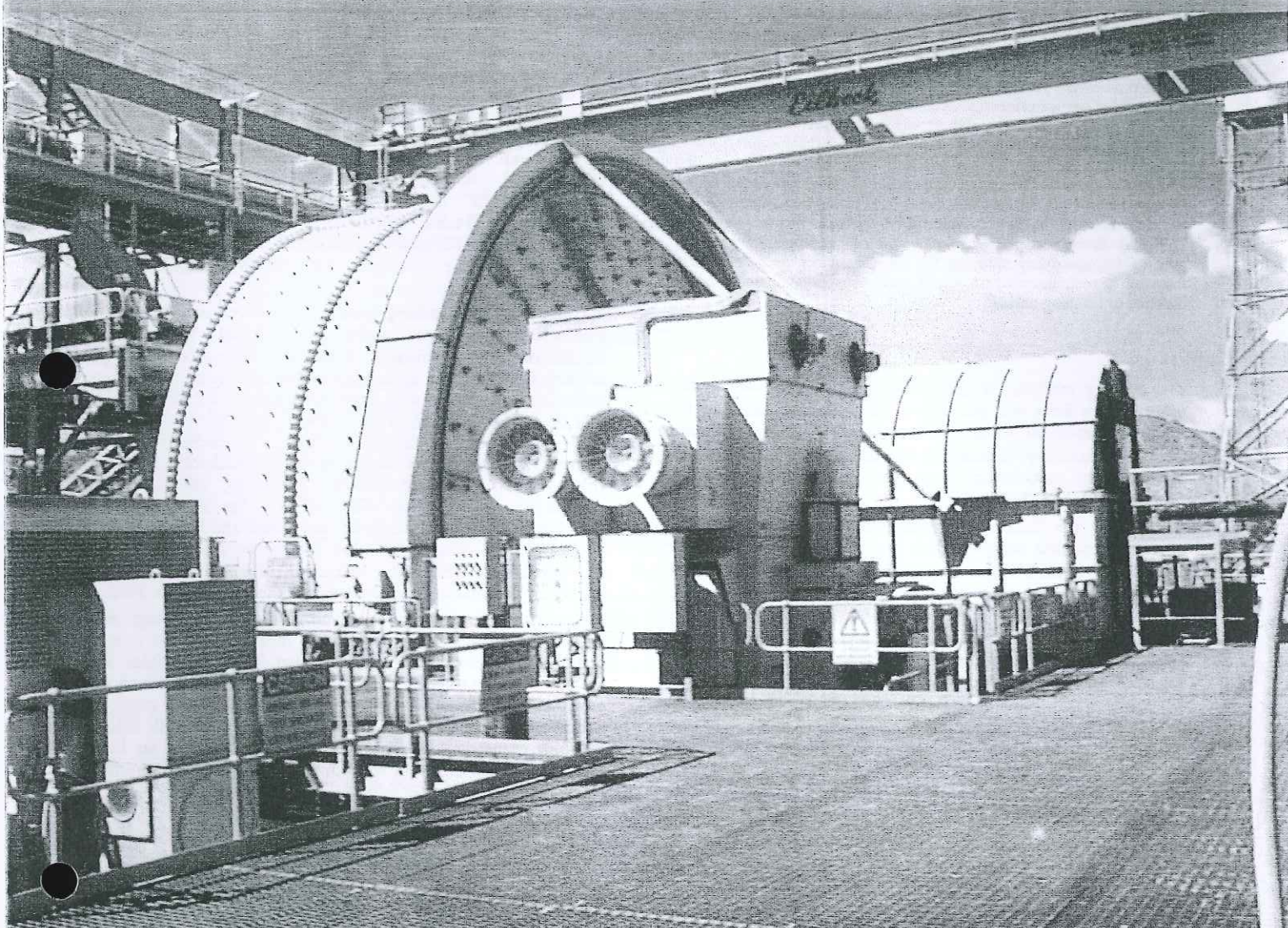


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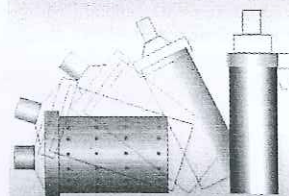
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Application of Alternative Lixiviants for Secondary Heap Leaching of Gold

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ABSTRACT

Some preliminary results on the secondary leaching of previously heap leached gold ore are presented. Alternative lixiviants for gold comprising chlorine, thiourea and thiosulphate were compared with cyanide using bottle roll tests. Chlorine was subsequently selected for column leaching tests. Column tests at 1.0, 0.1 and 0.01 gL⁻¹ Cl₂ at pH 2 were conducted. The results indicated that about 23 per cent of the gold was leached over 45 days using 1 gL⁻¹ Cl₂ at pH 2. The experiments conducted proved that the chlorine/chloride system has good potential for further extraction of gold and silver from the existing cyanide heap leach residues and a process for secondary leaching of gold has been proposed. Further testwork is recommended to extend conditions, sample types, and the duration of leaching period.

INTRODUCTION

The primary leaching of gold in dumps or heaps with cyanide often suffers from low recoveries. The extended leaching time offered by multiple lifts or layers can improve recovery, however the final recovery is limited by the degree of liberation, mineralogical associations and slow diffusion rates of the residual gold in the heap.

Currently the Telfer gold mine has processed 115 million tonnes of cyanide dump-leached ore with an overall recovery estimated at about 47.6 per cent. The material remaining in these heaps is estimated to have a grade of 0.38 g/t Au and so represents a potential resource of about 1.4 million ounces (Dunne and Reeve, 2000). Methods of increasing the recovery of gold from dumps and heaps that have undergone primary leaching are deserving of study. The potential of applying a secondary leach using a lixiviant other than cyanide was the subject of this study. In so doing, a change from alkaline cyanide to an acidic environment with chloride as a lixiviant was found to offer the hope of increased recovery of gold that is refractory or inaccessible to the primary leach system.

Besides better utilisation of fresh orebodies, new and improved approaches to leaching could transform the often-neglected old heaps, residues, tailing dams, and wastes from previous operations into potential metal sources. The aim of a leaching operation is to selectively dissolve the maximum amount of the valuable metal(s) with minimal co-extraction of impurities. This can be obtained with appropriate engineering of the process, choice of lixiviants and control of the conditions, and requires a sound understanding of the physicochemical characteristics of the minerals present and reagents used.

Cyanidation remains the primary technology for gold extraction; it is well explained, offers high selectivity for gold and is simple to use. Yet, the environmental issues of cyanide use and the decline in the number of high-grade gold deposits, along with the discovery of numerous large low-grade refractory deposits prompt the development of ways of improving gold extraction from refractory ores using alternative lixiviants. The most promising of these in recent times are thiosulphate, thiourea, and various halides including chlorine/chloride.

In this context, thiourea has been tested and proven efficient, however it suffers from similar problems to cyanide in terms of its dissolution of heavy metals and toxicity. Thiosulphate, a promising alternative reagent, still suffers from relatively slow kinetics of dissolution and difficulties in controlling the process so at present it remains a subject of intensive research. On the other hand, the aqueous processing technology using chlorine/chloride has a significant potential in treating metallurgical wastes (Staunton, 1998) and recovery of commercially viable products, especially in terms of optimising the recovery, while complying with health and environmental regulations.

Chlorination has a long history in gold leaching technology. Before being almost entirely abandoned following the establishment of cyanidation it was the main process for gold extraction through the second half of the 18th century. The major difficulties associated with chlorine/chloride leaching of gold at that time were the high price of the reagent, the high reactivity with base metal sulphides (resulting in excessive reagent consumption), the weak nature of the gold-chloride complexes compared to the gold-cyanide complexes, and its highly corrosive nature in acidic solutions. Yet, the kinetics of gold dissolution in chlorine/chloride are twice the rate achievable under standard cyanide leaching conditions (Nicol, 1987), and this system provides better extraction of gold from otherwise refractory carbonaceous gold ores (Marsden and House, 1992).

In recent years some of the main problems (ie the high price, unsuitability for tank leaching and lack of chlorine resistant equipment) have been overcome (Fagan, 1991 and 1991a). With the development of chlorinating cells (which allow production of cheap chlorine from sodium chloride), solar powered generators and modern heap leaching technology, combined with chlorine resistant materials, many of the old problems are no longer limiting. Chlorination in certain cases may offer significant advantages.

The following study was carried out in order to evaluate the potential benefit from further leaching of residual gold, particularly for secondary heap leaching, through application of cyanide, chlorine, thiourea, thiosulphate and hydrochloric acid. The experiments conducted proved that the chlorine/chloride system has good potential for further extraction of gold and silver from the existing cyanide heap leach residues and a process for secondary leaching of gold has been proposed.

DISSOLUTION OF GOLD IN THE CHLORINE/CHLORIDE LEACHING SYSTEM

Most of the leaching processes involve anodic or cathodic electron transfer from the metal element, countered by an equal but opposite transfer of electrons from the oxidising or reducing agent involved in the reaction. Gold commonly occurs in metallic form so the leaching involves oxidation of the metal. In order to simplify these reactions, they can be broken into two half-reactions and observed separately. The formal potential for a reversible half-reaction is given by the Nernst equation. The formal potential of the oxidising reagent has to be always more positive than the formal potential of the metal undergoing oxidation. A mixed potential, which has a value between the two formal potentials, is generated at the interface between the short-circuited cathodic and anodic sites, and is related to the rate of dissolution.

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The Au(I) and Au(III) ions are considered the only two significant oxidation states of gold. Gold is a typical 5d transition metal, where Au(I) has a 5d¹⁰ electronic configuration and Au(III) a spin-paired 5d⁸ electronic configuration, with polarising powers of different intensity. Owing to the lower polarising power, the Au(I) ions tend to form stronger bonds with less electronegative or soft donor ligands, while the Au(III) ions tend to form stronger bonds with more electronegative or harder donor ligands (Nicol, 1998). To be more precise, being soft metal ions both Au(I) and Au(III) tend to form strong bonds with the soft donor group of ligands which form p-bonds (ie cyanide, iodide, and ligands containing sulphur, selenium, phosphorous and arsenic donor atoms). However, the higher cationic charge of the Au(III) ion impedes the charge donation to the ligand and weakens the bond. In contrast, with harder donor ligands (ie chloride, amines, ammonia, nitrate, azide, and pyridine), where the bonding occurs by σ -bonding instead of π -bonding, the higher polarising power of the Au(III) ion results in strengthening of the σ -bond and Au(III) complexes form more readily than Au(I) complexes.

This rule is useful in predicting the nature and stability of the gold complexes and points to Au(I) as the prevailing state of gold where cyanide is the ligand and Au(III) as the prevailing state where chloride is the ligand (Nicol, 1998).

Gold is a very stable metal in pure water over a wide range of pH. The standard reduction potential of gold is higher than the standard reduction potential of water and for this reason the oxygen in water is not able to permanently oxidise gold to either Au(I) or Au(III) ions, as these ionic species are readily reduced back to metallic gold (Equations 1 and 2), and the water spontaneously oxidised back to oxygen (Equation 3). The standard reduction potentials for these half reactions (Lide and Frederikse, 1997) are given as:



However, with addition of suitable complexing agents (ie cyanide, chloride, thiosulphate or thiourea) which bond with the oxidised Au(I) or Au(III) ions and form complexes of lower standard potentials (see Equations 4 and 5) the equilibrium of the anodic half-reaction can be altered. Gold oxidised by a suitable oxidant (ie oxygen, chlorine, ferric ion) in aqueous solution can form a stable complex and remain in solution (Nicol, 1980; Hiskey and Atluri, 1988). This characteristic highlights the basis of the aqueous dissolution of gold.

The oxidation of gold and its complexation in acidic aqueous chloride solutions was found to form both Au(I) and Au(III) species by anodic half-reactions (Gallego *et al*, 1975; Nicol, 1980; Marsden and House, 1992; Schmid, 1985; Lide and Frederikse, 1997) given as:



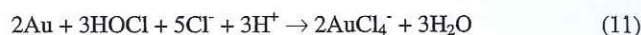
The cathodic reactions in the absence of oxygen are proposed as:



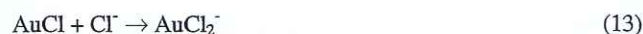
The full reactions for the process of dissolution of gold as Au(I) and Au(III) complexes respectively in chloride solution with chlorine as the oxidising agent can be represented with the following reactions:



Similarly, with hypochlorite as the oxidising agent the reactions would have the following form:



The mechanism for the dissolution of gold in acidic aqueous chlorine solutions (Equation 4) could involve initial formation of intermediate Au(I) chloride (Nicol, 1980) on the surface of the gold metal, followed by formation of secondary intermediate AuCl₂⁻ ions via reactions envisaged as:



The AuCl₂⁻ ions formed can either diffuse into the solution or in the presence of excess chlorine be further oxidised to Au(III) by the reaction:



The formal potential (E) for these reactions depends on the concentration and can be calculated from the Nernst equation. For Equation 4 it will have the following form:

$$E = E^\circ + RT/nF \ln [\text{AuCl}_2^-]/[\text{Cl}^-]^2 \quad (15)$$

Where the standard potential (E^o) relates to the stability constant for the formation of the complex (AuCl₂⁻) by the free energy changes ($\Delta G^\circ = -nFE^\circ$) for the referred couple, and n is the number of electrons involved in the reaction.

The electrochemical dissolution of gold in acidic chloride solutions takes place at potentials below 1.2 V with the formation of both Au(I) and Au(III) species (Nicol, 1980). It has been reported that at the potentials below 0.8V gold dissolves as Au(I) species, while at potentials of above 1.1 V it forms Au(III) species (Frankenthal and Siconolfi, 1982). In the potential range of 1.2 to 1.4 V, the reactions attain limiting current density controlled by the diffusion of chloride ions to the gold surface. At potentials above 1.5 V an oxide layer forms on the surface of the gold and hinders further dissolution, and at potentials above 1.6 V evolution of oxygen and chlorine gas takes place (Nicol, 1980).

Besides the oxidising effect of chlorine, the concentration of chloride in the leach solution has also been found to have a strong influence on the gold species formed (Equations 8 to 11). Nicol (1980) noted that the concentration of Au(III) decreases with the increase in chloride concentration, and increases with the increase in potential and stirring rate. On the Eh-pH diagram for Au-Cl-H₂O system (Figure 1), the boundary lines for the oxidation of gold to AuCl₂⁻ and AuCl₄⁻ shift to less positive potentials as the chloride concentration is increased.

Whilst the thermodynamics predict whether a reaction is possible or not, it is the kinetics which determine whether it actually occurs in a finite time and in a time frame acceptable for industrial application. The dissolution of gold in chloride

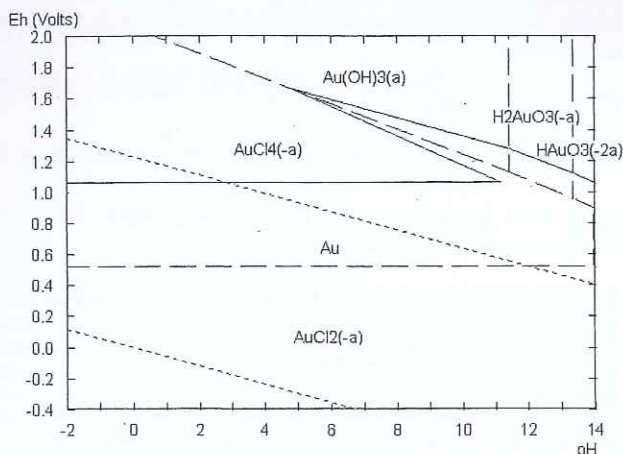


Fig 1 - Eh-pH diagram for the Au-Cl-H₂O system at 25°C, [Au] = 10⁻⁵ M and [Cl] = 10⁻² M.

solutions is controlled by the diffusion of either chlorine or chloride ion through the Nernst boundary layer to the gold surface.

The general requirement for a leaching process to occur is that at steady state the rate of the sum of the anodic reactions (r_a) is equal to the rate of the sum of the cathodic reactions (r_c):

$$r_a = r_c \quad (16)$$

For the full reaction in Equation 10, the rate of the anodic reaction (Equation 4) assuming a diffusion-controlled process with chloride concentration as in the bulk solution, $[Cl]_b$, where k is constant and D_{Cl} diffusion coefficient is given by:

$$r_a = k D_{Cl} [Cl]_b / 2 \quad (17)$$

Similarly, the rate of the cathodic reaction assuming hypochlorite as the oxidising agent (Equation 7) with concentration as in bulk solution, $[HOCl]_b$, is given by:

$$r_c = 2k D_{HOCl} [HOCl]_b \quad (18)$$

By substituting the expressions for r_a and r_c into Equation 16 we obtain the expression for the kinetics of the reaction shown in Equation 10:

$$[Cl]_b = 4[HOCl]_b (D_{HOCl}/D_{Cl}) \quad (19)$$

- 1) The recovery of gold from chloride solutions (Filmer *et al.*, 1984) in the past has mainly been accomplished by the use of cheap charcoal or activated carbon where it can yield very high loadings (>50 kg Au/tonne) of metallic gold (Avraamides *et al.*, 1985). Unfortunately, at present there is no elution procedure available, and the gold is recovered by burning the carbon. Solvent extractants and resins can also recover gold from chloride solutions (Kganyago, 1997).

EXPERIMENTAL

The material used in this work was a sample of cyanide heap leach residue from the Telfer gold mine in Western Australia. The average metal grades in the residue sample were gold 0.2 g/t, silver 0.3 g/t, and copper 424.6 g/t. Initial testwork, the results of

which are not presented here (Nikoloski, 1998), involving small bottle-roll leaching tests with 150 g of solid samples at 45 per cent solids rotated at 80 rpm, indicated that a considerable part of gold could still be successfully extracted. Based on these preliminary findings, a series of large bottle-roll and column leaching experiments were performed and are presented.

The large bottle-roll experiments were performed with 500 g of solid sample at 50 per cent solids rotated at 80 rpm. The head-grades for each run were calculated after the assay of the tails.

Chlorine leaching was conducted with initial levels of NaOCl of 20 mL⁻¹ and NaCl of 50 gL⁻¹, at pH values of 2, 5.5 and 7, where the measured redox potentials were 1.37, 1.26 and 1.11 V/SHE respectively. A single leach was also done with hydrochloric acid at pH 2 for comparison. In the cyanide leach experiment the solution was prepared with an initial level of NaCN of 400 g/t and an initial pH of 12.1 adjusted by addition of 1.5 kg/t lime. The thiourea leaching was performed with CS(NH₂)₂ at an initial level of 2 gL⁻¹ and FeCl₃ of 1 gL⁻¹. The pH value of the slurry was 1.5 and the redox potential measured as 0.6 V/SHE. The thiosulphate leach was performed by addition of 0.1 molL⁻¹ Na₂S₂O₃ × 5H₂O, 0.1 molL⁻¹ NH₃ and 5 × 10⁻⁴ molL⁻¹ Cu as catalyst. The pH was adjusted at 9 and the redox potential measured 0.18 V/SHE.

Column leaching tests with chlorine were conducted in three columns for up to 45 days. The columns were all run at pH 2 and 1.0 gL⁻¹ sodium chloride (NaCl) but with different concentrations of chlorine in solution (1 gL⁻¹, 0.1 gL⁻¹ and 0.01 gL⁻¹ respectively). The experimental arrangement is shown in Figure 2.

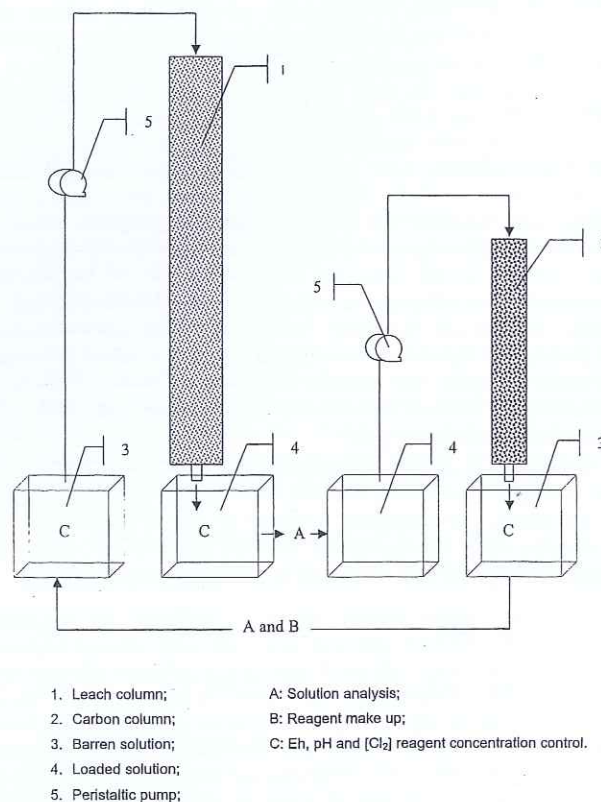


Fig 2 - Schematic presentation of a single column leach-carbon adsorption set-up.

At first, the leaching was carried out over a period of 14 days, during which time detailed analysis of samples were performed. To extract the leached gold, the solution coming out of each leach column was also run through a second column filled with 300 g of fresh coconut activated carbon. After the completion of the 14-day experiments the loaded carbon from each column was pulverised and sampled. The samples were placed in crucibles and burnt in a kiln at 830°C. The ash was digested in aqua regia and analysed by AAS.

After the first 14-day run the column leaching experiments were extended for an additional 30 days during which time only samples of the loaded solutions were taken for analysis. Carbon columns were not used. The concentration of reagents in the barren solution was made up to the required level and recirculated directly back into the leach column.

RESULTS AND DISCUSSION

Preliminary testwork involving small bottle roll tests indicated that even though the concentration of gold in the heap leach residue is very small a considerable part of it could still be successfully extracted. The best extractions were observed with chlorine, followed by cyanide, thiourea, and thiosulphate. The results from the large bottle-roll experiments confirmed these findings and provided more precise data for the leaching performance of the different types of lixiviants. As shown in Figure 3, the highest gold extraction of over 63 per cent after approximately 50 hrs is achieved with chlorine/chloride solution at pH 2.

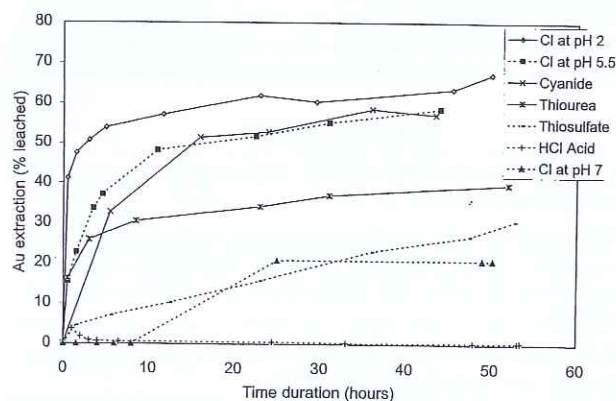


FIG 3 - Gold extraction from the large bottle roll leaching tests.

The extraction of silver (Figure 4) also triggers interest for further work. It appeared that 100 per cent extractions of silver are possible with the use of chlorine solutions at various pH values.

The observed extractions of silver from the large bottle roll tests appeared unpredictable later in the column leaching work. Rapid changes in the concentration of silver in the collected solution were observed and further testing is recommended. Based on the good results from the bottle roll leaching tests, the main interest was given to the chlorine/chloride leaching system and evaluation of the optimal conditions.

The dissolution of copper presented in Figure 5 was below 20 per cent with all of the reagents tested, except for thiourea which leached around 38 per cent of the copper.

A set of three leaching columns (160 mm dia; 2 m long) followed by carbon adsorption columns were set up to evaluate the leaching capacity of the chlorine/chloride system. The arrangement of the equipment was done in a way that simulated

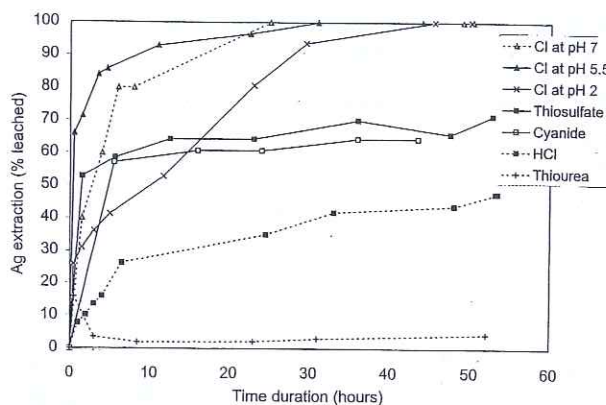


FIG 4 - Silver extraction from the large bottle roll leaching test.

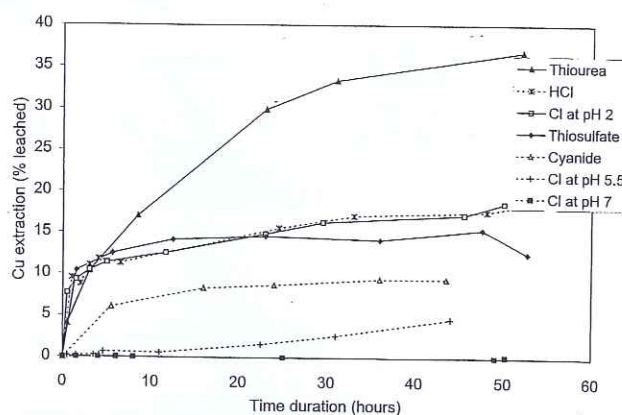


FIG 5 - Copper extraction from the large bottle roll leaching test.

a complete process of leaching, adsorption and elution, although the last of these operations did not give satisfactory results. The results indicated that although relatively slow, the dissolution rate for gold does not decrease with time and over 45 days approximately 23 per cent of the gold was extracted with a solution containing 1 gL⁻¹ chlorine at pH 2. The results look promising and suggest that over a longer leaching time higher final extractions can be reached. The dissolution curves of gold for the three different concentrations of chlorine in solution are presented in Figure 6. The shape of the curve for 1 gL⁻¹ indicated that the material in the column was still leaching when the test was terminated.

The lack of dissolution in the initial stages of the column leaching can be attributed to the time required for the solution to percolate through the column and the solution flow required for the chlorine/chloride solution at pH 2 to counter the remaining alkalinity of the material from the previous alkaline cyanide heap leach process.

The dissolution of silver and copper with time was also monitored and the corresponding dissolution curves as functions of time are presented in Figures 7 and 8.

Several forms of chloride may be considered for the chlorination of gold. Both sodium and calcium hypochloride are readily available, although the latter with sulphuric acid forms gypsum that might be deleterious to heap leaching by its precipitation and resultant loss of percolation. Bottled chlorine gas may also be considered, while an alternative is the on-site chlorination of salt water which is prevalent in WA.

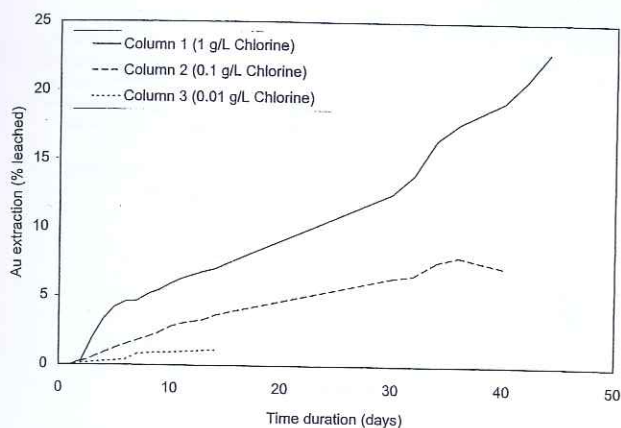


Fig 6 - Gold extraction from column leaching tests.

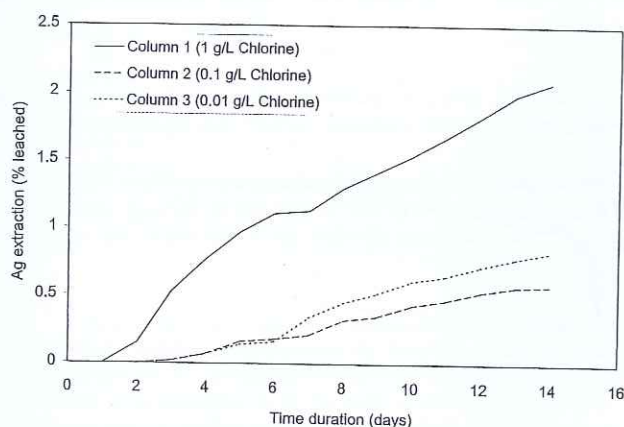


Fig 7 - Silver extraction from the column leaching tests.

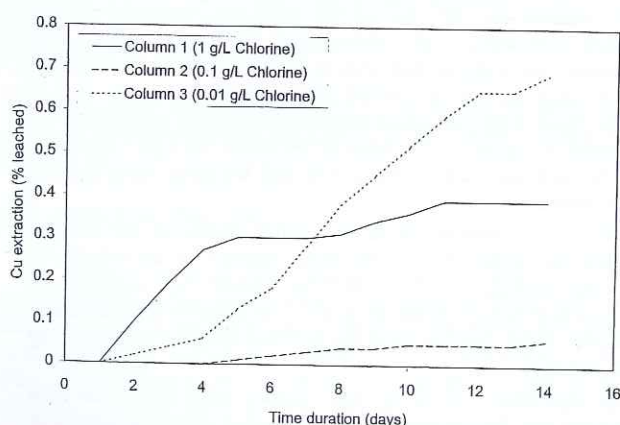


Fig 8 - Copper extraction from the column leaching tests.

The chlorination process could be automated by combining the heap leach system with solar energy sources for the pumps and electrolytic generation of chlorine as presented in Figure 9.

Solar arrays, solar pumping systems and chlorinating cells are nowadays readily available commercial products.

To reduce the evaporation of chlorine, the leach solution can be introduced with drippers buried below the surface of the heap. The process could operate with minimal supervision and the equipment could be transferred from one leached heap to another. Running a system like this over extended periods of time (such as six months or a year) could provide additional economic benefit for the mineral industry.

The proposed method for the gold recovery from solution is by carbon adsorption. The gold chloride complexes are readily deposited on activated carbon, but since gold from chloride complexes deposits on carbon in the form of metallic gold, a method for efficient elution is not available. A simple process for recovering the gold in this study was burning the carbon followed by digestion of the ash in aqua regia. The burning accounted only for 50 per cent of the expected seven per cent of gold from the first 14-day run, but at the low gold concentrations on the carbon this is likely to have been due to experimental or analytical errors.

Indeed analytical errors do cause concern when dealing with such low head grades and solution concentrations associated with secondary heap leaching. A pilot plant run over a longer period of time could test the efficiency of the process and also provide higher gold concentrations which in turn will reduce analytical errors.

Under industrial conditions, the gold could effectively be recovered from solution by the use of cheap charcoal, burnt after the gold deposited on it reaches a sufficient concentration. This would not be an ideal solution, but until an efficient way of eluting this gold from carbon is found or suitable solvent extractants or resins for recovery from acidic chloride solutions is developed, carbon burning may prove an economical solution.

CONCLUSIONS

The testwork carried out during this project leads to the following conclusions:

- The application of a chlorine/chloride leaching system for secondary heap leaching provides significant additional extraction of gold and silver from the primary leached residue.
- Additional work is recommended to test the efficiency of the process over extended periods of time.
- The availability of chlorinating cells and solar energy provide conditions for automated application of secondary leaching with minimal operator assistance.
- Carbon loading can be used as a simple and effective method for gold loading, but requires burning the carbon to recover the gold.

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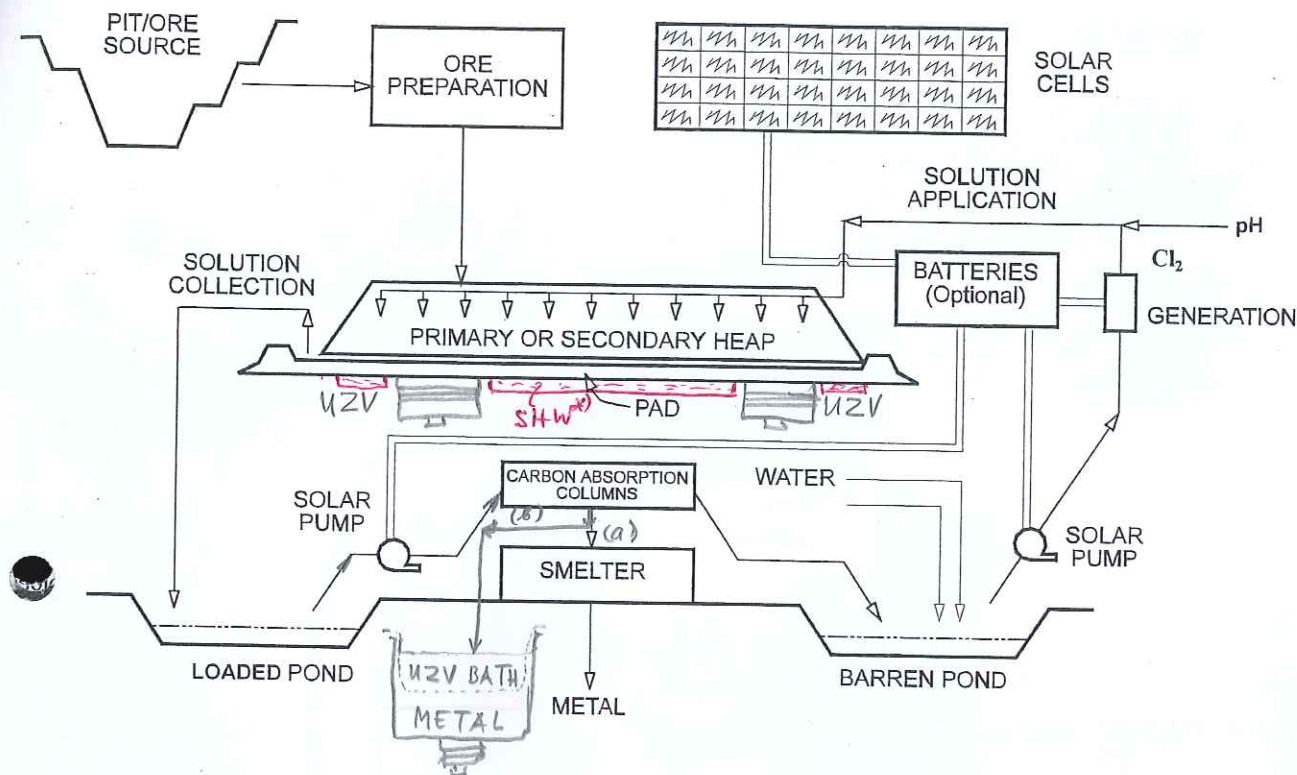


Fig 9 - Conceptual flowsheet for the proposed chlorine/chloride secondary heap leach process (after Nikoloski, 1998).

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$$E = [h\nu] = h \frac{c}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$E = 1 \text{ eV} = 1.6 \cdot 10^{-19} \text{ J}$$

$$\lambda = 1,24 \text{ } \mu\text{m}$$

