

Elution behaviour of metals from carbon

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This study investigated the elution of precious and toxic metals from activated carbon. Gold and mercury are of primary interest, due to their value and environmental impact respectively. A laboratory elution rig was commissioned to simulate industrial Zadra and AARL carbon elution conditions. Mercury was found to elute most effectively in strong caustic cyanide solutions; gold was found to elute most effectively in hot low ionic strength solutions. As cyanide decomposes on contact with activated carbon at high temperatures, optimum elution conditions for gold conflicts with those for mercury —no practical compromise in conditions was found. However, sequential elution allowed reasonable recovery of both metals. Ongoing work is looking at the deportment of other metals under elution conditions.

Introduction

Gold can be extracted industrially from ores by a variety of processes, and one of the most successful methods is the carbon-in-pulp (CIP) process. In CIP processing, ore is mined, ground, and leached with alkaline cyanidic solution to solubilize the gold as a gold cyanide complex. The gold cyanide is adsorbed by activated carbon, which is subsequently eluted to produce a concentrated gold solution. The eluted solution is electrowon to recover the precious metals (alternatively, zinc precipitation may be used), and the carbon is treated in a kiln under a flowing steam atmosphere to reactivate its surface for reuse.

Many gold plants process ores containing traces of mercury, but the deportment of mercury through the entire plant under different operating conditions is poorly understood. It is known that generally mercury follows gold through the cyanide circuit (Zárate, 1985) and loads onto the activated carbon, but only partially elutes with the gold. This partial elution compounds the treatment difficulties, since a portion of the mercury reports to the electrowinning cells, and the remainder reports to the carbon regeneration kilns.

Mercury is a heavily regulated effluent from industrial processes and, in Western Australia, is listed as a controlled waste under Schedule 1 of the WA Environmental Protection (Controlled Waste) Regulations 2004. Compounds or solutions of mercury may not be discharged into the environment under Schedule 1 of the WA Environmental Protection (Unauthorized Discharges) Regulations 2004, as it is classified as ‘waste that can potentially accumulate in the environment or living tissue’ under Part 3 of the WA Environmental Protection Regulations (1987).

This paper presents results from fundamental studies of the elution behaviour of mercury and gold under simulated industrial conditions. Conditions that favour mercury and gold desorption have been established, and a process for the treatment of mercury-containing CIP carbon is proposed.

Method

Elution rig

A laboratory-scale elution rig was commissioned to simulate Zadra and AARL carbon elution conditions, see Figure 1. The majority of the system was constructed from stainless steel tubing and Swagelok fittings. The elution column was ~600 mm long with an internal diameter of 25 mm, and a capacity of ~100 g of granulated activated carbon per experiment. The void volume of the system, when loaded with carbon, was ~150 mL. Solutions were pumped through the column with a high pressure positive displacement pump with a flow rate of 9.9 mL/min unless noted otherwise. A pressure relief valve (Figure 1) was set to 1 400 kPag as a safety precaution, but was not triggered in the experiments as routine operating pressures were well below this threshold.

Heat was maintained with electrical heating tape wound around the main column, controlled by a thermocouple inserted through the top of the column, connected to a PID controller. Temperature control was accurate to within $\pm 2^\circ\text{C}$ over the normal course of an experiment. Solutions were preheated prior to entering the column by five turns of tubing, wound with the same heating tape. Metal foil loosely bound around the column and heating tape provided convective insulation for the system.

Samples

Samples of granulated activated carbon were received from an industrial CIP plant. The samples were either barren, loaded, or acid washed (barren was taken after elution but before regeneration, loaded was from the adsorption train, and acid washed was taken immediately before elution). The metal loadings on each sample are given in Table I. Gold loadings were measured by FAAS on aqua regia digestions of ashed carbon samples, while mercury loadings were measured by CVAAS on microwave-assisted acid digestions of as-received samples.

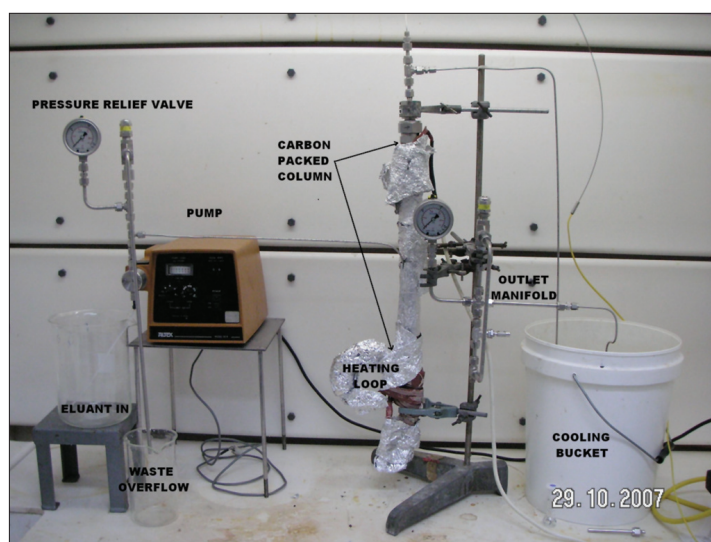


Figure 1. Photograph of the elution rig

Table I
Metals on carbon samples

| Sample | Gold loading (g/ton) | Mercury loading (g/ton) |
|----------------|----------------------|-------------------------|
| C1 loaded | 909 | 187 |
| C1 acid washed | 1 140 | 229 |
| C2 acid washed | 355 | 92 |

Due to the greater ease and precision with which higher element concentrations can be measured, the majority of experiments were performed with representative portions of C1 acid washed carbon.

Conditions

The standard operating procedure was to load the column with a known weight of acid washed carbon, fill the rig with deionized water, pump 150 mL of 2% w/v NaCN + 2% w/v NaOH solution into the rig, seal and soak the carbon at 130°C for ~30 minutes, then pump 9.9 mL/min of deionized water through at 130°C (AARL type elution). Output from the rig was collected in ~100 mL portions, weighed, and assayed for gold and mercury concentrations.

Pressure inside the elution rig was maintained by restricting the flow rate from the outlet manifold with the PD piston pump able to maintain pressures in excess of 1 MPa in the system. When pumping was stopped (such as during the soak stage), the rig was sealed to maintain the high pressures required to prevent the solution boiling.

Variations on this base method are noted for each run. The effects of modifying temperature, pressure, cyanide concentration and eluant composition were investigated.

Results and discussion

The concentration profiles shown are calculated from the metal assays of each sample and the masses of each solution. The recovery profiles shown are calculated as the normalized integrated concentrations of each metal, assuming that the density of each solution sample is equal to that of pure water. Simple density measurements on selected solution samples indicated this to be a reasonable approximation.

Commissioning data

During the commissioning of the column, a number of experiments were conducted at various temperatures and pressures to ascertain that the elution circuit was operating with similar characteristics to that of industry. Initially the C2 acid washed carbon was eluted at a typical elution pressure and temperature of 200 kPag and 130°C. The gold profile data is shown in Figure 2. The elution profiles (closed symbols) represent the metal assays from each sample with the recovery profiles provided by the cumulative metal values (open symbols). From the concentration profile, it was clear that during the initial stages of elution, which corresponds to the flushing of the NaCN + NaOH solution from the column, the elution of gold was poor. However, as the soak solution was displaced with distilled water, there was a large peak in the concentration profile, followed by a tail which was typical of elution processes. The recovery profile showed that within 2 200 g of eluant (~15 BV), the recovery of gold was >90%, and the profile was similar to that reported in the literature (Marsden and House, 2006). An elution experiment was also carried out at 700 kPag, and the data (Figure 2) showed that both

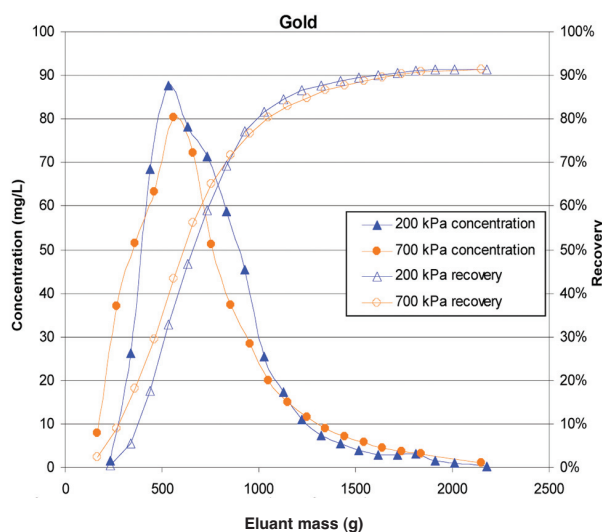


Figure 2. Effect of pressure on the concentration of gold in the eluant and the cumulative recovery for an AARL style elution at 130°C

the recovery and concentration profiles were similar at the two elution pressures. Such a result was not surprising, as it would be expected that pressure would not impact on the elution process, providing that it was maintained above the vapour pressure of the eluant solution.

An important operational observation from the elution experiments at the two different pressures, however, was that pressure control was less reproducible at 200 kPag. The outlet valve needed to be continually manipulated to prevent large changes in pressure, and hence flow rate, which affected the stability of the column temperature. In contrast, at 700 kPag, the elution operated more smoothly, with little change required in the valve position during the course of the experiment. This variability is evident in the gold concentration profile, where the main peak is less uniform at the lower pressure. Therefore, the remainder of the experiments were conducted at the higher column pressure to take advantage of the improved pressure, flow and temperature control.

The gold elution profiles at 130°C and 700 kPag for the other two carbon samples, C1 acid washed, and C1 loaded were compared to the profiles for the C2 acid washed carbon, as shown in Figure 3. From the gold recovery curves, it was evident that both the C1 and C2 carbon samples eluted in a very similar manner, despite the loading for the C2 carbon being significantly less than the C1 carbon. It was also clear that the acid washing stage had little impact on the elution of gold.

For each of the carbon samples eluted at 130°C and 700 kPag, the concentration and recovery profiles for mercury were also measured, as shown in Figure 4. These profiles are significantly different from those for gold, with the concentration of mercury peaking in the second eluant batch collected, and then rapidly dropping to zero. The recovery profiles indicated that only < 60% of the mercury had been eluted from the carbon, compared to > 90% for gold. These results indicate that distilled water is not effective at eluting mercury from carbon. The recovery of mercury from both the acid washed carbon samples was similar at ~57%, but recovery from the loaded (not acid washed) carbon was significantly lower at 41%. The mechanism by which acid washing improves mercury desorption has not yet been determined.

During the commissioning trials, elutions were conducted at a range of temperatures, with data obtained at 130 and 160°C, as shown in Figure 5. As expected, the elution of gold was more effective at higher temperatures, producing a sharper gold concentration profile, and

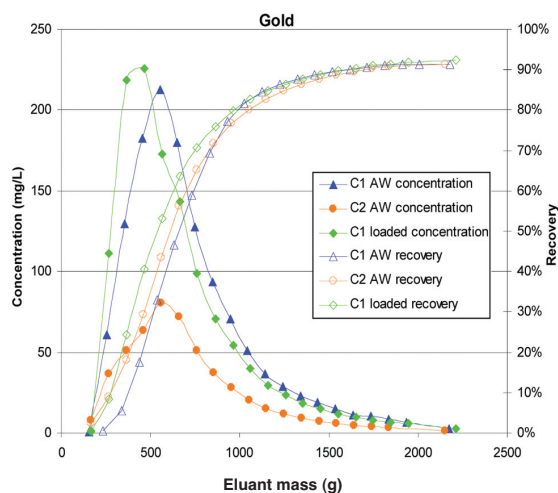


Figure 3. The concentration of gold in the eluant and the cumulative recovery for an AARL style elution at 130°C of three difference carbon samples

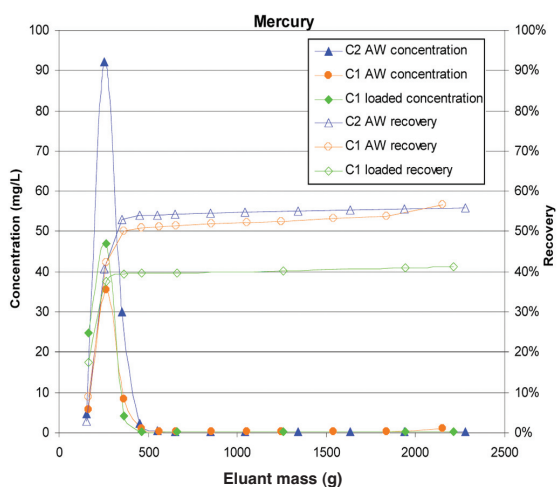


Figure 4. The concentration of mercury in the eluant and the cumulative recovery for an AARL style elution at 130°C of three difference carbon samples

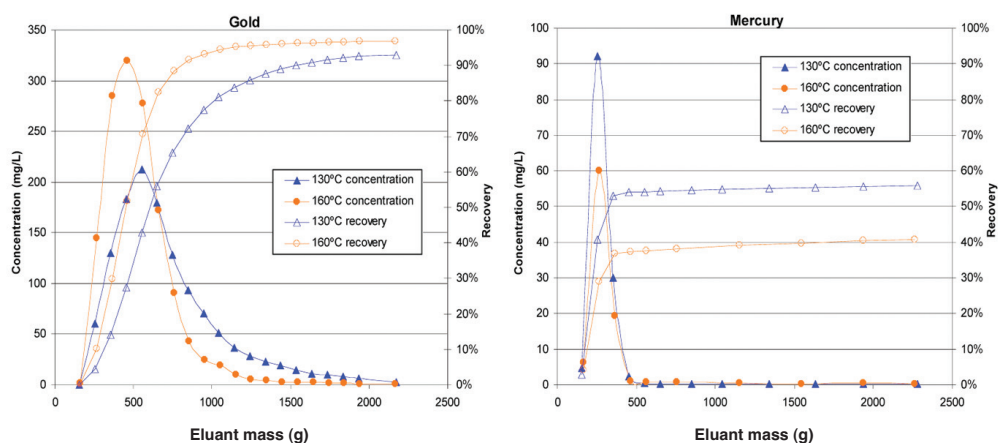


Figure 5. Effect of temperature on the concentration of gold and mercury in the eluant and the cumulative recovery for an AARL style elution

hence a more concentrated pregnant eluant at the higher temperature. The overall recovery was also superior at the higher temperature, 97%, compared to 93% at 130°C. These results are consistent with the data reported in the literature (Marsden and House, 2006). An interesting observation was that the elution of mercury was less effective at the higher temperature, with the peak concentration and recovery of mercury, lower at 160°C (40% recovery) than at 130°C (57% recovery). The data shown in Figure 4 suggest that cyanide is important for the elution of mercury, since the peak mercury concentration corresponded to the period in which the caustic cyanide soak solution was flushed from the column. The data obtained at 160°C are consistent with this hypothesis, since cyanide is known to decompose on activated carbon at elevated temperatures, resulting in a lower free cyanide concentration at higher elution temperatures.

Effect of cyanide concentration in the AARL soak stage

The effect of varying the cyanide concentration in the soak stage of the AARL elution on the metal elution was investigated. This work was undertaken as the commissioning data suggested that cyanide played an important role in the elution of mercury. The C1 acid washed carbon was soaked at 130°C in 2% w/v NaOH solutions containing 0, 2, and 5% w/v NaCN prior to the standard deionized water elution. The results are shown in Figure 6.

The data obtained for the gold profiles indicate that although a soak solution containing no cyanide could be utilized prior to the elution, the recovery of gold under these conditions was slow and that the recovery of gold was incomplete. Gold elution rates increased with increasing NaCN in the soak solution, with profiles approaching a similar overall recovery of gold. This data is also consistent with the literature, which shows the rate of gold elution from carbon utilizing a Zadra system at 95°C increases with increasing cyanide concentration. (Adams and Nicol, 1986). Mercury desorption was even more markedly affected by the presence of cyanide, with the peak mercury concentration very low from a caustic-only soak, resulting in an overall mercury recovery of only 6%. This data clearly indicated the importance of cyanide in the elution of mercury, and were consistent with the data in Figures 4 and 5. When 5% NaCN was adopted in the presoak, the concentration peak and overall recovery of mercury were higher, but still nowhere near complete (<65%). The reason for this is that for the AARL type elution, cyanide is used only in the presoak solution, and hence the elution of mercury ceases once this is flushed from the column with the distilled water.

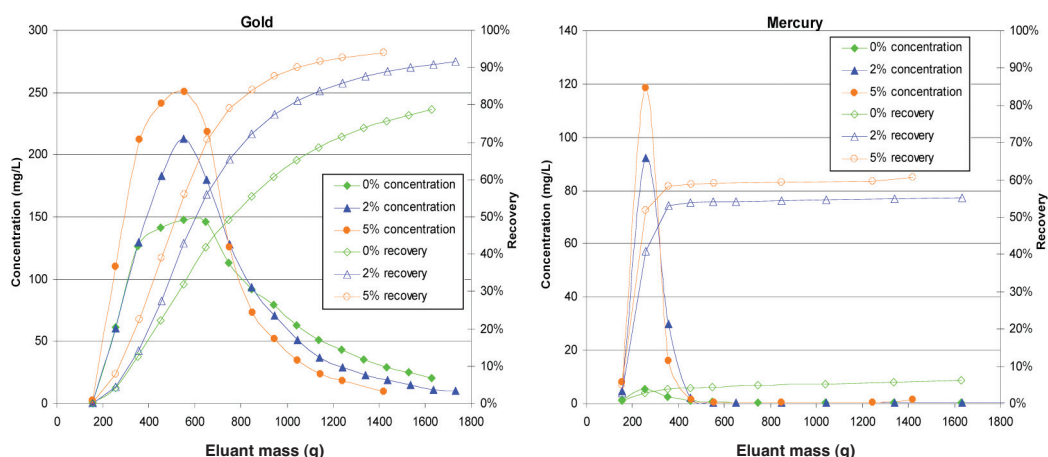


Figure 6. Effect of cyanide concentration in the soak stage on the concentration of gold and mercury in the eluant and the cumulative recovery for an AARL style elution

Pressure Zadra elution with high cyanide

The effectiveness of eluting metals with cyanidic eluant in place of deionized water was tested by utilizing a pressurized Zadra type elution at 130°C with 2% w/v NaCN + 2% w/v NaOH. This was undertaken in an attempt to establish whether the Zadra type systems are more effective at eluting mercury than the AARL process. The gold and mercury profiles are shown in Figure 7. It is interesting to note that the concentration profile for gold was poorer for the Zadra system, which was expected due to the high ionic strength of the eluant. However, the elution had not reached a plateau when the experiment was ceased, and the recovery profile indicates that given more time, the ultimate recovery of gold would be comparable to the AARL elution. The concentration profiles for mercury do not tail off as rapidly for the Zadra elution as they do for the AARL elution, providing further evidence that the presence of free cyanide is necessary to elute mercury from carbon. Even though the recovery of mercury with the pressure Zadra system was higher than the AARL system (76% and 56% respectively), the barren carbon still retained significant concentrations of mercury.

It should be noted that there is a small hump in the gold profile after 1 200 g of eluant; at this point, the flow was ceased, the column sealed and soaked at 130°C for 30 minutes prior to recommencing the flow. This was primarily done to assess whether additional soaking would improve the mercury elution. It is clear from Figure 7 that the gold concentration peaks and the mercury concentration dips temporarily, most likely as a result of the increased degradation of cyanide during the 30 minute soak period.

A further Zadra style elution was performed at the lower temperature of 110°C with 2% w/v NaCN + 2% w/v NaOH solution and no soak stage. The resulting profiles for gold and mercury are shown in Figure 8, along with the standard AARL elution profiles for comparison.

At 110°C, not surprisingly, the gold elution was significantly curtailed due to the combined effect of the higher ionic strength and lower temperature. The maximum gold concentration was only 19% of the peak value obtained with the AARL elution, and the gold recovery was only 34% after 1 900 g of eluant. Mercury elution, however, was much more effective at the lower temperature with cyanide, with an overall recovery of 87% being obtained. These results indicate that at 110°C, the degradation of cyanide in the column is significantly reduced, resulting a higher cyanide concentration, and hence better mercury recovery at the lower temperature.

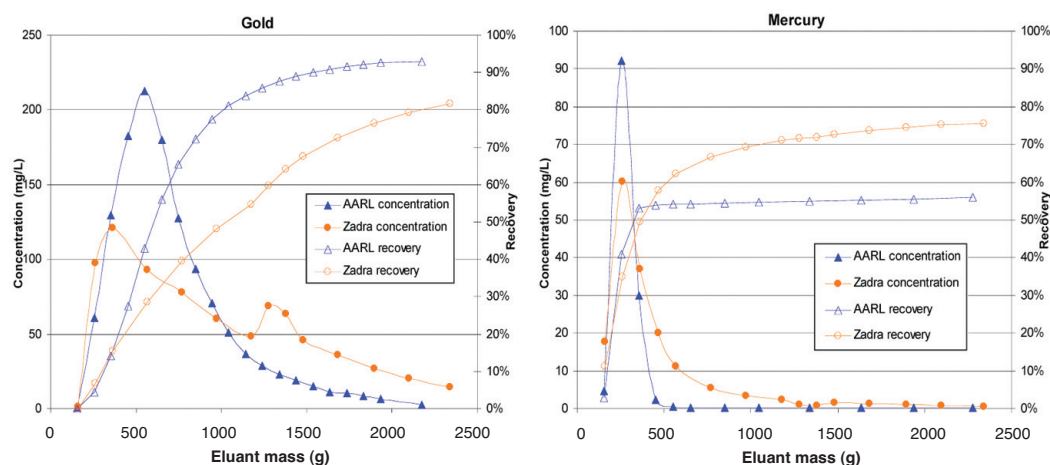


Figure 7. Comparison of Zadra and AARL style elution systems showing the concentration of gold and mercury in the eluant and the cumulative recovery of each metal at 130°C

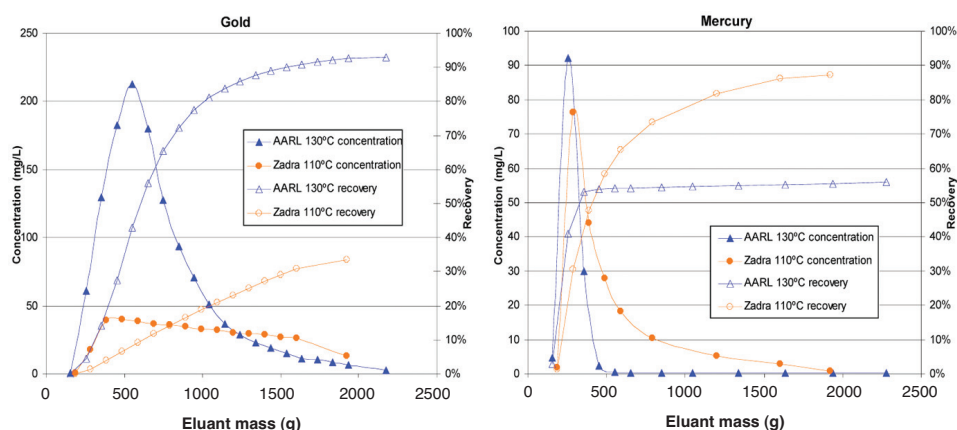


Figure 8. Comparison of Zadra elution at 110°C and AARL elution at 130°C, showing the concentration of gold and mercury in the eluant and the cumulative recovery of each metal

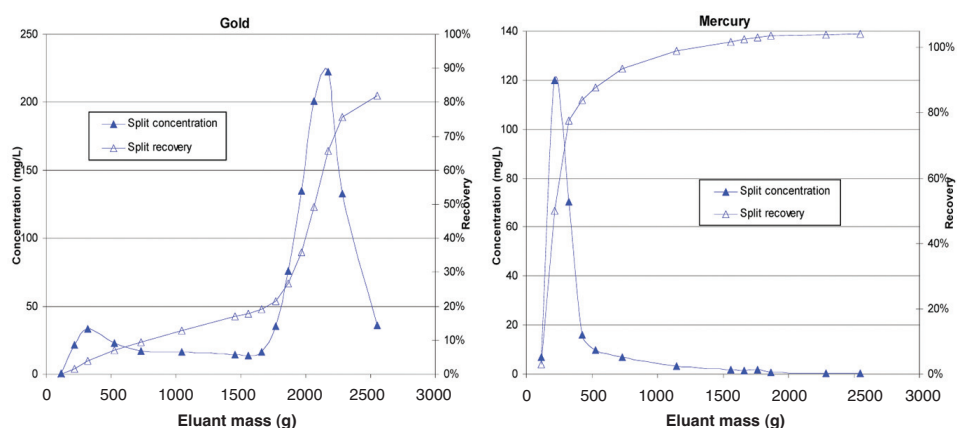


Figure 9. Split (two-stage) elution, with Zadra type eluant for the first 1 500 g, then a soak, followed by AARL elution at 130°C

Split elution: recovery of mercury and gold in separate eluant streams

An ideal elution is rapid, complete, and produces a concentrated solution of the metal of interest. The results presented so far indicate that optimum elution of mercury occurs under Zadra type conditions with a high concentration of cyanide and low temperature. In contrast, the optimum conditions for gold elution requires hot solutions with low ionic strength solution (i.e. AARL conditions). These conditions are mutually exclusive, and no viable balance between them was found where a high recovery of gold and mercury was obtained with a single eluant in a reasonable period of time. However, a split elution could be adopted where the mercury is initially eluted with a cyanide solution, followed by gold elution with distilled water. Figure 9 shows the profiles for such an arrangement, where ~1.5 L of NaCN + NaOH solution was passed initially at 90°C, followed by a soak stage at 130°C, and then ~1 L of deionized water. It can be seen that in this arrangement, almost complete mercury recovery was obtained within the first stage of elution. In the second stage of elution, the gold concentration profile was similar to the standard AARL profiles, and the recovery incomplete only as the experiment was truncated.

The split elution produces a gold-rich/mercury-cyanide-poor stream, and a mercury-cyanide-rich/gold-poor stream, and hence there is the possibility of treating the two streams separately. For example, the mercury-rich stream could be treated with sulphide to precipitate

the mercury as cinnabar (HgS, see Equation [1]) before recycle to avoid loss of gold, while the gold-rich stream can be directly electrowon.



Conclusions

Under the conditions employed, mercury elutes only in the presence of free cyanide. Gold elutes best in low ionic strength solutions at high temperatures (after being soaked in concentrated cyanidic solution). Cyanide decomposes on hot activated carbon, so mercury and gold elution require opposing conditions for efficient desorption. A split (or two-stage) elution system may allow for the practical elution of both metals and the possibility of separate treatment for each stream.

Future work

Optimization of the split elution conditions to achieve economic recovery and better separation of the two metals of interest are underway. Investigation of the deportment of other trace metals under elution conditions is also in progress.

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Matthew Jeffrey was awarded a Bachelor of Engineering (Chemical) with first class honours from the University of New South Wales in 1994, and a Doctor of Philosophy, from Curtin University (AJ Parker CRC for Hydrometallurgy) in 1998. Matthew has extensive research experience in hydrometallurgy, being based at Monash University for 8 years as a senior lecturer prior to joining CSIRO Minerals. He has published over 70 papers in the field, and holds a patent. Matthew is currently the CSIRO Research Program Leader for Gold Hydrometallurgy, and the Parker Centre gold market leader. Matthew's expertise and research interests include:

- Processing of gold using cyanide or thiosulfate
- Leaching and electrochemistry of gold and base metals
- Electrowinning
- Resin and carbon adsorption and elution
- Modelling and solution speciation
- Ion chromatography (for determining sulphur and cyanide speciation).

