

SELECTIVE COPPER REMOVAL FROM CUPRIFEROUS GOLD CONCENTRATE^①

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ABSTRACT Oxygenated chloride leaching process was tested on a Telfer off-grade copper-gold bulk concentrate to justify the pretreatment of gold materials containing considerable copper sulfides. It has proven to be feasible for extracting copper under rather mild conditions and leaving pyrite intact. Nearly 98% of copper was leached by this process using 0.5 mol/L chloride at 85 °C and only 0.2 g/L iron was transferred into the pregnant solution.

Key words: copper selective leaching cupriferous gold concentrate

1 INTRODUCTION

Copper minerals come only after pyrite and arsenopyrite as the primary host metal sulfide minerals associated with gold. Most copper deposits were found to contain gold to more or less extent. It is preferable to produce by flotation a concentrate suitable for smelting and refining on site or for shipment to a smelter. This leaves the contained gold to be recovered from anode slimes. Unfortunately, many respond poorly to flotation. This is particularly true when ores are oxidized partially or completely, and/or contain too small an amount of copper or too great an amount of pyrite. The exploitation of such copper-gold resources represents a great challenge to mineral industry.

Telfer is a very large copper-gold mine in Western Australia. It currently produces a copper-gold bulk concentrate from its high grade ores using controlled potential sulfidization (CPS)-flotation process and ships it to Japan for smelting the copper and recovering the contained gold from the anode slimes. With an increase in the content of pyrite in the high grade copper-gold ores, the bulk concen-

trate has suffered from the entrainment of pyrite. The attempts to reject pyrite from the concentrate have failed because a discardable tailing cannot be produced. Only a floatation concentrate of 15~20% Cu is obtained from a feed containing 3~4% Cu, which makes the shipment of the concentrate overseas uneconomical. Therefore, an alternative process is needed to be developed for recovering both copper and gold from such a low-grade concentrate. As copper minerals are cyanide materials it is proposed to leach copper prior to the recovery of gold by cyanidation^[1]. The process selection for the copper leaching from the concentrate was based principally on its mineralogy:

(1) The dominant copper minerals in the concentrate are chalcocite/digenite, which are rather easy to leach using relatively moderate conditions.

(2) More than 99% of gold in the concentrate is accessible to cyanide solution and little is locked in pyrite. It is not, therefore, required for gold recovery to decompose pyrite prior to cyanidation.

(3) Pyrite accounts for almost half of the concentrate mass and contributes more than

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three fourths its sulfur content, significant additional benefits can be expected from the avoidance of pyrite oxidation in the pretreatment process.

Oxygenated chloride leaching process was chosen to be investigated due to its high selectivity over pyrite and its ability to leach a wide range of copper minerals at moderate temperature without requiring expensive autoclaving or roasting.

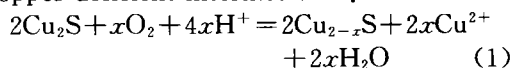
2 RESULTS AND DISCUSSION

Oxygenated chloride leach processes use oxygen in the presence of chloride to oxidize mineral sulfide to sulfur thereby releasing the metal values associated with it to solutions. The processes operate in dilute sulfuric acid with low chloride concentration, relatively moderate temperature and atmospheric pressure. Preliminary tests showed 95% Cu was readily extracted in 2 h under the following conditions: 0.3 mol/L H_2SO_4 , 0.5 mol/L NaCl, 150 mL/min O_2 , L/S ratio (v/w) 25:1, 85 °C, therefore these were taken as the standard leach conditions in this study, unless otherwise stated. It should be noted also that the leach pulp was oxygenated for 2 h at leaching temperature before the commencement of a test by introducing lixiviant into the solution. The main test results are given below.

2.1 Copper Leaching as Function of Time

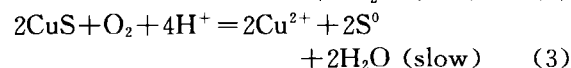
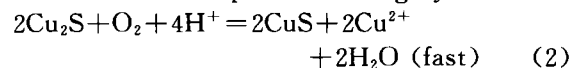
The copper extraction from Telfer chalcocite concentrate under the standard leaching conditions is depicted as function of time in Fig. 1. The leaching proceeded very fast initially then slowed down and finally reached a plateau.

It is generally agreed that chalcocite dissolution takes place in two stages^[2]. It is oxidized stepwise at first to covellite via a series of copper deficient intermediates:



where $x \rightarrow 1$, which corresponds the formation of covellite. The intermediates identified in-

clude: djurleite $\text{Cu}_{1.96}\text{S}$, digenite Cu_9S_5 and a new copper sulfide Cu_7S_5 ^[3] and a new copper sulfide Cu_7S_4 . The produced covellite is oxidized further to cupric ions, and the reactions involved can be represented roughly as



with the net reaction as



The oxidation of covellite actually occurs in parallel to that of the remaining chalcocite but at a much slower rate. The first part of chalcocite leaching curve does not, therefore, represent the true dissolution behaviour of chalcocite but the combined dissolution of chalcocite and covellite. However, the contribution of covellite dissolution to the copper extraction is very small initially. The first stage, commonly taken as up to 40% copper extraction, can be considered to describe approximately the rate of chalcocite dissolution.

2.2 Effect of Copper(II)

As shown in Fig. 1, no difference was

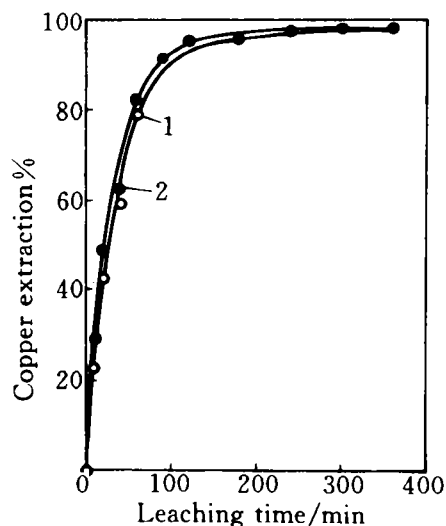


Fig. 1 Oxygenated leaching of a chalcocite concentrate in acidified brine solution

NaCl 0.5 mol/L; H_2SO_4 0.3 mol/L; O_2 150 mL/min, 85 °C; 1—Cu(II) 0 mol/L; 2—Cu(II) 0.1 mol/L

made by adding 0.5 mol/L CuCl_2 , provided preoxygenation of the slurry is carried out (see below). This reflects that the high reactivity of chalcocite and the ease of oxidation of Cu (I) by oxygen in the system.

2.3 Effect of Chloride Concentration

A series of tests were run with different concentrations of chloride using 0.3 mol/L H_2SO_4 , 150 mL/min O_2 at 85 °C to examine the effect of chloride concentration. As can be seen from Fig. 2, the leaching proceeded slowly without chloride addition, but the copper extraction was speeded up significantly by adding chloride up to 0.1 mol/L NaCl, at which chloride level nearly 95% copper in concentrate was leached within 3 h. Further increases in the chloride concentration did not show additional benefit for copper extraction. This contrasts with the cupric chloride leach system which required much higher total chloride concentrations, e. g. 5 mol/L, for satisfactory copper leaching, as seen previously^[1]. The difference in chloride requirements be-

tween the two leach systems can be explained as follows. The leached copper is in the cuprous state in the cupric chloride leach system but essentially in the cupric state in the chloride-oxygen leach system. Therefore chloride required for coordination with cuprous to prevent it from conversion into covellite by elemental sulfur is much lower for the latter than for the former. Furthermore chloride does not affect the Eh and mixed potential for leaching in the oxygen system. The very low chloride concentration requirement is the principal advantage of the chloride-oxygen leach system.

2.4 Effect of Sulfuric Acid

The leaching rate of copper increased as sulfuric acid was added up to a concentration of 0.3 mol/L, but further increases in sulfuric acid concentration made little difference as shown in Fig. 3. This is another difference from the cupric chloride leach system, where sulfuric acid showed little effect. The increase in sulfuric acid concentration promotes the copper extraction as expected from equation

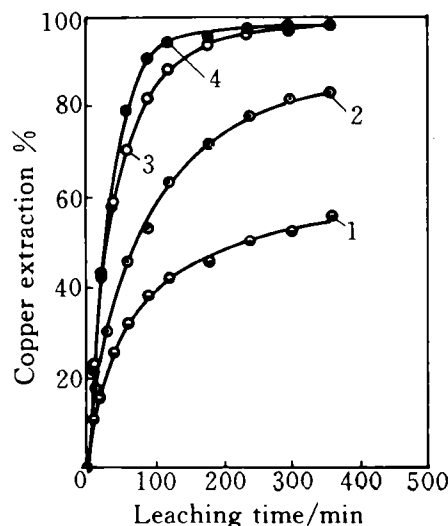


Fig. 2 Effect of chloride concentration on leaching

H_2SO_4 0.3 mol/L; O_2 150 mL/min;
L/S=25:1 v/w, 85 °C

1—chloride 0 mol/L; 2—chloride 0.04 mol/L;
3—chloride 0.1 mol/L; 4—chloride 0.5 mol/L

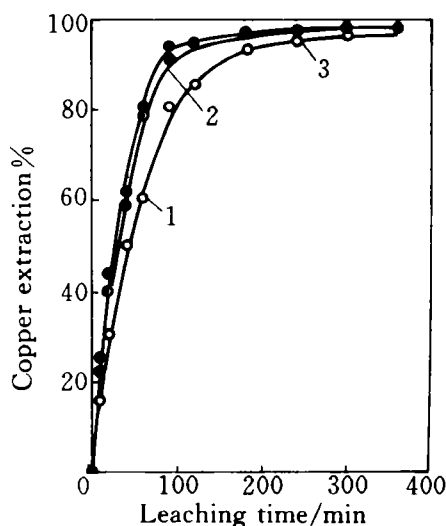


Fig. 3 Effect of sulfuric acid on the leaching

NaCl 0.5 mol/L; O_2 150 mL/min;
L/S=25:1 v/w, 85 °C

1— H_2SO_4 0.1 mol/L; 2— H_2SO_4 0.3 mol/L;
3— H_2SO_4 0.6 mol/L

(2) and (3) but reaches a steady oxygen diffusion controlled rate once sufficient acid is present. High acid and salt concentrations can be expected to decrease oxygen solubility^[4] and hence the rate of leaching.

2.5 Effect of Oxygen Flowrate

Fig. 4 shows the effect of oxygen flowrate on the chalcocite leaching in 0.3 mol/L sulfuric acid solution with 0.5 mol/L NaCl at 85 °C. The copper leaching rates increased initially with an increase in the oxygen flowrate then becomes constant, indicating that the pulp was saturated with oxygen. The total copper extraction as high as 98% was achieved after 4 h leaching for all oxygen flowrates tested.

2.6 Effect of Pre-oxygenation

All the tests above made use of 2 h pre-oxygenation to saturate the leaching solution and pulp minerals with oxygen. Several pairs of comparative tests were run under identical conditions but with different extent of pre-

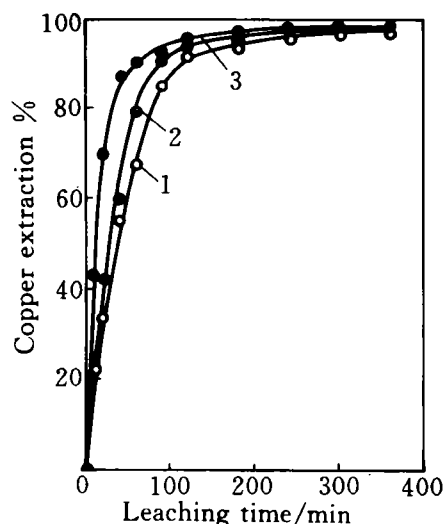


Fig. 4 Effect of oxygen flowrate on the leaching

NaCl 0.5 mol/L, H₂SO₄ 0.3 mol/L, 150 mL/min, L/S=25:1 v/w, 85 °C
1—O₂ 50 mL/min; 2—O₂ 150 mL/min;
3—O₂ 300 mL/min

oxygenation. Fig. 5 indicates that under the three leaching conditions tested the copper extractions without pre-oxygenation occurred much slower. This once again shows the importance of the oxygen concentration in the leach pulp, and saturation of the mineral surfaces and pores with oxygen. The relative importance of the dissolved oxygen in solution and adsorbed oxygen on mineral surfaces however remains to be evaluated. It was not possible to directly measure dissolved oxygen at the temperature employed in these tests but it can be predicted to be $<1 \times 10^{-3} \%$ ^[4].

2.7 Effect of Liquid to Solid Ratio

Tests with three liquid to solid ratios were done to examine its effect. Higher L/S ratios were shown to be favourable for copper leaching as seen in Fig. 6, but leaching dilute pulp obviously decreases throughput. On the other hand, similar copper extraction can be achieved with a relatively low L/S ratio pro-

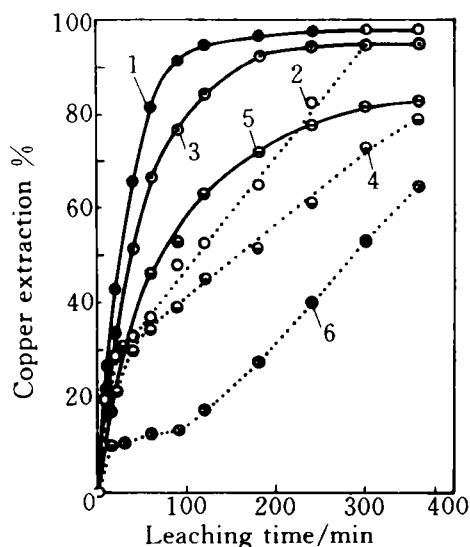


Fig. 5 Effect of leach slurry preoxygenation on the leaching

curves	NaCl/ mol·L ⁻¹	H ₂ SO ₄ / mol·L ⁻¹	O ₂ / mL·min ⁻¹	S/L (%)
1	0.5	0.3	600	4
2	0.5	0.3	600	4
3	0.5	0.6	1200	10
4	0.5	0.6	1200	10
5	0.04	0.3	600	4
6	0.04	0.3	600	4

1, 3, 5—2 h preoxygenation; 2, 4, 6—no preoxygenation

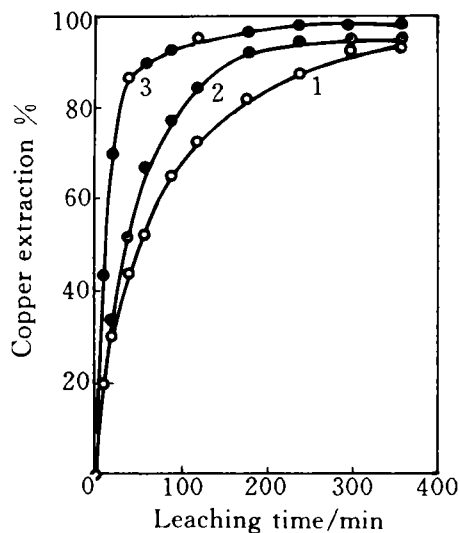


Fig. 6 Effect of liquid to solid ratio on the leaching

NaCl 0.5 mol/L; H_2SO_4 0.6 mol/L;
 O_2 300 mL/min, 85 °C

1—L/S=5:1 V/W; 2—L/S=10:1 V/W;
 3—L/S=25:1 V/W

vided that the leaching time extended appreciably. The proper compromise between L/S ratio and leaching time depends principally on the concentrate grade, and on the efficiency of oxygen mass transfer to the solution.

2.8 Fate of Pyrite

The pyrite in the concentrate was found to remain essentially untouched, as expected, and iron in the pregnant liquor was therefore less than 0.2 g/L. This offers additional benefits because of saving the reagents for pyrite oxidation and subsequent neutralization of leaching solution and by passing the troubles caused by iron in the solution.

2.9 Effect of Temperature

Temperature dependency was not tested. It is expected that a rise in leach temperature will enhance leaching on the one hand, but on the other hand decrease the solubility of oxygen in unpressurized vessels, which will affect the leach reaction adversely. Thus there

should be an optimum temperature range. In practice, the appropriate temperature range for chloride-oxygen leaching of copper sulfide is recommended to be 85 ~ 90 °C^[5,6]. Hence leaching at 85 °C was used in this work which proved to be sufficient. Of course pressured vessels will allow higher temperatures and use of higher pulp densities but this needs to be justified and is outside the scope of this study.

3 CONCLUSIONS

A copper sulfide concentrate from the Telfer Mine was tested with chloride-oxygen leach system. The results obtained showed:

(1) The oxygenated leaching in acidified brine solution proves to be efficient for leaching a Telfer off-grade copper-gold bulk flotation concentrate which contains chalcocite as the dominant copper mineral. Nearly 98% of copper present in the concentrate was leached within 4~5 h

(2) The leaching process studied shows rather selective over pyrite, which remains intact during the leaching and iron in the pregnant solution was found to be less than 0.2 g/L. This avoids iron contamination of the pregnant liquor and reduces the amount of oxidant required as well as the amount of elemental sulfur or sulfuric acid produced. It also simplifies the downstream recovery of copper and gold;

(3) Oxygenated sodium chloride leaching of the concentrate can be operated under milder conditions than cupric chloride leaching, with chloride addition as low as 0.5 mol/L and a leaching temperature of 85 °C. With pre-oxygenation of the pulp, it was not necessary to add copper(II) salt to initiate the reaction.

(4) More than 95% of reacted sulfide sulfur is present as elemental sulfur, which account for about 8% of residue mass. This sulfur is expected to interfere with gold cyanidation of the residue, thereby necessitating a search for a process suitable for either gold extraction from sulfur bearing materials, or to sulfur removal prior to cyanidation of the residues.

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(From page 24)material comminution.

(2) Proceed from catastrophe, irreversibility, state deviating far from equilibrium in the process of material comminution, the fundamental conditions forming dissipative structure are studied.

(3) Proceed from the unstability and stability of the state of material system, the mechanism research of material comminution is carried to the category of nolinear thermodynamics and nonlinear dynamics.

(4) System response to nonequilibrium constraints of outside is better described when extra entropy is regarded as the Lyapounov function of material system in order to judge the stability of the system.

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