The dissolution of gold from roasted pyrite concentrates

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SYNOPSIS

A study of the dissolution of gold from a pyrite concentrate and from various calcines is reported. The percentage extraction of gold was found to decrease with increasing sulphur content in the material leached because of the porosity of the materials, and particularly because of the passivation of the anodic dissolution of gold when the gold was in contact with other conducting minerals. This is explained in terms of the current-potential curves for the oxidation of gold and the reduction of dissolved oxygen.
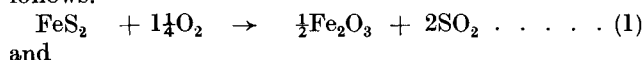
SAMEVATTING

Daar word verslag gedoen oor die oplossing van goud uit 'n pirietkonsentraat en uit verskillende kalsiene. Daar is gevind dat die persentasie goudekstrak afneem met'n toenemende swawelinhoud in die materiaal wat geloog word vanweë die poreusheid van die materiale en veral omdat die anodiese oplossing van goud gepassiveer is waar die goud in aanraking met ander geleidende minerale was. Dit word verklaar in terme van die stroompotensiaalkrommes vir die oksidasie van goud en die reduksie van opgeloste suurstof.
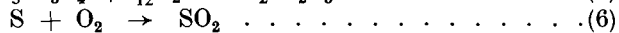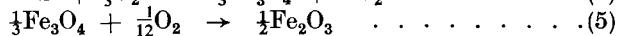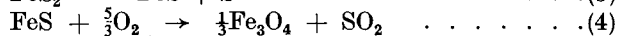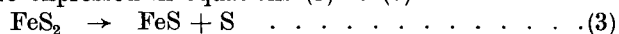
Introduction

Gold that occurs in association with pyrite or arsenopyrite is often not amenable to extraction by cyanidation. For this reason, several plants for the recovery of gold include flotation of a sulphide concentrate and roasting of this material at 700 to 850°C.

The reactions that take place can be expressed as follows:

$$FeS_2 \quad + 1\tfrac{1}{4}O_2 \quad \rightarrow \quad \tfrac{1}{2}Fe_2O_3 + 2SO_2 \quad \ldots \ldots (1)$$

and

$$FeAsS + \tfrac{5}{2}O_2 \quad \rightarrow \quad \tfrac{1}{2}Fe_2O_3 + \tfrac{1}{2}As_2O_3 + SO_2 \quad (2)$$
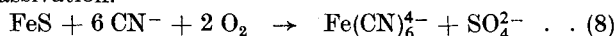
This treatment liberates the gold, making it more amenable to extraction, and produces sulphur dioxide, which can be converted into sulphuric acid. The roasting of the sulphide is a complex reaction, and several intermediate materials are formed during the process. These are expressed in equations (3) to (7)

$$FeS_2 \rightarrow FeS + S \quad \ldots \ldots \ldots \ldots \ldots .(3)$$
$$FeS + \tfrac{5}{3}O_2 \rightarrow \tfrac{1}{3}Fe_3O_4 + SO_2 \quad \ldots \ldots .(4)$$
$$\tfrac{1}{3}Fe_3O_4 + \tfrac{1}{12}O_2 \rightarrow \tfrac{1}{2}Fe_2O_3 \quad \ldots \ldots \ldots .(5)$$
$$S + O_2 \rightarrow SO_2 \quad \ldots \ldots \ldots \ldots \ldots .(6)$$
$$SO_2 + \tfrac{1}{2}O_2 \rightarrow SO_3 \quad \ldots \ldots \ldots \ldots .(7)$$

Since not all the particles are at equilibrium during the roasting process, a mixture of these products might be obtained. To maximize the production of sulphuric acid, the sulphur content of the calcine must be reduced to a minimum, but the roaster must operate under a slight deficiency of oxygen to prevent the formation of sulphur trioxide. The gold extractions from the resulting calcine were found to increase with the degree of oxidation. In plant practice, a compromise is reached between the production of sulphuric acid and of gold, a calcine being produced that contains predominantly hematite with some magnetite. The reasons for the poor gold extraction from incompletely roasted calcines have not been established conclusively, and form the subject of this paper.

Factors that affect the extractability of gold from

calcines are the roasting temperature[1,2], the residual sulphur in the calcine[3], and the degree of sulphation of the calcine[4]. The poor extractions obtained at high roasting temperatures are thought to be due to the sintering of the particles, resulting in physical encapsulation of the gold. The effects of residual sulphur on the extraction of gold during leaching has been attributed to a number of factors. These include the consumption of oxygen in the leaching solution by reactions like those expressed in equations (8) and (9), i.e. the consumption of cyanide by the same reactions, incomplete formation of the porous oxide structure during roasting (which means that less gold is exposed to the leaching solution), and the formation of a film of reaction products on the surface of the partially leached gold thus causing passivation.

$$FeS + 6CN^- + 2O_2 \rightarrow Fe(CN)_6^{4-} + SO_4^{2-} \quad . \quad . \quad (8)$$
$$S_2O_3^{2-} + CN^- + \tfrac{1}{2}O_2 \rightarrow SCN^- + SO_4^{2-} \quad . \quad . \quad .(9)$$

No reasons have been proposed for the effect of sulphation roasting on the subsequent gold extraction. However, the lower roasting temperature appears to be the principal factor affecting the subsequent dissolution of the gold.

The dissolution of gold in cyanide media is known to be due to an electrochemical reaction. The anodic reaction is the dissolution of gold,

$$Au + 2CN^- \rightarrow Au(CN)^- + e^-, \quad \ldots \ldots (10)$$
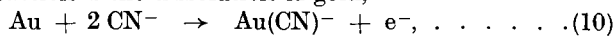
whereas the cathodic reaction is the reduction of oxygen,

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-, \quad \ldots \ldots \ldots (11)$$
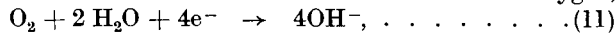
The anodic reaction has been studied extensively and was reviewed fairly recently[5]. It will therefore not be dealt with in detail in this paper. Instead, the combination of the two half-reactions and their effects upon each other during the reactions will be discussed.

Experimental

A sample of pyrite concentrate and calcine from a local gold mine were used in this study, and several partially roasted calcines were produced at the National Institute for Metallurgy, now the Council for Mineral Technology (Mintek). The analyses of these materials are given in Table I. All the other materials used in the study were of chemically pure grade or better.

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TABLE I

TABLE I

ANALYSIS OF MATERIALS USED IN THIS STUDY

Material	Analysis	
	Sulphur %	Gold p.p.m.
Pyrite concentrate	43	3,56
Calcine	0,10	4,35
Partially roasted calcine A	13,5	4,02
Partially roasted calcine B	6,7	4,10

Roasting

The pyrite concentrates were roasted in a continuous fluosolids roaster 6 inches in diameter. The contents of the roaster were heated externally by a gas flame to 700°C, and the overflow from the bed was collected for this study. The extent of oxidation of the calcines was varied by the alteration of the flowrate of air in relation to that of the concentrate.

Leaching

The solids were leached in open 2-litre bottles. Reagents were placed in the bottles, which were then rolled for the appropriate time at approximately 8 r/min. The slurry was then filtered, and the residue was washed with copious quantities of water.

Apparatus

A gold rod of 8 mm diameter and of greater purity than 99,9 per cent was sealed in a Teflon rod and connected to the normal rotating-electrode assembly. A potentiostat (Princeton Applied Research Model 371), an X–Y recorder (Hewlett Packard Model 7046A), and a speed controller and sweep generator constructed at Mintek were used. Potentials were measured relative to the saturated calomel electrode and are quoted as such. The solutions were equilibrated by the bubbling of the required gas through the solution prior to each run. All the experiments were carried out at ambient temperature, i.e. approximately 22°C. The gold electrode was polished with alumina paste before each experiment.

Analysis

The solutions were analysed by atomic-absorption spectrophotometry. Gold in the calcines was analysed by the fire-assay methods and sulphur by the Leco combustion technique. The concentrations of residual cyanide were determined by titration with silver nitrate, potassium iodide being used as the indicator.

Results and Discussion

The extraction of gold from the various head materials

TABLE II

EFFECT OF THE SULPHUR CONTENT ON THE EXTRACTION OF GOLD

Leaching conditions
Solids: 50g NaCN: 2,5g CaO: 2,5g H_2O: 100ml Time: 24h

Material	Sulphur %	Gold extraction %
Pyrite concentrate	43	17
Partially roasted calcine A	13,5	28
Partially roasted calcine B	6,7	40
Calcine	0,1	82

was found to decrease with increasing sulphur content (Table II). The possible reasons for this phenomenon will be discussed in turn, and a combination of physical encapsulation and electrochemical passivation proposed to explain the behaviour.

Consumption of Cyanide

The leaching of a partially roasted calcine results in a much higher consumption of cyanide than does the leaching of the completely roasted material (Table III). Only a slight excess of cyanide is used in plant practice, and this has been postulated as the reason for the low gold extractions. In these experiments, however, a large excess of cyanide was used; hence the consumption of cyanide is not the principal reason for the poor extractions.

TABLE III

EFFECT OF CYANIDE CONSUMPTION ON THE EXTRACTION OF GOLD

Leaching conditions
Solids: 50g CaO: 2,5g H_2O: 100ml Time: 24h

Material	Initial NaCN %	Final NaCN %	Gold extraction %
Calcine	2,5	2,25	82
Calcine	0,25	0,13	82
Partially roasted calcine A	2,57	1,71	28

Consumption of Oxygen

Under certain conditions, the dissolution of gold from the calcine can be controlled by the rate of reduction of oxygen. Depletion in the concentration of oxygen may therefore result in a decrease in the rate of dissolution of the gold. Reactions such as the dissolution of iron sulphide consume oxygen, and it is therefore possible that, in the presence of partially roasted calcine containing large quantities of iron sulphide, an oxygen deficiency occurs in solution. However, the use of oxygen instead of air as the oxidant had no effect on the extent of the reaction after 24 hours. If any oxygen deficiency had been the cause of the poor extraction from partially roasted calcine, additional dissolution would be expected in the presence of an oxygen atmosphere.

A second experiment, in which 25 g of partially roasted calcine A and 25 g of calcine were mixed prior to leaching, yielded the same gold extraction as would have been expected if the materials had been treated separately. If an oxygen deficiency occurred during the leaching of the partially roasted calcine, it should also have affected the dissolution of gold from the calcine when the two were combined in the same leaching vessel. The consumption of oxygen is therefore not the principal reason for the poor extractions from partially roasted calcine.

Physical Encapsulation

When pyrite is roasted, the particles become porous owing to a change in structure and volume of the solid. This is illustrated by the increase in surface areas recorded in Table IV. The gold extraction increases with this increasing porosity, and it is therefore possible that the poor gold extraction from pyrite and partially roasted calcine may be due to physical encapsulation of
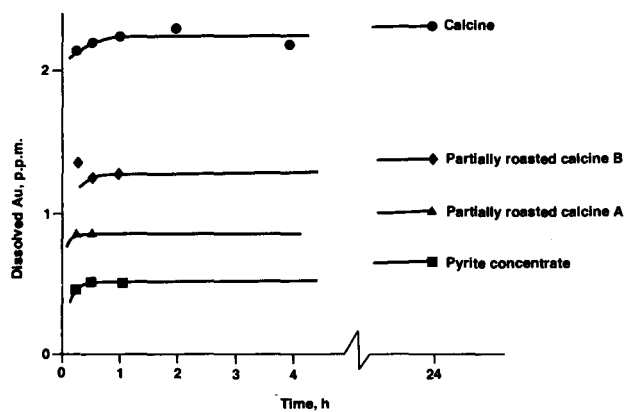
Fig. 1—Rates of gold dissolution

TABLE IV

THE EFFECT OF ROASTING AND GRINDING ON SURFACE AREAS

Leaching conditions

Solids: 5,0g   NaCN: 2,5g   CaO: 2,5g   Time: 24h

Material	Before grinding		After grinding	
	Surface area $m^2.g^{-1}$	Gold extraction %	Surface area $m^2.g^{-1}$	Gold extraction %
Pyrite	0,9	17	6,4	71
Partially roasted calcine B	2,1	40	7,5	72
Calcine	3,0	82	7,9	87

the gold. This possibility is supported by the rate of reaction illustrated in Fig. 1. The initial gold extraction is fast for all the samples but virtually ceases after 1 hour, thus indicating that a proportion of the gold is readily amenable to dissolution but that, for some reason, the remainder is unable to dissolve readily in the cyanide.

When the samples were ground very fine, the gold extractions were higher. However, despite their considerably higher surface areas, the extractions from finely ground pyrite and partially roasted calcines were still significantly lower than from the untreated calcine. This indicates that exposure and, possibly, complete liberation of the gold from the pyrite and partially roasted calcine increases its ability to dissolve, but that some factor is still responsible for the poor dissolution of the gold. The exposure of gold caused by the breaking of particles during the roasting process is significant, since it contributes to the improved gold extraction. However, it is not the only contributing factor.

Passivation of Gold in the Calcine

The oxidation of gold in a cyanide solution is a complex reaction that has not yet been explained satisfactorily. All the workers in this field have shown that oxidation initially follows normal Tafel behaviour, but that passivation occurs as the potential is shifted anodically. The anodic current achieved prior to passivation is dependent on the cyanide concentration and on the concentration of the impurities in solution[5]. Curve B in Fig. 2 illustrates

the current–potential curve for a freshly polished gold electrode immersed in a pure solution and scanned anodically afterwards. After the electrode has stood in the solution for several minutes, or when lead or thallium salts have been added, Curve A (Fig. 2) is obtained for the current–potential curve. Scanning of the potential of the gold surface (A) to a value of −0,4V, followed immediately by another potential sweep from −0,9V, yields a curve similar to that of B. The reason for this behaviour is not well understood but, for the purposes of this paper, the two distinct forms of gold surface can be adequately described as active and passive. When held at a potential cathodic to −0,6V, passive gold usually reverts to the active state, whereas active gold becomes passive at potentials anodic to −0,6V. A comparison of the current–potential curve for the reduction of oxygen on the surface of the gold with the curves for the oxidation of active and passive gold surfaces shows that in both cases dissolution will occur at a current of approximately 200 $\mu A.cm^{-2}$. Since the size and shape of the gold particles in a calcine are not known, this figure cannot be converted direct into a leaching rate, but it is clear that the rate is reasonably high.

Mineralogical studies of the calcine particles indicate that the gold is present in intimate contact with the surrounding minerals. If the contacting mineral is electrically conductive, the reduction of oxygen can take place over the entire surface of the mineral. The magnitude of the current for the reduction of oxygen may exceed that for the oxidation of gold in the region cathodic to the potential where the passivation of gold occurs. This is illustrated schematically in Fig. 3, from which it can be seen that, under these conditions, the mixed potential at which dissolution occurs is shifted to an anodic value and the gold surface is passivated. The rate of dissolution of gold under these conditions is slow. The approximate conductivities of the minerals associated with the gold on the concentrate and the calcine are illustrated in Table V. Magnetite, pyrite, and pyrrhotite have high conductivities, whereas hematite is virtually an insulator. Gold that is in contact with magnetite, pyrite, and pyrrhotite would be expected to
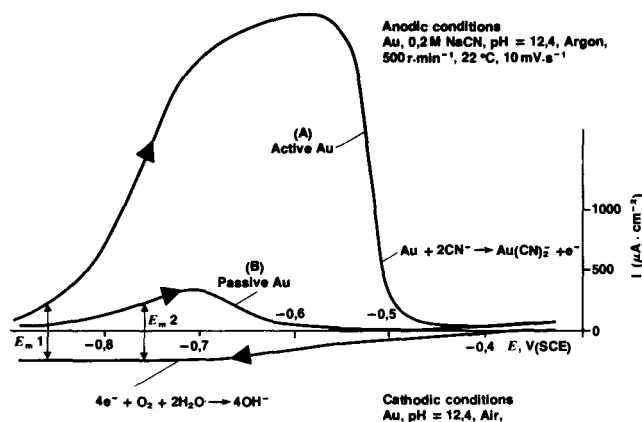

Fig. 2—Current-potential curves for gold oxidation and oxygen reduction

passivate as a result of the enhanced magnitude of the cathodic current.

In completely oxidized calcine, only hematite is present; hence, oxygen would not be reduced except at the surface of the gold. Dissolution of the gold would not be retarded under these conditions. In the presence of other conducting minerals (i.e. in partially roasted calcine and pyrite), the gold-dissolution current could be expected to drop to below $10 \mu A.cm^{-2}$. Again, the particle size of the gold in the calcine is not known, and this value cannot be converted direct into a leaching rate. However, the rate will be much slower than that for the dissolution of unpassivated gold. Fig. 1 indicates that the dissolution of active gold probably takes only a few hours; that of passive gold should take several days.

Mrkusic[3] has suggested that the passivation of gold is due to film formation, and that this film results from dissolved components of the calcine. This appears unlikely, since current–potential curves for the oxidation of gold in pure solutions are very similar to those in solutions arising from leaches in which poor gold extractions occurred. However, it is possible that dissolved components from individual ores may have a slight effect on the rate of dissolution, it having been found[5] that the dissolution current of gold prior to passivation depends on impurities in the solution (e.g. lead, thallium, mercury, and bismuth.) This would change the tendency of gold to go into the passive state.

The enhanced dissolution of gold from pyrite and partially roasted calcines subsequent to fine grinding can be explained partially in terms of the passivation of gold. As the material is ground, increasing amounts of gold are separated from the conductive host materials and no longer passivate during leaching, since the reduction of oxygen occurs on a relatively smaller surface area. This

TABLE V

CONDUCTIVITIES OF VARIOUS MINERALS

Mineral	Conductivity S.m^{-1}
Hematite	10^{-4} to 1
Magnetite	$2 + 10^4$
Pyrite	$1 + 10^3$
Pyrrhotite	10^5

The values are averages of those given by Shuey[6]

$Au + 2CN^- \rightarrow Au(CN)_2^- + e^-$

I

E

E_m

$4e^- + O_2 + 2H_2O \rightarrow 4OH^-$
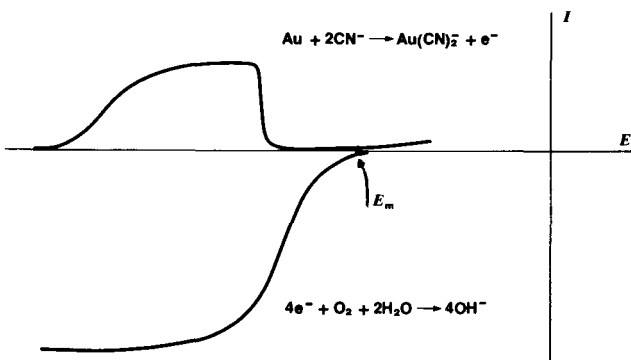
Fig. 3—Current–potential curves in the presence of additional cathodic area

Leaching conditions
Solids: 50g   NaCN: 2,5g   CaO: 2,5g   Temperature: 22°C
H$_2$O: 100ml

Material	Gold extracted	
	24 h	21 d
Calcine	82	82
Partially roasted calcine B	40	65
Pyrite concentrate	17	28
Reduced calcine	60	N.D.

N.D. — Not determined

gold is therefore amenable to complete dissolution within the 24-hour leaching period. However, the reduction in gold dissolution recorded from pyrite and partially roasted calcine cannot be wholly attributed to these reasons as will be explained later.

Confirmation of the passivation mechanism for the retardation of gold dissolution was obtained in two experiments (Table VI). In the first experiment, the three head materials were leached for a period of 21 days. No further dissolution occurred from the fully oxidized calcine, but significant dissolution occurred from the partially roasted calcine and the pyrite concentrate, indicating that a very slow reaction was taking place. If the low dissolution from these materials in the first 24 hours were due purely to physical encapsulation, no additional leaching would occur. The extraction of gold from the calcine was unchanged after the extended period, which indicates that the remainder of the gold is not accessible to the leaching solution. After 21 days one would expect, from the relative dissolution currents, all the exposed but passivated gold to be dissolved. The extraction from the pyrite and partially roasted calcine was significantly lower than that from the calcine, showing that a proportion of the gold had not been exposed to the leaching solution. This confirms that physical encapsulation is part of the reason for poor gold extractions from partially roasted calcine.

The base-metal concentration in solution after the extended leaching period was not significantly different from that after 24 hours. The additional dissolution of gold recorded for pyrite and partially roasted calcine is therefore not considered to be due to the dissolution of the minerals that encapsulate the gold.

In the second experiment, a sample of calcine was reduced under hydrogen gas at 700°C to a material containing a proportion of magnetite. The dissolution of gold from this material in 24 hours was significantly less (Table VI), although the surface area was unchanged by the pretreatment. This can be attributed only to the slower dissolution of the gold in contact with magnetite and, hence, in its passive state.

The passivation of gold in cyanide media is known. It was used by Cathro[7] to explain the decrease in the dissolution rate of gold when the atmosphere was changed from air to oxygen, and was suggested by Mrkusic[3] as one of several possible reasons for poor gold extractions. In the present work it has been shown to be

one of the reasons for the effect of incomplete roasting on the subsequent dissolution of gold. This incomplete roasting also limits the exposure of the gold to the leaching solution. In practice, the only way in which the subsequent gold dissolution can be optimized is the production of an extensively oxidized calcine, or dissolution of the incompletely oxidized material prior to cyanidation.

Conclusions

The poor extraction of gold from incompletely roasted calcines can be attributed partly to incomplete development of the pore structure. However, there is another reason for the observed behaviour: passivation of the gold caused by an increase in the possible surface area upon which the reduction of oxygen can occur. Depletion of the oxygen in solution and excessive consumption of cyanide did not play any role in the experiment carried out in this study but may decrease the dissolution rates on a plant scale.

References

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Precious metals

The International Precious Metals Institute (IPMI) has announced that its Sixth International Conference is to be held in Newport Beach, California, from 7th to 11th June, 1982. The theme is 'Precious metals today serving mankind tomorrow'.

Enquiries should be directed to IPMI, 2254 Barrington Road, Bethlehem, PA 18018, U.S.A.

Fluid engineering

BHRA Fluid Engineering will hold an international conference on Flow Induced Vibrations in Fluid Engineering from 14th to 16th September, 1982. The meeting will be held at the University of Reading, England. Offers of papers are invited.

The vibration of components subjected to dynamic fluid forces is a problem experienced by a range of industries from power generation to chemical processing. The occasional, but well publicized, failure of an offshore or coastal platform, traced to the effect of wind, waves, or tidal currents, first highlighted the urgent need for further data on the mechanism of flow-induced vibrations. This information would be of equal value to designers of such large highly stressed structures on the one hand and to those responsible for the thermal efficiency and reliability of shell and tube heat-exchangers on the other. The demand for better thermodynamic performance of heat-exchangers has led to longer, more slender tubes, which are closely spaced, and higher fluid flowrates. Tube failures caused by excessive vibrations are likely to increase as a result, and the direct and indirect costs of such failures can be very high. This new international conference aims to bring together specialists from the various industries involved so that experiences and ideas can be exchanged and successful practical solutions examined in the light of the different industrial environments.

The conference will cover prediction and analysis; practical experiences; input forces; vibration monitoring; and economics, but papers on related topics such as flow-induced noise will be considered.

Further details are available from the Organizing Secretary, Flow Induced Vibrations Conference, BHRA Fluid Engineering, Cranfield, Bedford MK43 OAJ, England; telephone Bedford (0234) 750422, telex 825059.