Effect of Liquid-to-solid Ratio

Further light may be shed on the re-adsorption phenomenon by consideration of the effect of the liquid-to-solid ratio on the batch elution of gold from activated carbon using fresh sulphide solutions. The results in Figures 5 and 6 show that re-adsorption occurs when the liquid-to-solid ratio is low, and not when the solution volume exceeds about 200 ml for a 5 g batch of loaded carbon.

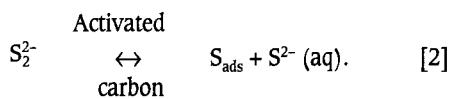
Effect of Na_2S Concentration

The effect of Na_2S concentration on the batch elution of gold from activated carbon at high liquid-to-solid ratios is shown in Figure 7. Complete elution was achieved in about 1 hour from a 1,0 M Na_2S solution, and in 36 hours from a 0,1 M Na_2S solution. No re-adsorption effect was evident under these conditions.

Figure 7 shows that re-adsorption occurred after 36 hours when 0,01 M Na_2S was used, which suggests that the re-adsorption phenomenon is related to the ratio of activated carbon to sulphide concentration in the solution, as well as to the liquid-to-solid ratio. The fact that the pH shifts slightly is probably also a factor. It is evident that re-adsorption is associated with small amounts of sulphide present in relation to the amount of gold in the system. No elution was obtained in the case of 0,001 M Na_2S solution. Possibly a greater degree of oxidation of sulphide to polysulphide occurs when the initial sulphide concentration is low:



This type of reaction occurs slowly¹⁵ when alkali sulphide solution stands in air. Activated carbon is known^{16,17} to catalyse the reaction, with the ultimate formation of products such as elemental sulphur and $\text{S}_2\text{O}_3^{2-}$. This is in direct agreement with the observations made during the present experiments: that the initially colourless Na_2S solutions rapidly turned yellow in colour owing to the formation of intermediate polysulphides¹⁸ (S_2^{2-} to S_4^{2-} are yellow in colour, S_5^{2-} to S_7^{2-} are orange, and S_8^{2-} to S_9^{2-} are red). The yellow colour tended to disappear after about 1 to 2 hours of reaction, which suggests that either the carbon eventually reduces the polysulphide back to sulphide, or that elemental sulphur was deposited on the carbon surface in a secondary reaction, e.g.



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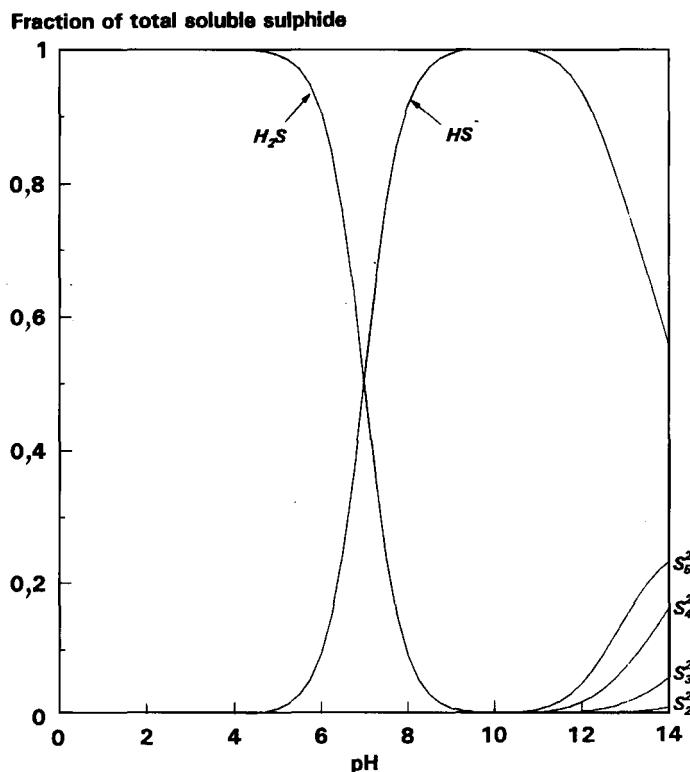
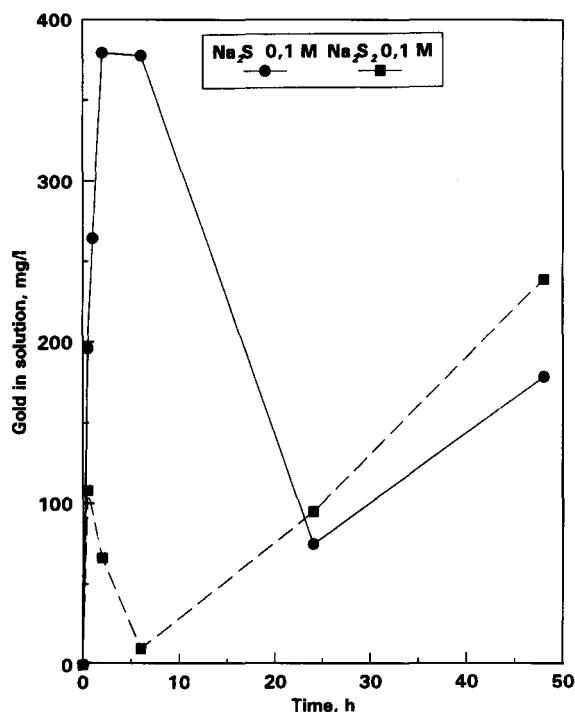


Figure 3—Distribution of polysulphide species in the S-S²⁻-H₂O system with variation in pH (0,2 M S₄²⁻)



Conditions: pH 13,5
Carbon mass 5 g; solution volume 50 ml
Initial gold on carbon 12800 g/t; temp. 25°C

Figure 4—Effect of polysulphides on the batch elution of gold from activated carbon at low liquid-to-solid ratios

These reactions are substantiated by measurements of the visible spectra of various solutions. Giggenbach¹⁹ measured such spectra and assigned bands to individual polysulphides, as detailed in Table II.

Table II

Visible absorbance bands due to polysulphide ions in aqueous solution (after Giggenbach¹⁹)

| Ion | Wavelength, μm |
|------------------------------|----------------|
| SH ⁺ | 229 |
| S ²⁻ | 250 |
| S ₂ ²⁻ | 358 |
| S ₃ ²⁻ | 417; 303 |
| S ₄ ²⁻ | 368; 303 |
| S ₆ ²⁻ | 375; 299 |

The peak maxima of the various solutions measured in the present study are shown in Table III. Large amounts of polysulphides were found to be present in Na₂S + S mixtures, particularly after being boiled. No evidence for polysulphide species was found in fresh 0,1 M Na₂S solution; however, some polysulphides, mainly S₂²⁻, were detected in the solution after it had been exposed to the atmosphere for 1 week.

Polysulphides were detected in 0,1 M Na₂S solutions that had been contacted with activated carbon for periods of up to 24 hours. However, no polysulphides were found to be present after 96 hours.

In the eluates of batch sulphide elutions with and without gold present, polysulphides were detected after 2 hours, but not at 24 hours and 48 hours, which is consistent with reactions [1] and [2].

Despite the re-adsorption that occurs under certain conditions, a 95 per cent elution of gold from carbon at room temperature in less than 1 hour in a batch system is a significant improvement on that achieved under comparable conditions with the conventional caustic cyanide eluant.

Elution of gold using sulphide solutions

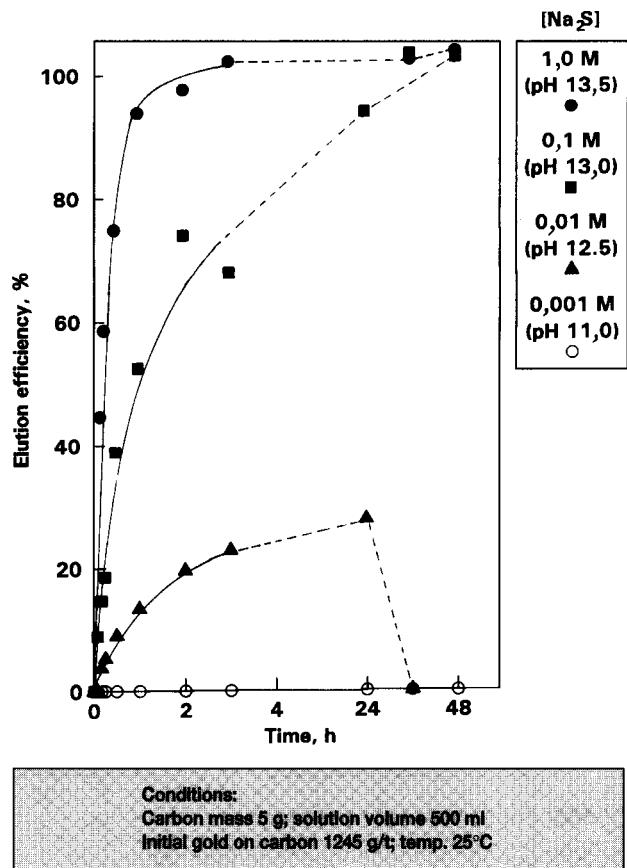
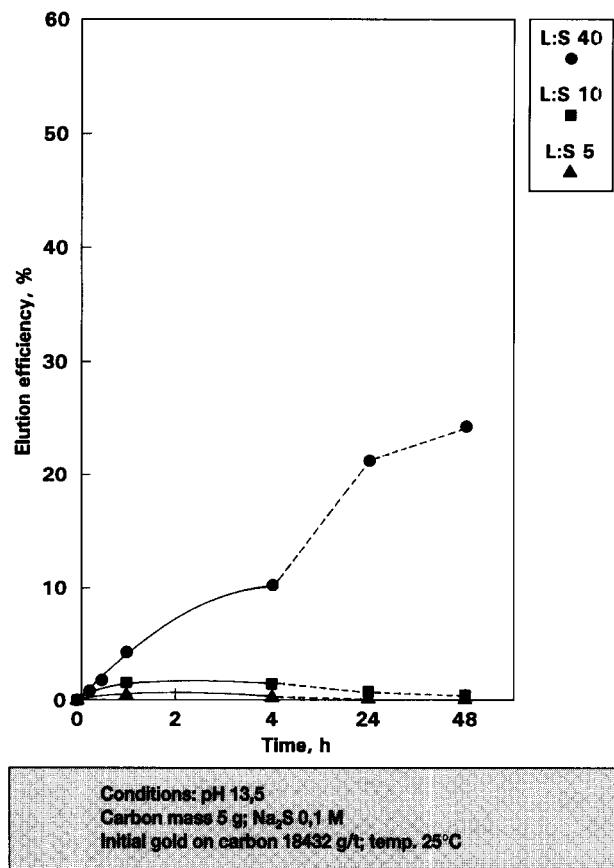


Figure 5—Effect of liquid-to-solid ratio on the batch elution of gold from activated carbon at high initial gold loading

Figure 7—Effect of Na₂S concentration on the batch elution of gold from activated carbon

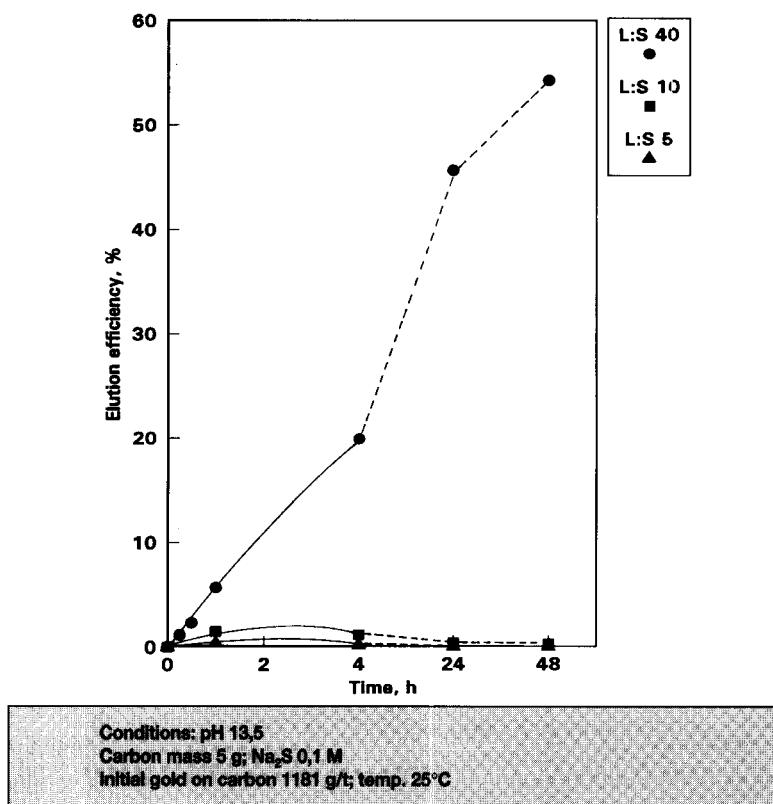


Figure 6—Effect of liquid-to-solid ratio on the batch elution of gold from activated carbon at low initial gold loading

Effect of pH Value

The form in which the sulphide is present depends on the pH value of the solution, as shown in Figure 1. The free S²⁻ species is present to any significant extent only at values above 13; the HS⁻ species predominates between pH values of 6 and 13; and the H₂S species predominates at pH values below 6. The effect of eluant pH on the efficiency of gold elution is shown in Figure 8. A high degree of elution is achieved only at pH values above 13, which suggests that it is the free S²⁻ ion that reacts most readily with the adsorbed aurocyanide species. This result is in contrast to those obtained by Green *et al.*²⁰ on a different system—the elution using thiourea of gold that had been adsorbed as aurocyanide onto strong-base ion-exchange resins. In that work²⁰, it was found that acidic solutions were necessary to achieve acceptable elution efficiencies. In that instance, acid destabilization of the Au(CN)₂⁻ complex is necessary in order to replace the strongly held cyanide ligand ($\log \beta_2 \text{Au}(\text{CN})_2^- = 39,7$) with the less strongly held thiourea ligand ($\log \beta_2 \text{Au}(\text{SC(NH}_2)_2)^+ = 23,3$):

Elution of gold using sulphide solutions

Table III

Visible spectral data for sulphide and polysulphide solutions

| Solution | Contact time | Absorbance* | | | |
|--|--------------|----------------------------------|--|---|--|
| | | SH ⁻ 250 to 270 nm | S ₂ ²⁻ 295 nm | S ₂ ²⁻ + S ₂ ²⁻ 366 nm | S ₃ ²⁻ 415 nm |
| Synthetic solutions: | | | | | |
| A. Na ₂ S 0.1 M + S 0.1 M Warmed | 5 min | vs | s | w | vw |
| Boiled | 5 min | vs | vs | vs | |
| Boiled | 3 h | vs | vs | | |
| B. Na ₂ S 0.1 M Open to atmosphere | — | vs | | | |
| C. Na ₂ S 0.1 M + carbon | 1 week | vs | w | | |
| | 2 h | vs | w | | |
| | 24 h | vs | s | w | |
| | 96 h | vs | | | |
| Batch eluates: | | | | | |
| A. 0.1 M Na ₂ S; 50 ml; 5 g carbon; initial gold on C; 12800 g/t; 25°C (Figure 4) | 2 h | vs | s | | |
| | 24 h | vs | | | |
| | 48 h | vs | | | |
| B. 0.1 M Na ₂ S, 50 ml; 5 g carbon; no gold; 25°C | 2 h | vs | s | w | |
| | 24 h | vs | | | |
| | 48 h | vs | | | |

* v—very strong, s—strong, w—weak, vw—very weak

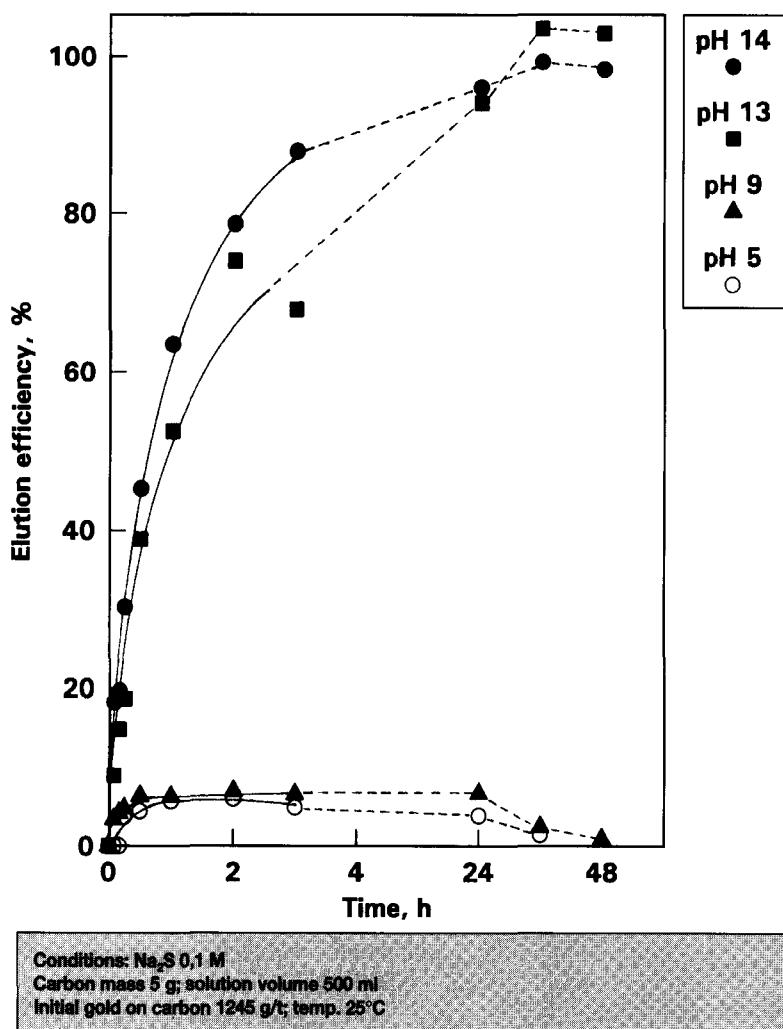
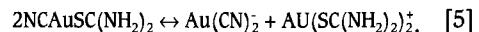
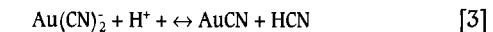


Figure 8—Effect of pH on the batch elution of gold from activated carbon



The stability constants for gold complexes with several sulphide ligands were measured, and these complexes were found to have a much higher degree of stability than the gold thiourea complex²¹ (Table IV), which is consistent with the notion that gold sulphides may form in sulphide eluate solutions.

Seward²¹ and Renders and Seward²² have demonstrated the predominance of the $\text{Au}(\text{SH})_2^-$ complex between pH 4 and 10, and the increasing predominance of species such as $\text{Au}_2\text{S}_2^{2-}$ at pH values greater than 10 (Figure 9 and Table IV). However, this is not the only possible species present in the alkaline region since the data were scattered and somewhat ambiguous in that region²¹. Other complexes that may be present under alkaline conditions²¹ include $\text{Au}_2\text{S}_3^{4-}$, $\text{Au}_2\text{SHS}_3^{3-}$, $\text{Au}_2\text{S}_2^{3-}$, $\text{Au}_2(\text{SH})_2\text{S}_2^{2-}$, AuSHS^{2-} , $\text{Au}_2(\text{SH})_3^{2-}$, Au_2SHS^- , and AuS^- . The presence of multi-charged gold complexes such as AuS_2^{2-} in alkaline sulphide solutions is therefore consistent with the present experimental results.

It is proposed that the elution of gold by sulphide solutions proceeds by means of an initial step that involves the polysulphide ion, expressed as S_2^{2-} for clarity:



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Acknowledgements

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Table IV

Stability constants for several Au(I) complexes at 25°C (after Seward²¹)

| Complex | $\log \beta$ | Complex | $\log \beta$ |
|---|--------------|---|--------------|
| AuI_2 | 19,0 | $\text{Au}_2\text{S}_2^{2-}$ | 41,1 |
| AuBr_2 | 12,4 | $\text{Au}(\text{HS})_2^-$ | 30,1 |
| AuCl_2 | 9,2 | AuHS^0 | 24,5 |
| AuF_2 | — | $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ | 26,0 |
| $\text{Au}(\text{CN})_2^-$ | 38,7 | $\text{AuCH}_2\text{N}(\text{SNH}_2)_2^+$ | 22,2 |
| $\text{Au}(\text{SCN})_2^-$ | 16,8 | | |
| $\text{Au}(\text{CS}(\text{NH}_2)_2)_2^+$ | 23,3 | | |

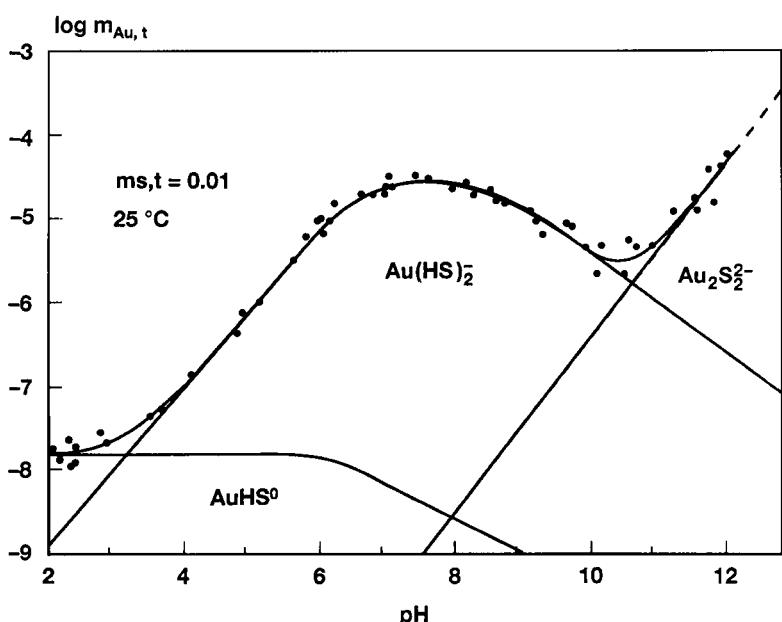
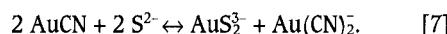


Figure 9—The solubility of Au_2S at 25°C as a function of pH (after Renders and Seward²²)

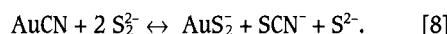
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This mechanism is substantiated by evidence from current work for the presence of AuCN on carbons that have been eluted by sulphide solutions, and by the presence of SCN^- in the eluates as measured by ion chromatography.

The elution behaviour of gold depends on the relative concentrations of sulphide and polysulphide ions in solution. In the presence of a small amount of polysulphide, it is postulated that gold is converted into a multi-charged anion that has little affinity for activated carbon, and is eluted:



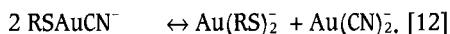
When a large amount polysulphide is present, the gold is proposed to be converted into a singly charged anion that has a relatively high affinity for activated carbon, and is re-adsorbed:



The type of re-arrangement reaction, represented by [7] and [8], between gold cyanide and another ligand has been demonstrated previously for thiosulphate²³:



and for thiols (RS^-)²⁴:



Effect of Initial Gold Loading on Carbon

The initial gold loading on carbon does not have a great effect on the elution efficiency, as shown in Figure 10. However, high gold loadings of about 10 000 to 50 000 g/t depress the elution slightly when compared with an initial loading of 1000 g/t. This is consistent with the results shown in Figures 5 and 6, and confirms that high molar ratios of gold to sulphide depress the elution of gold.

Effect of Polysulphides at High Liquid-to-solid Ratios

The effect of polysulphides on the elution efficiency at high gold loadings (12 800 g/t) and relatively low liquid-to-solid ratios (about 10) are shown in Figure 4. A comparison of these results with those obtained at low gold loadings (1245 g/t) and high liquid-to-solid ratios (about 100) is interesting, as shown in Figure 11. There is now no evidence of re-adsorption from 0,1 M Na_2S solution with no added polysulphides. The re-adsorption effect in the presence of polysulphides is still evident at high liquid-to-solid ratios but is much less marked, with the re-adsorption equilibrium predominating only after 48 hours, as compared with 1 hour in the low liquid-to-solid experiment.

Elution of gold using sulphide solutions

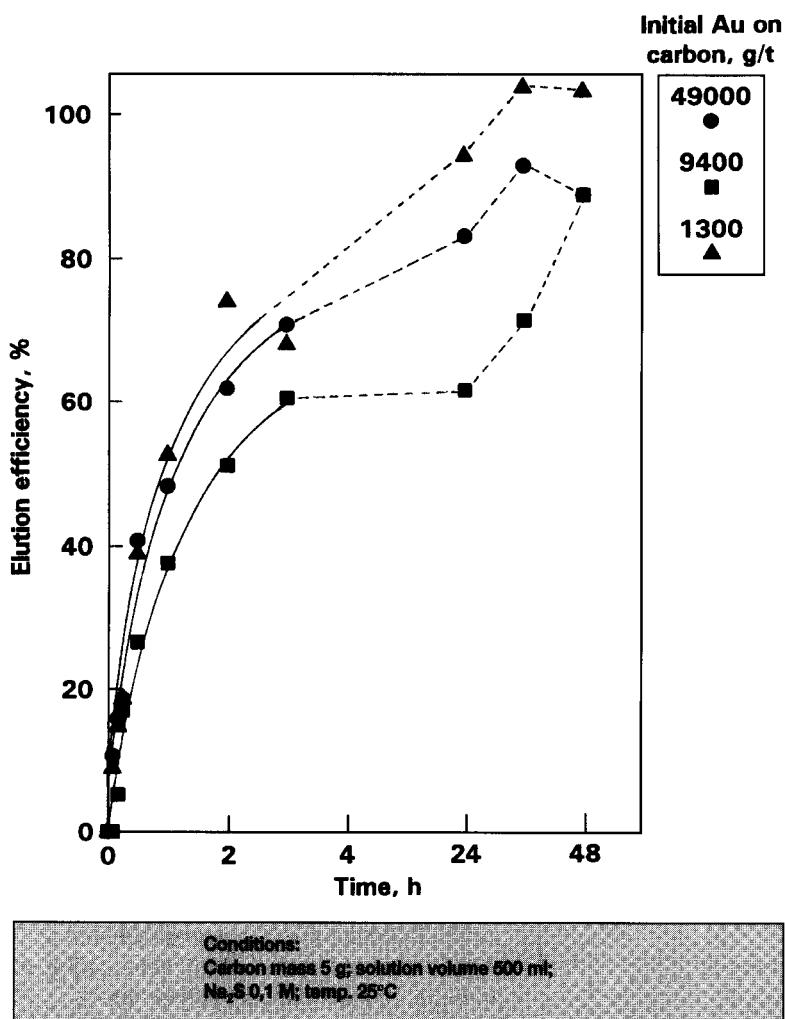


Figure 10—Effect of initial gold loading on the batch elution of gold from activated carbon

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There is very little information available regarding the complexes that are formed between gold and polysulphide in aqueous solution, although polysulphides have been shown²⁵ to leach gold from the arsenical stibnite concentrate. Mellor²⁶ states that the solubility of gold in polysulphide solution is due to the formation of AuS_2^- and AuS_2^{2-} species. The predominance of species like these in the early stages of elution, where the S_2^{2-} polysulphide species were found to be present, would account for the re-adsorption phenomenon mentioned earlier, since these singly negatively charged complexes are likely to have a high affinity for activated carbon²⁷.

Single-pass Elution of Gold Cyanide with Sodium Sulphides

The batch experiments that were discussed in the previous section may be useful in the interpretation of some of the effects that were observed in the single-pass elution experiments.

Effect of Na_2S Concentration

As observed previously, the rate of elution is enhanced at higher sulphide concentrations. At lower sulphide concentrations, the elution is very slow, as shown in Figure 12. After a time that is approximately inversely proportional to the Na_2S concentration, there is a sudden and dramatic increase in the elution rate. For example, with 0,05 M Na_2S , this increase occurs after 2,3 hours; with 0,1 M Na_2S , after 1,2 hours; and with 0,2 M Na_2S , after 0,5 hours. The batch elution experiments showed that, at low sulphide-to-gold ratios, there is a predominance of polysulphide in solution, and the re-adsorption equilibrium [9] predominates. When the polysulphide concentration has been sufficiently lowered by adsorption onto the activated carbon, reaction [2], there is a significant amount of sulphide ion in solution, and the elution equilibrium, reactions [7] and [8], predominates. The application of UV-visible spectrophotometry to the eluates revealed the presence of polysulphides (absorbance at 295 nm) in regions of high elution rate. These results are consistent with the batch results, and corroborate the hypothesis that polysulphides are associated with re-adsorption effects. Eluants containing 0,4 M Na_2S or higher were found to result in the elution of about 98 per cent of the gold from the carbon in about 4 hours at these flowrates.

Adams and Nicol¹⁰, using an identical experimental arrangement with cyanide and hydroxide solutions, found the kinetics of elution to be first order and to be described by the rate equation

$$-\frac{dc}{dt} = k(C - KS), \quad [13]$$

where C and S are the concentrations of gold on the carbon and in solution, respectively, and k and K are constants. The incorporation of this equation in the mass balance yields the relation

$$\ln C = \ln C_0 - k't, \quad [14]$$

where C_0 is the initial concentration of gold on the carbon, t is the time from the start of elution, and k' depends on the experimental conditions and diffusion coefficients.

Whereas data from the equivalent cyanide and hydroxide elutions yielded linear relations when $\ln C$ was plotted against t , this was not the case for the sulphide elutions, as shown in Figure 13. The initial region with the slower rate corresponds to the region where polysulphides were detected in the eluates. This results in a delayed onset of elution.

Elution of gold using sulphide solutions

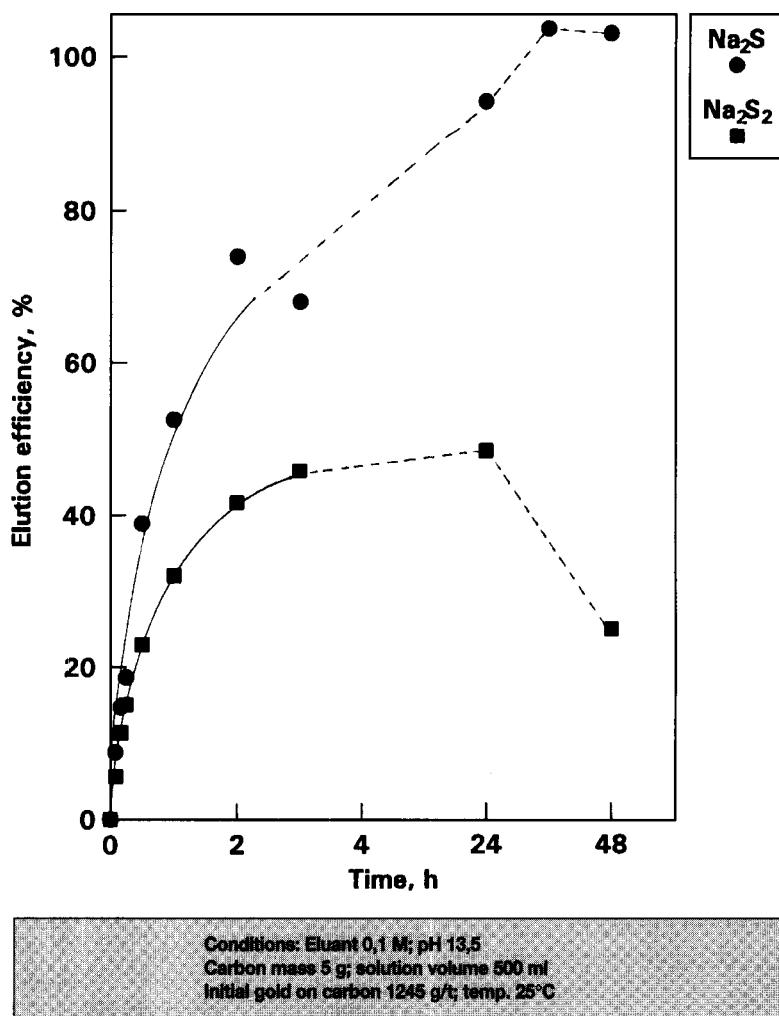


Figure 11—Effect of polysulphides on the batch elution of gold from activated carbon at high liquid-to-solid ratios

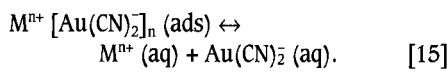
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Effect of NaOH Concentration

The pH value of a 0,2 M Na₂S solution is approximately 13. The addition of NaOH causes a shift to a higher pH region, where the fraction of S²⁻ species is higher. This results in a concomitantly higher elution rate, as shown in Figure 14.

Effect of NaCl Concentration

The ionic strength has a marked effect on the elution of gold from activated carbon with cyanide or caustic solutions because of the effect of the Mⁿ⁺ cation on the equilibrium:



The results in Figure 15 show that the ionic strength had a negligible effect on the elution with sulphide solution; so, the simple equation [15] does not hold in this case. Owing to the very stable gold sulphide complexes that form in aqueous solution (Table I), and the tendency²² of thiol ligands for the displacement of cyanide from Au(CN)₂⁻, it is suggested that the mechanism of sulphide elution involves a similar type of ligand displacement reaction, with the formation of a multi-charged gold complex that has little affinity for carbon^{23,24}.

Effect of Temperature

The results in Figure 16 show that the initial rate of elution is enhanced at higher temperatures. However, increasing amounts of adsorbed gold are presumably deposited as an insoluble form, such as Au⁰, resulting in the plateau effect in the high-temperature curves in Figure 16. This premise could not be confirmed by XRD analysis owing to the low gold loading that was present.

Effect of Other Anions

The addition of sulphite and, to a greater extent, thiosulphate ions to the eluant results in enhanced rates of elution, as shown in Figure 17. These ions may assist by reducing any polysulphides back to sulphide ion. Figure 17 also shows the slight depressing effect of 0,2 M S, and the dramatic effect when 0,6 M S is added to the eluant, which virtually completely eliminated the elution. The 0,2 M Na₂S conditions are equivalent to the 0,1 M S₂²⁻ conditions used in the species distribution diagram in Figure 2. At pH 13, there are substantial concentrations of polysulphides (comparable with the concentration of S²⁻), which would result in a depression of the elution kinetics. This would also be affected by the adsorption of polysulphides via reaction [2].

In the case of 0,6 M S, the conditions are equivalent to the 0,2 M S₄²⁻ conditions used in the species distribution diagram in Figure 3. In that case, the concentrations of polysulphides were very much larger than the concentration of S²⁻ ions, and the solution remained yellow-orange in colour throughout the experiment. The ratio of AuS₂³⁻ to AuS₂²⁻ species was presumably very low, as evidenced by the negligible elution rate.

Elution of gold using sulphide solutions

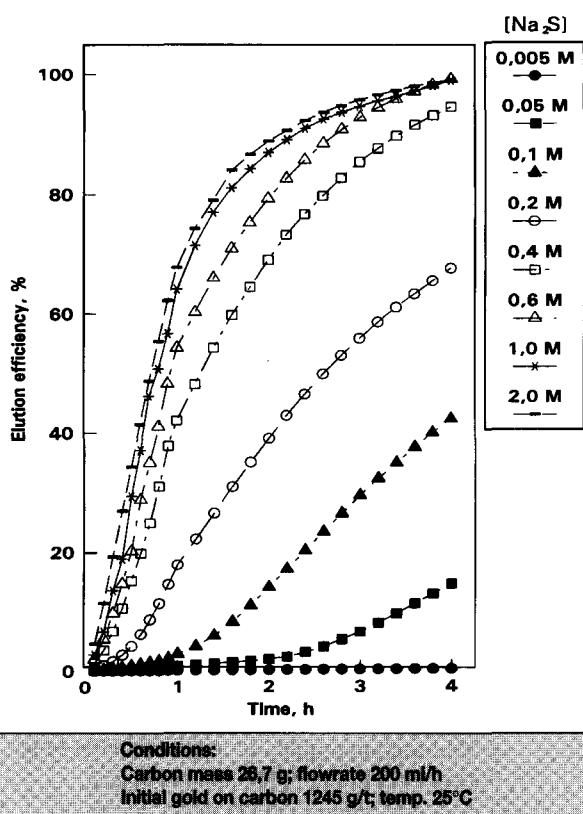


Figure 12—Effect of Na₂S concentration on the single-pass elution of gold cyanide from activated carbon

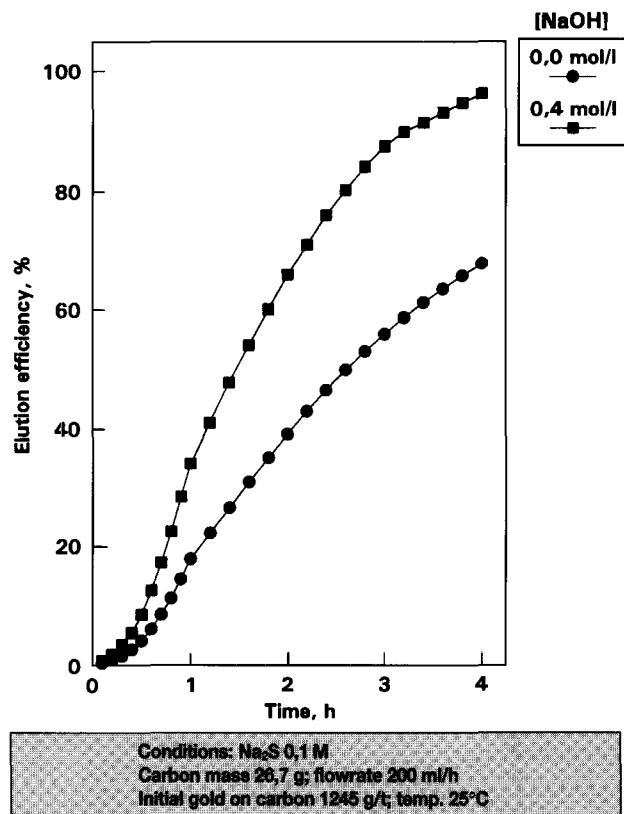


Figure 14—Effect of NaOH concentration on the single-pass elution of gold cyanide from activated carbon

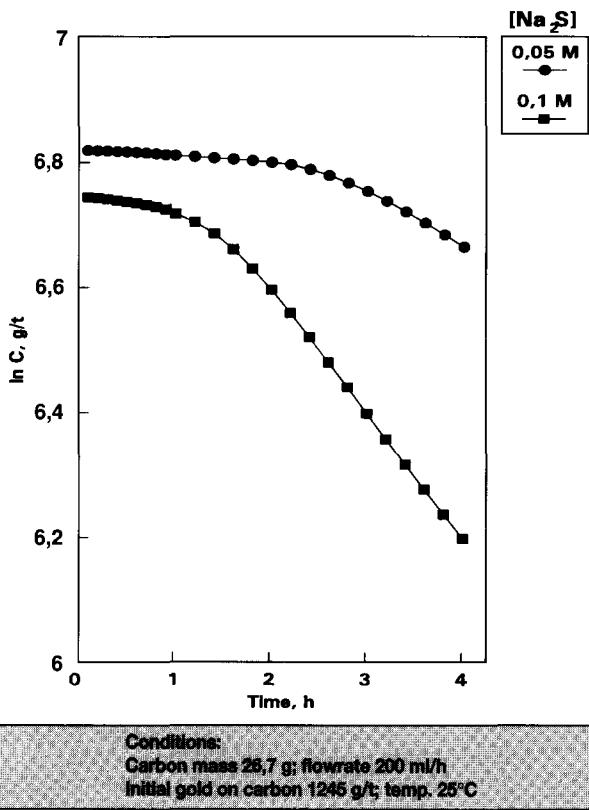


Figure 13—Plot of ln C versus t for the elution of gold from activated carbon at different sulphide concentrations

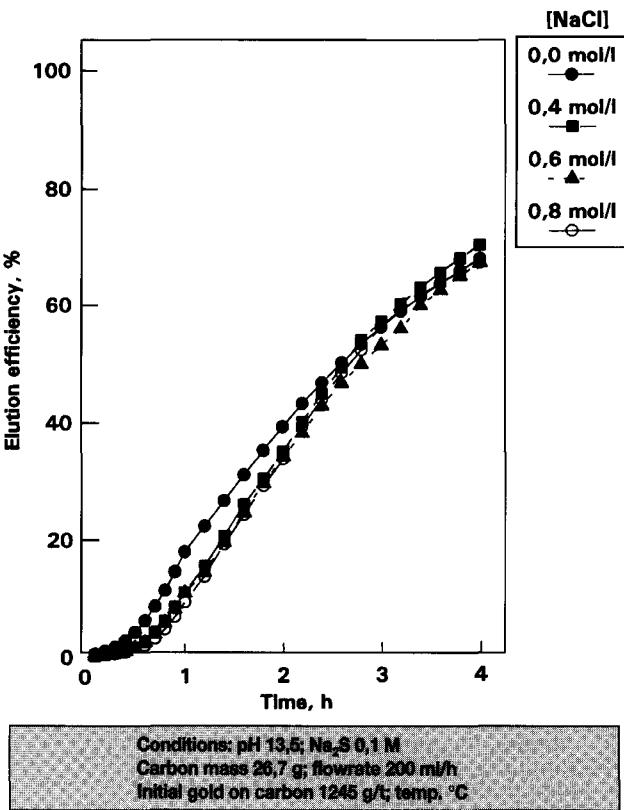


Figure 15—Effect of NaCl concentration on the single-pass elution of gold cyanide from activated carbon

Elution of gold using sulphide solutions

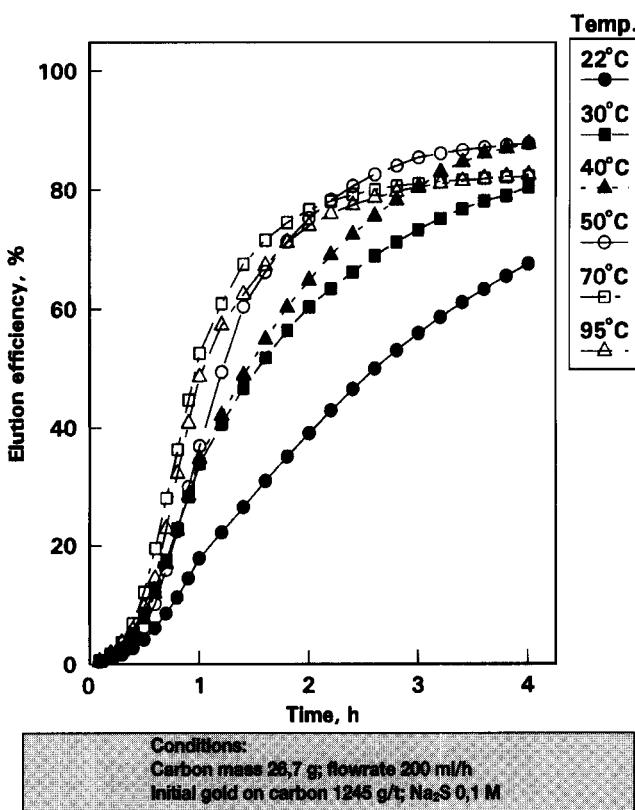


Figure 16—Effect of temperature on the single-pass elution of gold cyanide from activated carbon

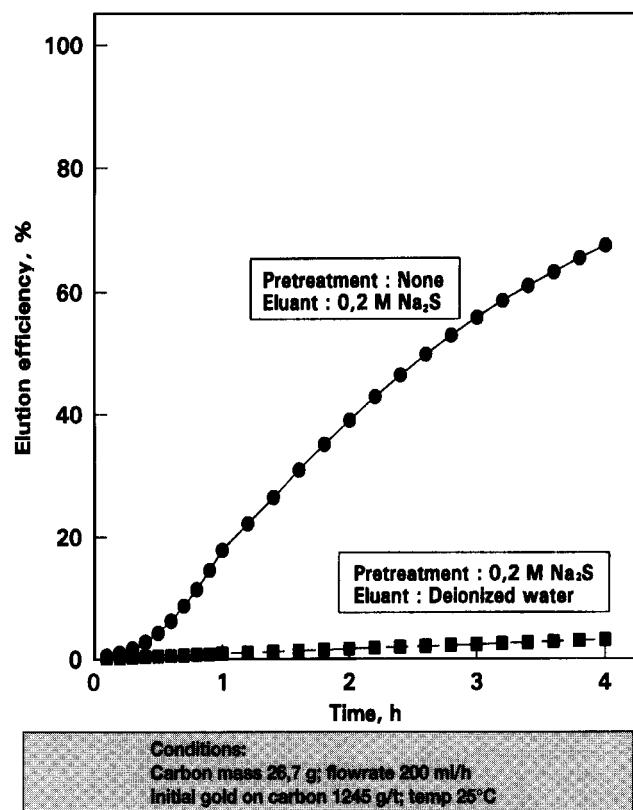


Figure 18—Effect of pretreatment on the single-pass elution of gold cyanide from activated carbon

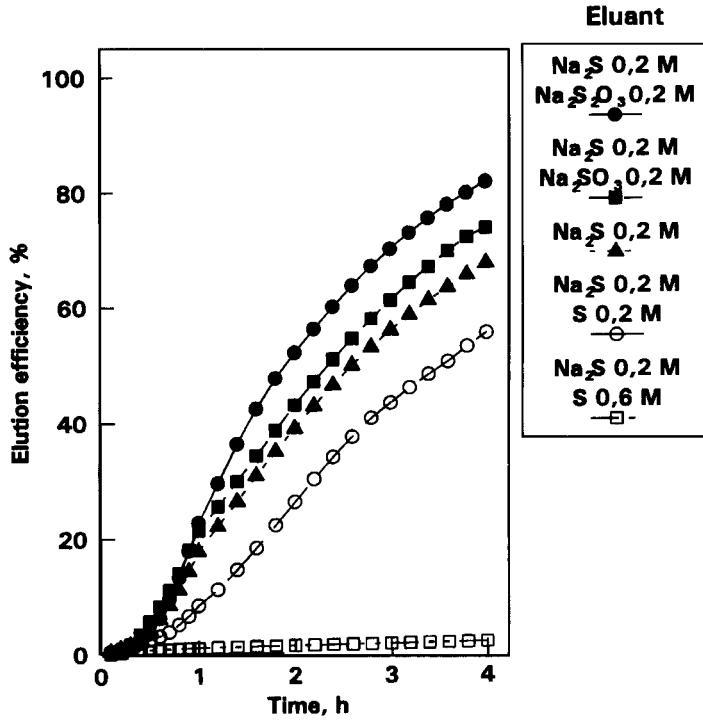


Figure 17—Effect of other anions on the single-pass elution of gold cyanide from activated carbon

Effect of Sulphide Pretreatment Followed by Elution with De-ionized Water

In an attempt to extend the concept of sulphide elution to the AARL method, loaded carbon was pretreated with 0,2 M Na₂S for 4 hours, before being drained and eluted with de-ionized water. The experiment was unsuccessful, as shown in Figure 18. This is attributable to the fact that alkaline solution is necessary²¹ for the stabilization of gold in the elutable Au₂S₂²⁻ form. Figure 15 shows that Au(HS)₂ is the predominant form between pH 4 and 10, and this singly negatively charged species would probably^{27,28} be strongly adsorbed by activated carbon.

Stripping of Silver from Sulphide-eluted Carbons

Several experiments were carried out on the feasibility of stripping the silver, in particular, from the carbon in a step subsequent to sulphide elution. Gold was first eluted batchwise from carbon containing 1000 g/t of gold and 200 g/t of silver with a 0,2 M Na₂S solution. The results obtained by several different stripping methods are shown in Table V, and indicate that it is possible to remove most of the silver from sulphide-eluted carbon. These procedures could undoubtedly be optimized further.

Elution of gold using sulphide solutions

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Table V
Stripping of silver from sulphide-eluted carbon by various methods

| Pretreatment | Stripping solution | Silver on carbon, g/t | | Ref. |
|--|---|-----------------------|-------|------------------|
| | | Initial | Final | |
| 1. None | 5 M NH ₄ Cl 90°C pH 7.0 (HCl/NH ₃) S:L 40 6 h | 200 | 20 | 29 |
| 2. 0.5M HCl 105 g/l FeCl ₃ ·6H ₂ O 90°C S:L 13 6 h | 0.5M Na ₂ S ₂ O ₃ 25°C pH 7.0 S:L 40 6 h | 200 | 52 | 30; this work |
| 3. As for (2) | 0.5M Na ₂ SO ₃ 25°C pH 6.0 S:L 40 6 h | 200 | 170 | 30; this work |
| 4. As for (2) | 50 g/l NaCl 90°C pH 7.0 S:L 40 6 h | 200 | 188 | 30; 31 |

Zadra⁹ has shown that carbon can be recycled between loading and stripping many times without a loss in efficiency. It is conceivable that the form of the silver and base-metal sulphides that are produced inside the carbon during sulphide elution and subsequent regeneration is such that some cyanide leaching of these species occurs during the subsequent adsorption step. This could result in equilibrium loadings of these elements eventually being reached, with no further detrimental effect on gold recovery.

Conclusions

Elution efficiencies of around 96 per cent were obtained with a single pass of eluant containing 0.2 M Na₂S and 0.4 M NaOH in 4 hours—about 10 bed-volumes of eluant. The initial rate was slow over the first hour of elution, probably because the activated carbon catalysed the oxidation of sulphide to polysulphide.

Elution efficiencies of around 100 per cent were also obtained in batch elutions of carbon in less than 4 hours at liquid-to-solid ratios of about 100. Lower liquid-to-solid ratios resulted in re-adsorption of the gold, probably owing to the oxidation of sulphide to polysulphide with the resultant formation of less elutable gold complexes.

No attempt was made to fully optimize the elution conditions, but several trends were evident. Improved rates of elution were obtained at higher sulphide concentrations and pH values greater than about 13.

Increasing temperature raised the initial elution rate, but lowered the overall extraction efficiency, probably owing to the deposition of elemental gold on the carbon.

Increased ionic strength, by means of NaCl addition, had no effect on the elution, which confirms that the elution mechanism in the case of sulphide is different from that when cyanide or hydroxide is used as the eluant.

The elution of gold by sulphide solutions is proposed to proceed by means of an initial step that involves the reaction of polysulphide ions with the adsorbed aurocyanide species, forming AuCN on the carbon and thiocyanate in solution. This is followed by the formation of poorly adsorbed complexes with sulphide ions, such as AuS₂³⁻. The presence of polysulphides, whether generated *in situ* by the catalytic oxidation effect of activated carbon or by the addition of elemental sulphur, serves to reduce the elution rate and efficiency dramatically. This is probably due to the formation of complexes such as AuS⁻ and AuS₂, which have a high adsorption affinity.

Sodium sulphide solutions are rapid and effective for the elution of gold from activated carbon at room temperature. As silver and base metals are not eluted, the technique is suitable for applications where the carbon is not intended for re-use, for example, in the elution of gold from carbon fines. ♦