

# The roasting and leaching of Witwatersrand pyrite concentrates

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## SYNOPSIS

Many of the pyrite concentrates produced at South African gold and uranium mines contain economically significant amounts of nickel, copper, and cobalt, apart from gold and uranium. In some cases these concentrates are leached for uranium, followed by roasting and cyanidation of the calcine for the extraction of the gold. Even if their intrinsic value is excluded, the presence of appreciable amounts of base metals can lead to excessive consumption of cyanide and zinc in the conventional process for the recovery of gold from calcines.

The extent to which base metals, particularly cyanocides in the calcine, can be made soluble in water or in dilute acid by variation of the pyrite roasting conditions was investigated. An important finding of the investigation was that the conditions producing favourable base-metal sulphation (and hence solubility in water) also produced good sulphation of the uranium values that had not been extracted in a conventional leach of the original pyrite. Thus, if the pyrite is subjected to a sulphating roast followed by quenching in water (or dilute acid), it should be possible for the uranium to be extracted in improved yield. The need for leaching of the pyrite would therefore fall away.

It was noted that sulphation roasting also resulted in improved gold extractions when the calcine was subsequently subjected to conventional cyanide-extraction procedures.

From well-sulphated calcine, the dissolution of base metals and uranium appeared to be fairly independent of leaching pH, time, and temperature. On an inadequately sulphated calcine, low pH values during leaching gave increased extraction of copper and uranium but did not have a significant effect on the dissolution of nickel and cobalt. The extraction of uranium increased with increasing leaching time and temperature, while only longer times at a low pH value markedly improved the extraction of copper. The extraction of cobalt was fairly independent of leaching time and temperature, but the results were insufficient for a conclusive evaluation to be made of their effects on the dissolution of nickel.

A cursory economic assessment indicated that sulphation roasting applied to the pyrites investigated is likely to be very profitable.

## SAMEVATTING

Baie van die pirietkonsentrate wat by Suid-Afrikaanse goud- en uraanmyne geproduseer word, bevat aansienlike ekonomiese hoeveelhede nikkal, koper en kobalt, afgesien van goud en uraan. Soms word hierdie konsentrate gelooë vir uraan, gevolg deur roosterling en sianiedbehandeling van die kalsien om die goud te ekstraheer. Sels wanneer hul intrinsieke waarde uitgesluit word, kan die teenwoordigheid van aansienlike hoeveelhede van hierdie basiese metale lei tot oormatige sianied en sink verbruik in die konvensionele herwinningprosesse vir goud uit kalsiene.

Die mate waartoe basiese metale in kalsien oplosbaar gemaak kan word in water of verdunde suur deur die piriet roostingstoestande te varieer is ondersoek. 'n Belangrike bevinding van die ondersoek was dat toestande wat gunstige sulfatering van die basiese metale veroorsaak het, (en daarom ook wateroplosbaarheid) ook geskik was vir sulfatering van uraan wat nie ge-ekstraheer is gedurende die konvensionele logging van die oorspronklike piriet nie. Dit behoort dus moontlik te wees om die logging van die piriet voor roosterling uit te skakel, aangesien 'n hoër opbrengs gesulfateerde uraan ge-ekstraheer kan word deur die kalsien met water (of verdunde suur) te loog. Gesulfateerde basiese metale sal tegelykertyd ge-ekstraheer word. Dit was opgemerk dat sulfateerroosterling ook verbeterde goud-ekstraksies opgelewer het wanneer die kalsien daarna met sianied behandel is.

Die uitwerking van loogparameters soos pH, tyd en temperatuur op die oplossing van basiese metale en uraan uit kalsien is ook ondersoek. Ekstraksies blyk redelik onafhanklik van hierdie veranderlikes te wees met deeglik gesulfateerde kalsien. Met kalsien wat onvoldoende gesulfateer is, het lae pH waardes gedurende logging tot toenemende koper- en uraan-ekstraksies gelei maar met geen betekenisvolle uitwerking op die oplossing van nikkal en kobalt nie. Uraan-ekstraksie neem toe met toenemende loogtyd en temperatuur, terwyl slegs langer loogtye by laër pH waardes koper-ekstraksie merkbaar verbeter. Kobalt-ekstraksie is redelik onafhanklik van loogtyd en temperatuur. Die gegewens was onvoldoende om 'n afdoende evaluasie van die effek van loogtyd en temperatuur op die oplossing van nikkal te maak.

Oppervlakkige ondersoek dui daarop dat sulfateerroosterling van die piriet bestudeer ekonomies winsgewend kan wees.

## Introduction

Many of the pyrite concentrates produced in South Africa from Precambrian conglomerates of the Witwatersrand type contain appreciable quantities of gold, together with uranium and base metals such as copper, cobalt, and nickel. Experience gained over many years in the roasting of these concentrates for the production of sulphuric acid has led to an understanding of the effect of roasting conditions on the gold extraction from the resulting calcine. However, little was known about the possible effects of the roasting conditions on the extraction of uranium and base metals from the calcine.

Pilot-plant tests and large-scale plant operations in

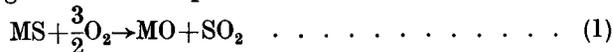
many parts of the world have established that a sulphation roast can convert the base metals in sulphide concentrates from oxides or sulphides to water-soluble sulphates. For example, sulphation roasting has become an industrial reality in Katanga<sup>1</sup> (where a copper cobalt sulphide concentrate is sulphation roasted), at Falconbridge in Canada<sup>2</sup> (where non-ferrous metals are recovered from a nickeliferous pyrrhotite after sulphation roasting), and at Outokumpu Oy in Finland<sup>3</sup> (where dead-roasted calcine is reacted at about 700°C with fresh pyrite to achieve sulphation of the copper, cobalt, nickel, and zinc). Because of the different nature of these raw materials, it was not possible to infer, from their behaviour, how South African pyrites would react to sulphation roasting. Research was therefore initiated to establish quantitatively the influence of various para-

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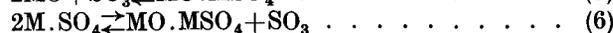
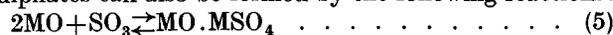
meters on the roasting of Witwatersrand pyrite and on the subsequent extraction of gold, uranium, and base metals from the calcines.

### Mechanism of Sulphation Roasting

Sulphation roasting is carried out below the decomposition temperatures of the sulphates, when the following reactions take place:



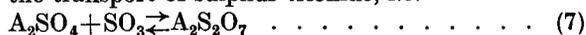
Reaction (3) is catalysed by metal oxides. Basic sulphates can also be formed by the following reactions:



The preferred temperature for sulphation roasting is between 650 and 700°C, a range at which iron sulphates are unstable; the preferred reactor is a fluidized bed.

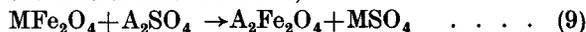
Alkali sulphates promote the formation of sulphates. Various authors<sup>4</sup> attribute this effect to the following reactions:

(i) the transport of sulphur trioxide, i.e.



(ii) a stabilizing effect of the alkali salt on the metal sulphate (perhaps the formation of double salts)

(iii) the destruction of ferrites, i.e.



Fletcher and Shaelef<sup>4</sup> have indicated that a combination of the above factors is probably responsible for the catalytic effect of the alkali sulphates.

### The Experimental Roasting Plant

The sulphation experiments were conducted in a fluidized-bed reactor, which formed the central part of the roasting plant depicted in Fig. 1. The flowsheet of the plant, illustrating its major components, is given in Fig. 2.

A variable drive (1) operates a screw feeder (2), which withdraws the dry feed material from a feed hopper (3). At the end of this screw, the material is picked up by the fluidizing air and transported pneumatically to the bottom of the fluidized-bed reactor (6). Provision was also made to feed material from the side of the reactor into the middle of the fluidized-bed section. The fluidized-bed reactor is made of 316L stainless steel, and consists of a bed section (200 mm in diameter and 1250 mm high) and an expanded free-board section (430 mm in diameter and 3200 mm high). The bottom end of the bed section is sealed by a unit consisting of a tuyère plate and a windbox. The feed material enters the bed section together with about half of the fluidizing air through a funnel-shaped opening in the centre of the tuyère plate. A ball-bearing about 20 mm in diameter in the funnel-shaped opening in the tuyère plate acts as a non-return valve to prevent hot calcine from falling into the pneumatic feed pipe. The other half of the fluidizing air enters the bottom bed section from the windbox through three equally distributed tuyères. This arrangement ensures good fluidization of the bed material.

The level of the fluidized bed is kept constant by an overflow pipe at the top end of the bed section. The pipe discharges excess bed material into a collection hopper (9), from where the calcine can be discharged through a ball valve when required.

The gases and entrained dust leave the reactor through an opening at the top end of the freeboard section. They then enter a cyclone (7) (there are two parallel cyclones of 110 and 150 mm outer diameter, which can be used singly or together). The cyclone underflow material passes into a collection vessel (8), from where it can be discharged by a ball valve, while the overflow material passes through insulated pipes into a bag-house (10). The bag-house is made of stainless steel, and contains a fabric filter bag with a diameter of 200 mm and a height of up to 1800 mm. A rapping device at the top of the bag-house makes it possible for the collected dust to be dislodged from the filter fabric where it drops into the cone-shaped bottom of the bag-house. From here it can be discharged intermittently by means of a ball valve. The bag-house is insulated by a layer of high-temperature cement and a layer of weather-resistant cement.

From the exit of the bag-house, the clean exhaust gases are sucked by an air-operated ejector through rubber hoses to a high point in the vicinity of the plant, where they are vented. The ejector also provides a means for pressure control in the reactor, and can compensate for high pressure drops across the bag-house. It also

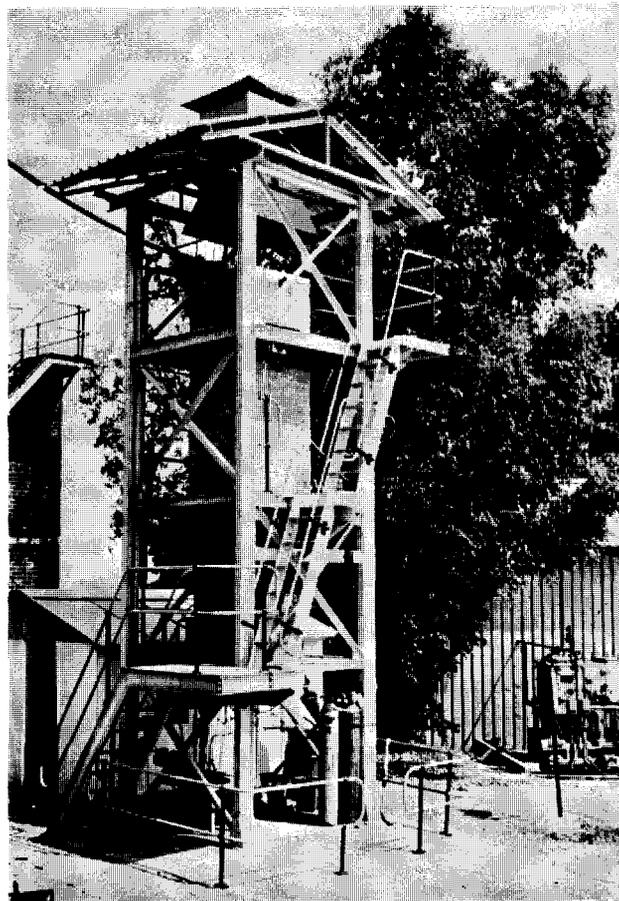


Fig. 1—Experimental fluidized-bed roasting plant at the Anglo American Research Laboratories

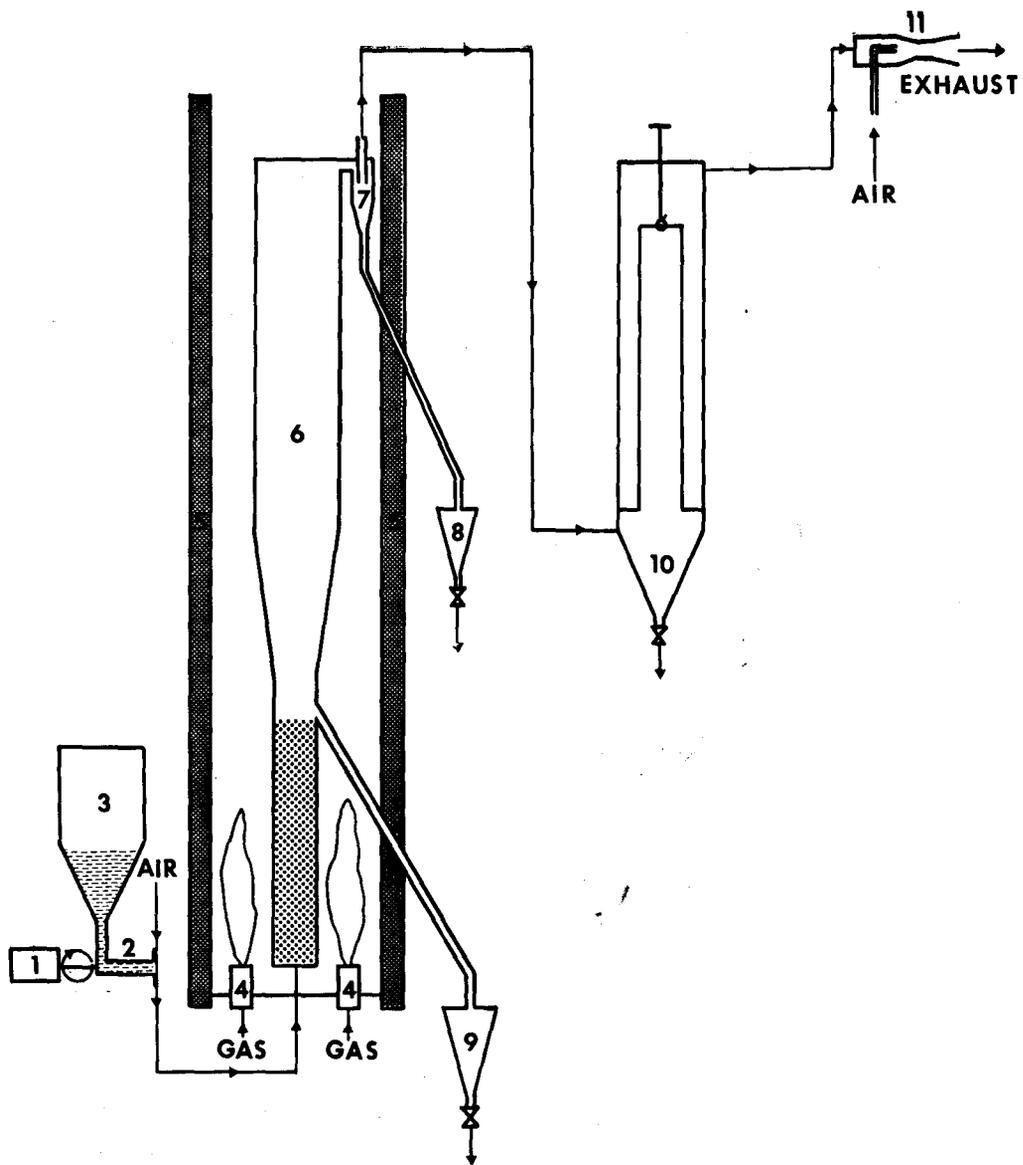


Fig. 2—Flow diagram of the experimental fluidized-bed roasting plant at the Anglo American Research Laboratories

- |                  |   |   |              |
|------------------|---|---|--------------|
| 1 Variable drive | 5 Firebricks                            | 8 Collection hopper for cyclone underflow     | 10 Bag-house |
| 2 Screw feeder   | 6 Stainless-steel fluidized-bed reactor | 9 Collection hopper for bed-overflow material | 11 Ejector   |
| 3 Feed hopper    | 7 Cyclone                               |   |              |
| 4 Burners        |   |   |              |

makes it possible for the reactor to be run under a slight vacuum.

The whole length of the stainless-steel reactor and the cyclones is enclosed by a double firebrick box, the bottom end of the box being sealed by an asbestos-cement plate in which four gas burners are situated. Six additional burners are placed along the freeboard section.

The plant equipment and brickwork are suspended from or supported by a framework of steel girders, as can be seen from Fig. 1. The actual reactor is suspended from steel brackets welded to the top of the freeboard portion, which permits unimpaired expansion of the reactor during heating.

The control equipment and most of the instrumentation for the plant are accommodated in the prefabricated hut next to the plant. A twelve-point temperature

recorder records the temperatures at important points along the reactor and the bag house. Pressure probes provide manometer readings of the pressures at various positions of the system and a differential pressure reading across the bag house. Another recorder provides a graph of the oxygen concentration in the exhaust gas. This recorder receives a signal from a paramagnetic oxygen meter through which a sample of gas is continuously passed. The gas sample is withdrawn from a position behind the cyclones. Flowmeters and pressure gauges give information on flows and pressures of fluidizing air, instrument air, and heating gas. A variable-speed pump permits the introduction of metered quantities of water into the reactor through an inlet probe.

The plant is capable of burning up to 10 kg of pyrite per hour. For the testwork, pyrite was fed to the roaster

until a stable bed had been attained. By that time, the temperatures and pressures in the system had stabilized and the collection vessels for bed overflow, cyclone underflow, and bag-house product were emptied. The roasting of additional pyrite then produced the calcine fractions on which the leaching tests were conducted.

### Materials

The pyrite concentrates used in the investigation were obtained by the flotation of slimes-dam material originating from Witwatersrand ore. The analyses of the pyrites are given in Table I. Pyrites 1 and 2 had already undergone a leach in sulphuric acid for the extraction of uranium, which accounts for their low uranium concentrations. Pyrite 2 is a highly cleaned concentrate, as indicated by the high sulphur and iron contents. Further cleaning of the other pyrites would improve not only the sulphur grade but also the concentrations of base metals and gold. The upgrading of the uranium in the cleaning stage is difficult.

### Dissolution of Copper, Cobalt, and Nickel

Of the three calcine fractions produced in the pyrite roasting tests, namely the bed overflow (B), the cyclone underflow (C), and the cyclone overflow, only the first two were leached. The iron content of the dust in the cyclone exhaust gases that collected in the fibreglass bag (10 in Fig. 2) was excessively sulphated because of the

low temperature of 200 to 300°C in the bag-house. The cyclone overflow underwent a mass loss of more than 50 per cent on being leached, thus rendering meaningless the results of the leaching tests on this fraction. In an industrial sulphation operation, in which the dust collection would be dry, the flue dust would be returned to the bed to decompose the iron sulphates formed (as, for example, described in reference 3). However, this was not practicable in the present investigation.

The effect of roasting temperature on the extraction of uranium and base metals is demonstrated in Table II. The table clearly shows that a reduction in roasting temperature significantly increases the extraction of all the elements. The higher extraction from the cyclone underflow as compared with the bed overflow is due not only to the lower temperature of the cyclone but also to the greater fineness of the cyclone material. The results also indicate that the leaching pH and/or leaching time have an effect on the dissolution of the metal values. These effects, as well as the influence of leaching temperature, were investigated in more detail on another sample, and the results are shown in Fig. 3.

As shown in Fig. 3, none of the following has a pronounced effect on the dissolution of cobalt: leaching temperature, time, or pH. The same applies to copper at the high leaching pH, but a significant increase in extraction is observed with decreasing pH. Increasing

TABLE I  
ANALYSES OF PYRITE CONCENTRATES

PYRITE	ANALYSES						
	g/t					%	
	Au	Cu	Co	Ni	U <sub>3</sub> O <sub>8</sub>	Fe	Sulphide sulphur
1	7,8	1400	890	2200	100*	28,6	28,6
2	16,8	1800	2000	3800	220*	42,0	41,4
3	8,50	1200	780	2500	310	25,0	25,5
4	4,85	900	760	2300	280	23,8	23,9

\*After sulphuric acid leach

TABLE II  
THE EFFECT OF ROASTING TEMPERATURE ON THE EXTRACTION OF BASE METALS AND URANIUM FROM CALCINES\*

Calcine no.	Roasting temp. °C		Leaching conditions			Extraction, %							
	Bed	Cyclone	pH	Time min	Liquid-to-solid ratio	Cu		Co		Ni		U	
						B	C	B	C	B	C	B	C
2	850	800	3	20	30	9	12	4	8	0,7	1,3	< 10	10
	780	470				17	51	10	49	1,5	9	< 10	14
	680	680				18	32	16	43	2,9	11	< 10	25
3	820	820	1,5	60	2	13	11	9	11	1	2	19	53
	690	640				43	69	19	59	10	12	21	80

\*B = Bed-overflow calcines  
C = Cyclone-underflow calcines

Roasting conditions Mean retention time: 2 h  
Na<sub>2</sub>SO<sub>4</sub> addition: Nil  
Free O<sub>2</sub>: 2 to 4 %

Calcine analyses before leaching, %

Calcine	Cu	Co	Ni	U
2 B	0,18	0,16	0,42	0,024
C	0,20	0,20	0,44	0,024
3 B	0,099	0,091	0,28	0,029
C	0,096	0,082	0,23	0,037

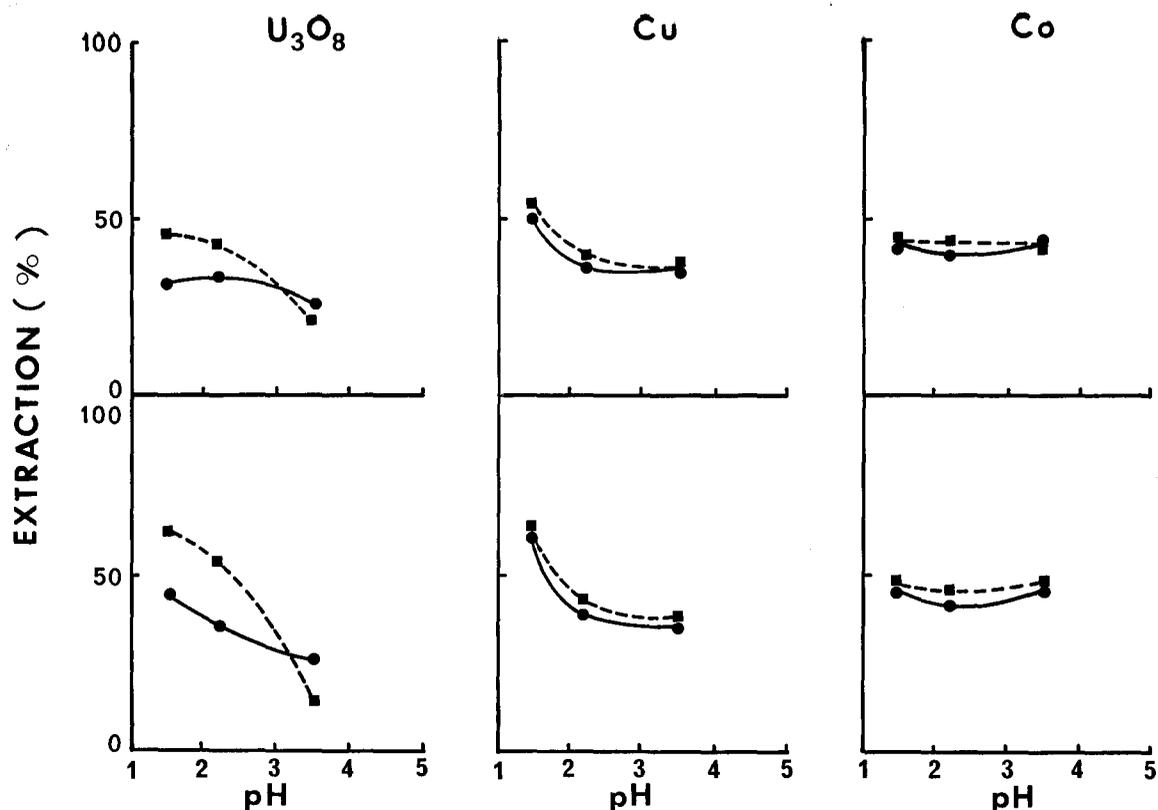


Fig. 3—Extraction of uranium, copper, and cobalt from cyclone-underflow calcine as a function of leaching pH

<b>Leaching conditions:</b>		<b>Roasting conditions:</b>	
Time	Top graphs 30 minutes, bottom graphs 120 minutes	Free O <sub>2</sub>	4 to 8%
Temperature	Full line 25°C, broken line 60°C	Temperature	690°C
Liquid-to-solid ratio	2	Na <sub>2</sub> SO <sub>4</sub> addition	Nil
Calcine analysis (per cent)	Cu 0,15 Co 0,11 U <sub>3</sub> O <sub>8</sub> 0,015	Retention time	≈ 2 h

time also appears to improve the copper extraction at a pH of 1,5. A longer leaching time, higher leaching temperature, and lower pH all have a promotional effect on the dissolution of uranium. A reversal in the extraction occurs at a pH value just above 3, as can be seen from the relevant curves. This is probably due to a temperature-dependent solubility phenomenon since precipitation of the dissolved uranium from solution can occur in this pH region.

The above findings demonstrate that the sulphated portion of the base metals dissolves rapidly, the dissolution being unaffected by leaching temperature, time, or pH (up to a pH value of 3,5). The unsulphated portion of the cobalt remains insoluble under all the leaching conditions investigated. Some of the unsulphated portions of copper and uranium can be extracted, the amount extracted increasing with decreasing pH and increasing leaching time. For uranium, an increase in the leaching temperature also has an accelerating effect on the rate of leaching. The nickel extraction in the above experiments was always low, and the effect of the various leaching parameters was therefore obscured. However, in general, the extractions of nickel appear to follow those of cobalt. This is confirmed by an investigation of the effect of sodium sulphate addition during roasting.

These results are shown in Fig. 4, where the leaching extraction (at different pH values) from calcines is plotted as a function of sodium sulphate addition during roasting. For insufficiently sulphated samples (low addition of sodium sulphate), the leaching pH has a significant effect on the extraction of copper and uranium but not on that of nickel and cobalt. At the higher additions of sodium sulphate, where the degree of sulphation improves, the pH effect disappears for all the metals studied. For copper, cobalt, and uranium, the extraction approaches a maximum at a sodium sulphate addition of about 4 per cent, and little further benefit can be derived from the addition of more sodium sulphate. On the other hand, the extraction of nickel, in particular from the bed-overflow material, continues to improve with the addition of sodium sulphate, even beyond the highest addition made, viz 6 per cent. This confirms the findings of other investigators<sup>4</sup> that nickel is very difficult to sulphate. Long retention times in the roaster, such as those used at Outokumpu Oy<sup>3</sup>, would probably reduce the need for high additions of sulphate. This is being investigated.

#### Gold from Calcines

The effect of various roasting parameters on the

dissolution of gold by cyanidation of calcine is shown in Table III. For all the four calcines investigated, the dissolution of gold improved significantly with the addition of sodium sulphate during the roast. Even more striking is the effect of the roasting temperature. For calcine 2, a lowering of the roasting temperature from 850 to 650 °C increased the gold extraction by more than 10 per cent, while an improvement of approximately 4 per cent was achieved by a decrease in the temperature from 820 to 690 °C in the case of calcine 3. An increase in the retention time of the calcine in the roaster from 2 to 4 hours also appeared to improve the gold extraction, as shown by the tests on calcine 4. However, in that case the higher oxygen partial pressure (14 per

cent as compared with 4 to 8 per cent for the other tests) may have had a compounding effect, which could not be defined by the limited number of experiments conducted.

The above results show clearly that sulphation roasting provides an economic incentive because of the extra gold recovery<sup>5</sup> that is possible and because of the benefits arising from rendering the uranium<sup>6</sup> and base metals water-soluble.

#### Dissolution of Base Metals, and Consumption of Cyanide

Base metals are dissolved to some extent when water-quenched calcine is cyanided. An attempt was

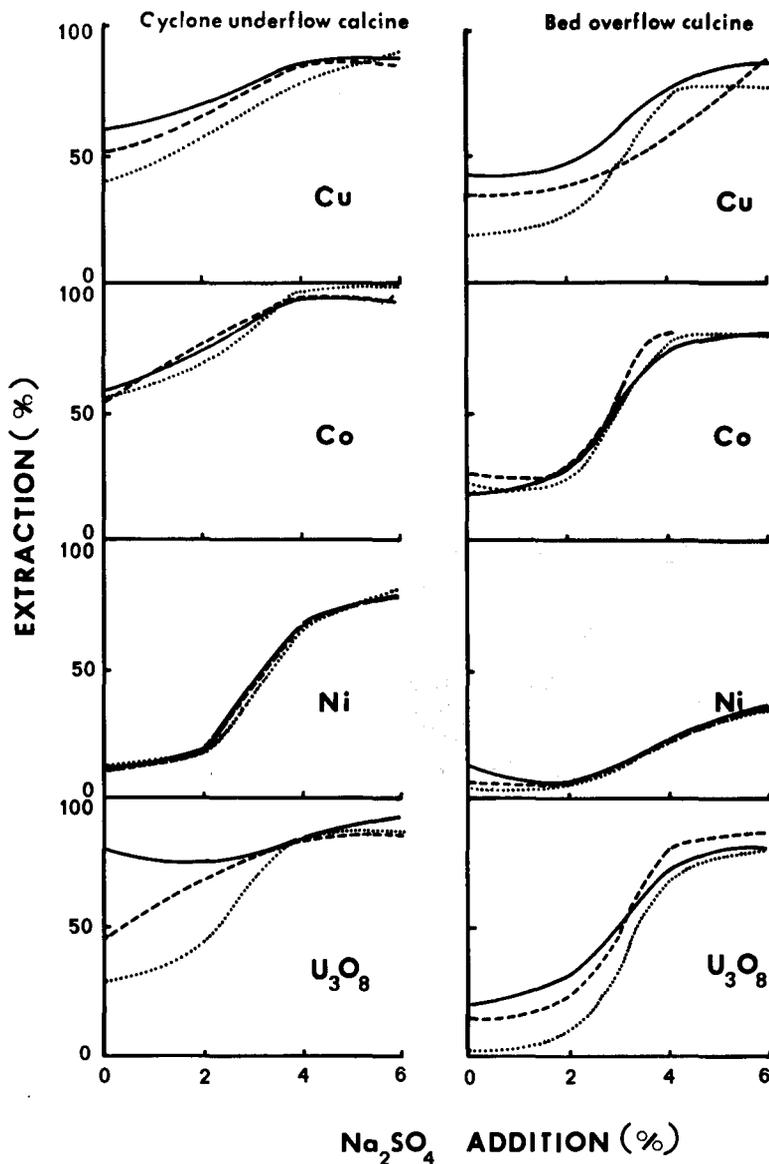


Fig. 4—Extraction of uranium and base metals (at different pH values) from calcines as a function of sodium sulphate addition

**Leaching conditions:**

Time 1 h  
 Temperature 60 °C  
 Liquid-to-solid ratio 2

pH

Solid line 1,5, broken line 2,2, dotted line 3,5

**Roasting conditions:**

Free O<sub>2</sub> 4 to 8%  
 Temperature 690 °C  
 Retention time ≈ 2 h

made to correlate the consumption of cyanide with the degree of base-metal dissolution during quenching and cyanidation. However, the study was not completely conclusive because of the wide scatter of the results, and the outcome can be discussed only in general terms.

The dissolution of base metals into the aqueous, as well as into the cyanide, leaching solution, and also the consumption of cyanide during gold leaching, is greater for the fine cyclone material than for the coarser bed-overflow material. The consumption of cyanide and the extraction of base metals into aqueous and cyanide solutions are low for roasting temperatures above 800°C. (The results were as follows: in the aqueous leach, the extraction of cobalt and nickel was less than 10 per cent and that of copper less than 20 per cent; in the cyanide leach, the extraction of copper, nickel, and cobalt was less than 10 per cent, and the consumption of sodium cyanide was less than 1 kg/t but increased with decreasing temperature.) The extraction of the base metals from calcine roasted at 690°C into the aqueous leach is shown in Table II. For the same roasting temperature, the extraction of copper and nickel into the cyanide liquor was up to about 25 per cent, and that of cobalt was up to 10 per cent. The cyanide consumption increased from about 1 kg/t to 2,5 kg/t. With an increasing degree of sulphation at a fixed temperature, a higher percentage of the base metals dissolved in the aqueous leach and less into the cyanide liquor; the consumption of cyanide was also lower. For most well-sulphated samples at 690°C, the extraction of the base metals into the cyanide solution and the cyanide consumption were similar to those for a sample roasted at a temperature of more than 800°C. The above correlation indicates that sulphation roasting will not lead to a marked

increase in cyanide consumption in the gold-recovery operation. Also, the sulphation roast will not result in increased base-metal dissolution into the cyanide liquor, which, if it took place, might increase the consumption of zinc in the gold-precipitation stage. On the contrary, for calcines roasted at temperatures lower than about 800°C, sulphation roasting has the advantage of making most of the base metals soluble in the aqueous leach, thus leaving only small quantities that can dissolve in the cyanide circuit.

Future investigations will be aimed at the expression of the above findings in more quantitative terms.

### Conclusions

The present investigation has outlined some developments that could change the pyrite-processing industry in South Africa. The fact that uranium is made water-soluble under the same conditions as the base metals could alter the conventional circuit from one including the leaching of pyrite concentrate to one involving the recovery of uranium (and base metals) from a sulphated calcine. Even dead-burnt calcines could yield their base-metal and remaining gold values after a roasting process similar to that practised since 1968 at the Kokkola Works of the Outokumpu Oy<sup>3</sup>, where about one-quarter to one-third green pyrite is sulphation roasted with three-quarters to two-thirds calcine. In the meantime, much work still remains to be done to provide answers to the questions posed by this investigation, to optimize sulphation conditions, and to develop methods for the recovery of base metals and uranium from calcine leach liquors. Once flowsheets have been worked out, an economic study will need to be undertaken to indicate the prospects of a sulphation enterprise. A cursory economic assessment indicates that the process can hardly fail to be profitable for the pyrite concentrates investigated.

### Acknowledgements

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TABLE III

THE EFFECT OF PYRITE ROASTING CONDITIONS\* ON GOLD EXTRACTION BY CYANIDATION

Calcine no.†	Roasting temp. °C	Mean roasting time h	Na <sub>2</sub> SO <sub>4</sub> ‡	Gold extraction§
			addition %	%
1	690	2	0	87,1
1	690	2	1	88,3
1	690	2	2	89,6
2	850	4	0	75,6
2	650	4	0	86,2
2	650	4	2	89,3
3	820	2	0	83,2
3	690	2	0	87,4
3	690	2	4	88,8
3	650	2	2	89,7
4	690	2	0	90,2
4	690	2	2	92,1
4°	690	4	2	94,0

\*Free oxygen 4 to 8%

†Bed-overflow material, gold head values,

g/t: 1=10,3 2=24,0 3=6,4 4=8,9

‡Na<sub>2</sub>SO<sub>4</sub> added to pyrite before roast

§Cyanidation conditions; Time: 16 h

pH: ≈ 11

Residual NaCN: ≈ 0,02%

Solid-to-liquid ratio: 0,5

Method: rolling bottle

°Free oxygen 14%