The flotation of gold, uranium, and pyrite from Witwatersrand ores


SYNOPSIS

The Witwatersrand reefs contain gold, uranium, and pyrite in the following average concentrations: 0.001 per cent, 0.02 per cent, and 1.7 per cent respectively.

The paper discusses the flotation of pyrite to produce a sulphide concentrate, reviews work done on the production of gold concentrates, discusses attempts to produce maximum concentrates, and closes with a review of processes for the simultaneous flotation of these three species.

It is concluded that high recoveries of all three species can be achieved only if a rougher concentrate of perhaps 20 per cent of the feed (by mass) is produced, and it is suggested that reverse leaching (leaching before cyanidation) of this concentrate, followed by a cleaning flotation step for the recovery of the pyrite, would be more efficient than the routes employed at present.

Introduction

It is apt that simultaneous consideration should be given to the flotation of gold, uranium, and pyrite because the association between these three constituents of the Witwatersrand reefs makes it difficult to consider them in isolation. Gold is probably the most floatable of all the constituents of the reef, but the close association between as much as 30 per cent of the gold and radio-active minerals (both uraninite and thucholite), and between as much as 20 per cent of the gold and the various sulphide minerals (pyrite) present in the reef, means that, in general, high recoveries of gold are associated with the simultaneous recovery of both uranium and sulphides. Similarly, the recovery of uranium is likely to result in the simultaneous recovery of gold and sulphides, and the recovery of sulphides to result in the simultaneous recovery of gold and uranium.

However, the reefs have an average sulphur content of about 1.7 per cent so that there has been considerable experience in the production of a relatively high-grade sulphide concentrate containing comparatively small amounts of gold and uranium. The gold is usually present in economic quantities in these concentrates, which therefore require cyanidation before being delivered to the end-user. The uranium is mainly present as thucholite in the concentrates, and is accordingly not generally present in economic quantities.

The concentration of gold in the reefs is about 0.001 per cent, so that there has been very little experience of the production of a gold concentrate by direct flotation from the ore. Instead, there has been some work on the use of flotation to produce a gold concentrate from a material prepared by some alternative technique of primary concentration to a gold content of about 0.1 per cent.

The uranium in the reefs is present at about 0.02 per cent on average, but there have been problems in the development of a flotation technique that will give a uranium concentrate because

(i) much of the uranium is present as uraninite, which is inherently difficult to float;

(ii) the uraninite tends to be very finely ground during milling, which makes its selective flotation even more difficult;

(iii) a small but significant fraction of the uranium is carried by siliceous minerals such as zircon, leucoxene, titanite, monazite, and various phyllosilicates, all of which are difficult to float selectively; and

(iv) thucholite is floated very readily, but tends to be rather coarse because its low density permits it to escape from milling circuits before being milled.

Accordingly, in this paper flotation to produce a 'pyrite' (sulphide) concentrate will first be discussed in detail; some work on the production of gold concentrates will be reviewed; there will be a short discussion of the attempts to produce uranium concentrates; and the paper will close with a review of processes involving the simultaneous flotation of all three species. The discussion will centre on the Witwatersrand ores; while flotation is important in the treatment of the arsenopyritic gold ores of the Barberton area, the economic importance of that area is too slight to justify detailed treatment. Similarly, the role of flotation in the production of uranium at Palabora is ignored.

Flotation of Pyrite

The purpose for which pyrite is usually concentrated by flotation is the production of sulphuric acid by the roasting of the concentrate and catalytic oxidation of

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the resultant sulphur dioxide. Accordingly, it is necessary to prepare a fairly high-grade concentrate that is relatively free of siliceous minerals. The need for a high grade arises partly from the fact that any gangue minerals in the concentrate tend to be fine, flaky phyllosilicates, which would make the concentrate difficult to thicken, dewater, and roast, and partly because the costs of transportation of the gangue minerals in some cases exceeds the cost of their removal.

The word pyrite is used generically for a range of metal sulphides present in the ore. Table I gives a list of the iron sulphides, many of which are present in the Witwatersrand reefs. In addition, there is a wide range of other sulphides such as bornite, pentlandite, galena, sphalerite, chalcopyrite, arsenopyrite, limonite, cobarite, and gersdorffite, in much lesser concentrations. All of these are likely to be floated into the 'pyrite' concentrate, and the residue that results from calcination may contain significant quantities of the base metals. Also in the concentrate are some of the products of the radioactive decay of the uranium and thorium present. The concentration of these products is low.

It has been found that most flotation reagents have a very deleterious effect on the cyanidation of gold. Accordingly, the flotation of pyrite is usually conducted after cyanidation. However, the effect of the flotation reagents can be destroyed by hot leaching with sulphuric acid and an oxidant for the recovery of uranium, and in these instances it is possible for the pyrite to be floated before the uranium and gold are recovered. However, as significant quantities of uranium and gold are also recovered in the flotation, these processes are considered later.

The fact that pyrite is normally floated after gold recovery leads to the most interesting aspect of pyrite flotation. Cyanide is inherently a depressant for pyrite, and the traces of cyanide present in the gold-plant residues are quite sufficient to have a significant effect.

Similarly, the lime used to ensure alkaline conditions during cyanidation can have a deleterious effect on flotation. This effect is believed to be not only one of pH, but also to be due to 'calcium activation of quartz'.

Accordingly, the pH value has to be adjusted into the acid range and the feed must be conditioned for a significant period before flotation, both to destroy the effect of the lime and to remove cyanide ions as free HCN. When reclaimed slime-dam material forms the feed, effective conditioning is particularly necessary.

A variety of collectors has been used. The chief collectors are xanthates, typically isopropyl or secbutyl xanthates. However, mercapto-benzo-thiazole, which is effective at somewhat lower pH values than xanthates, has found fairly wide use in the treatment of reclaimed slime-dam material or uranium-plant residues, which are inherently more acidic than gold-plant residues. Amines have found some use when employed at high pH values. Table II summarizes typical collector and pH conditions for various feeds.

A wide range of frothers has been used. Copper sulphate is often added as a sulphide activator when xanthates are used, particularly at high pH values. It has been suggested that the copper also forms complexes with free cyanide ions and thus reduces the depressant effect of cyanide, but the evidence in favour of this mechanism is slight.

Dextrin has found favour as a depressant for pyrophylite and other phyllosilicates, and certainly appears to assist in producing a clean concentrate when the feed is finely ground or has a high shale content. Another parameter that determines the quantity of siliceous material floated is the amount of water in the concentrate; the flotation cell acts to a certain extent as a classifier, and water in the concentrate tends to entrain fine particles into the concentrate without selectivity.

The operations at Government Gold Mining Areas and Virginia are fairly typical of pyrite-recovery plants in the industry.

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**TABLE I**

**COMPOSITION UNITS**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Atomic %Fe</th>
<th>Atomic %S</th>
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<th>Mineral</th>
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<td>47.06</td>
<td>125.89, 1.059.899</td>
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<td>FeS</td>
<td>50.63</td>
<td>49.37</td>
<td>1.026</td>
<td>Virginia</td>
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<tr>
<td>FeS</td>
<td>50.00</td>
<td>50.00</td>
<td>1.000</td>
<td>G.G.M.A.</td>
</tr>
<tr>
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<td>52.17</td>
<td>0.917</td>
<td>Loraine</td>
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<td>52.38</td>
<td>1.100</td>
<td>Fresh coarse ore</td>
</tr>
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<td>1.111</td>
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<tr>
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<td>60.00</td>
<td>1.500</td>
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<td>FeS</td>
<td>33.33</td>
<td>66.67</td>
<td>2.000</td>
<td>Fresh coarse ore</td>
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**TABLE II**

**COLLECTORS AND pH CONDITIONS ON TYPICAL FLOTATION PLANTS ON THE WITWATERSRAND**

<table>
<thead>
<tr>
<th>Mine</th>
<th>Feed to flotation</th>
<th>Collector</th>
<th>Rougher</th>
<th>pH</th>
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<tr>
<td>Merriespruit</td>
<td>Au residue</td>
<td>Xanthate</td>
<td>5.5</td>
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<tr>
<td>Virginia</td>
<td>U residue</td>
<td>Xanthate</td>
<td>4.9 to 5.7</td>
<td></td>
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<tr>
<td>G.G.M.A.</td>
<td>Au residue</td>
<td>Xanthate</td>
<td>5.4 to 5.8</td>
<td></td>
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<tr>
<td>Vogelstruisbl</td>
<td>Fresh coarse ore</td>
<td>Xanthate</td>
<td>5.8</td>
<td></td>
</tr>
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<td>Zandpad</td>
<td>Fresh coarse ore</td>
<td>Xanthate</td>
<td>10 to 11</td>
<td></td>
</tr>
<tr>
<td>Hartbeesfontein</td>
<td>Fresh coarse ore</td>
<td>Xanthate</td>
<td>9.9</td>
<td></td>
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<tr>
<td>Virginia</td>
<td>U residue</td>
<td>Mercapto</td>
<td>4.8 to 4.9</td>
<td></td>
</tr>
<tr>
<td>Free State Gedul</td>
<td>Various residues</td>
<td>Mercapto</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>President Brand</td>
<td>Various residues</td>
<td>Mercapto</td>
<td>4.5</td>
<td></td>
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<td>Buffelsfontein</td>
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<td>Mercapto</td>
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<td>Reclaimed dam</td>
<td>Mercapto</td>
<td>3.8 to 4.4</td>
<td></td>
</tr>
<tr>
<td>G.G.M.A.</td>
<td>Reclaimed dam</td>
<td>Mercapto</td>
<td>3.8 to 4.4</td>
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</tr>
<tr>
<td>Libanon</td>
<td>Fresh coarse feed</td>
<td>Amines</td>
<td>10 to 11</td>
<td></td>
</tr>
<tr>
<td>Venterspost</td>
<td>Fresh coarse feed</td>
<td>Amines</td>
<td>10 to 11</td>
<td></td>
</tr>
</tbody>
</table>
**Government Gold Mining Areas**

The flowsheet of the plant is given in Fig. 1. The incoming pulp was screened for the removal of trash, held in agitated pulpers, and then distributed to four banks of conditioners and rougher-scanvanger cells. The combined rougher concentrates were cleaned. The cleaner tailings and scavenger concentrate were combined and distributed to the four conditioners. The cleaner concentrate had a sulphur content of approximately 44 per cent, representing a recovery of 82 per cent from a feed with an average sulphur content of 3.3 per cent. Intensive conditioning and careful pH control were found to be essential.

**Virginia**

The flowsheet for the 'high grade' (pyrite) section of this plant is shown in Fig. 2. Adequate conditioning was obtained in the agitator, the conditioners originally installed ahead of rougher flotation being bypassed. The plant was a conventional rougher-scavenger-cleaner-reclaimer plant treating monthly 129 000 t of material with an average sulphur content of 1.55 per cent. The concentrate had a sulphur content of nearly 40 per cent, with the following grading: between 75 and 45 μm 14 per cent, and less than 45 μm 83.5 per cent. The sulphur recovery was 85 per cent.

**Flotation of Gold**

The first experiments on the flotation of gold from the whole ore were carried out in 1934, when it was reported that about 70 per cent of the gold in the sand fraction on the circuits then employed could be concentrated into a pyritic fraction that was only 2 per cent of the mass fed. The process was applied at Government Gold Mining Areas in 1935, and shortly after at Brakpan Mines15. At Government Gold Mining Areas, a rougher float using xanthate collector and cresylic acid frother at a pH value of 6.0 to 6.5 yielded a 7 per cent concentrate that contained 87 per cent of the gold in the 5 g/t feed.

It was noted in that work that, if the product was cleaned, an 'acid-grade' pyrite could be produced but this meant a loss of efficiency in the gold recovery, and accordingly the process was not pursued; instead, the plants were run primarily for the recovery of gold. No other plants have been run on the Witwatersrand specifically and solely for the recovery of gold from the ore, although, of course, flotation is the basis for the recovery of gold in the eastern Transvaal and elsewhere in the world. It should be noted, however, that at Hartebeesfontein 85 per cent of the gold was floated into a silicous concentrate that was 2 per cent by mass of the feed by the addition of only a frother and dithiophosphate16,17; and at Zandpan attempts were made to produce a tailing so low in gold that it was not economic to cyanide it18, but this did not prove to be possible.

However, it can be mentioned that the use of a frother alone yielded19 a gold recovery of 94.1 per cent into 52.5 per cent of the feed during the flotation of finely milled (67 per cent minus 75 μm) Elsburg ore; 90.8 per cent into 42.0 per cent of the feed during the flotation of Vaal Reefs ore ground to 77 per cent minus 75 μm; and 83.4 per cent into 18.7 per cent of the feed during the flotation of 44 per cent minus 75 μm Vaal Reefs ore. In each case, the recoveries of uranium and pyrite were similar to the fraction of feed floated, which indicates the inherent floatability of the gold.

Some accent was recently placed on the recovery of gold by flotation from gravity concentrates. At Village Main, a gravity concentrate is 'redressed' on a shaking table, and the cleaned concentrate is floated with a frother and dithiophosphate16. The recovery from the flotation is 95 per cent, and the flotation concentrate can be smelted directly to yield a bullion averaging 870 parts of gold per thousand. At Loraine, it was found20 that 90 per cent of the gold in the underflow from the tertiary cyclone could be floated into 1.2 per cent of the ore, and 98 per cent into 2.4 per cent of the ore, by use of the same combination of reagents with the addition of Zn(CN)₂₄ to suppress the pyrite that had been activated by the xanthate and copper sulphate added elsewhere in the plant.

Similarly, tests on the flotation of gold by an undisclosed procedure from a belt concentrate with a gold content of 2.5 kg/t have shown that 87.4 per cent of the gold can be concentrated into 3.9 per cent by mass of the feed, giving a product averaging 7.3 per cent gold by
However, an economic study showed that this process has little advantage over intensive cyanidation, which was then adopted for plant use.

**Flotation of Uranium**

As noted in the Introduction, there have been few full-scale applications of processes that have been designed solely for the concentration of uranium. The flotation of uranium has been the subject of intensive laboratory study for over three decades, and it is perhaps desirable that this work should be reviewed briefly.

Early work indicated that a 20 to 30 per cent recovery of uranium could be achieved by the use of a frother alone. The mineral floated was mainly thucolite. The addition of xanthate permitted additional thucolite to be recovered along with significant amounts of uraninite. A further float with oleic acid permitted a total recovery of as much as 80 per cent of the uranium in a concentrate that was 20 per cent by mass of the feed, but the oleic acid float was sensitive to the presence of lime and iron from the grinding circuit. A combined diphenyl-thioencarbazide–xanthate float yielded over 60 per cent of the uranium in over 15 per cent by mass of the feed, but was abandoned on the grounds of impracticability. A combination of a sulphonate and fuel oil gave a recovery of as high as 84 per cent in 29 per cent of the feed, but required very large quantities of reagents. Various sulphonates were tried, but all tended to float slimes preferentially, so achieving good recoveries at the expense of grade.

Interest in uranium concentration procedures waned once a satisfactory leaching procedure had been found for the whole ore, but was revived in the early 1960s, when the uranium market declined. In one process that was evolved, 87 per cent of the uranium was concentrated from a feed containing 0,15 kg of $\text{U}_3\text{O}_8$ per ton into 45 per cent by mass of the feed, by use of a combination of 0,035 kg of Cyanamid 404, 0,15 kg of TEB, 0,22 kg of di-ethyl acid pyrophosphate, 0,7 kg of o-xylated C-13 alcohol alkyl acid phosphate, and 0,10 kg of oleic acid per ton. The rate of flotation was slow.

As a further indication of the complexity that appears to be required of any potentially successful uranium float, the study of agglomeration flotation can be cited. Reagent additions were 10 to 12 kg of kerosene, 0,35 kg of Triton X-100, 1,4 to 3,2 kg of oleic acid, and 0,2 to 0,4 kg of sulphuric acid per ton. The pulp was conditioned at a density of between 30 and 50 per cent solids by mass by an impeller revolving at 1800 r/min for 30 minutes, and was diluted to 20 per cent solids before flotation. Recoveries of over 85 per cent in 30 per cent by mass of the feed were achieved from a feed containing 0,4 kg of $\text{U}_3\text{O}_8$ per ton. Of importance was the collection of fines by this process: over 97 per cent of the uranium in the minus 12μm fraction was recovered.

About the only process that has been adopted at full scale for the recovery of uranium was that used on the low-grade circuit at Virginia. The residue from the gold plant was acidified to a pH value of 5,3 by the addition of 1,5 kg of sulphuric acid per ton, conditioned in a pachuca for several hours, and given a rougher float in a single bank of thirty-eight 1,2 m³ Agitair cells. The reagents used were 20 g of cresylic acid, 40 g of xanthates, 33 g of Aerofloat 25, 2 g of creosote, 4 g of Aerofroth 65, and 1 g of Aerofroth 70 per ton. The concentrate, 20 per cent by mass of the feed, represented a 50,5 per cent recovery of uranium and 79,4 per cent recovery of pyrite. The sulphur grade was only 5 to 6 per cent in the concentrate, but the uranium was upgraded from 0,12 to 0,3 kg/t.

It can be concluded that a generally applicable process for the concentration of uranium will be difficult to find. Fortunately, the recent increase in the price of uranium has relieved the urgency for finding such a process.

**Simultaneous Flotation of Pyrite, Gold, and Uranium**

Until recently the simultaneous recovery of pyrite, gold, and uranium as a primary means for the production of all three minerals was practised on a few mines. Recently, however, the increase in the price of gold and uranium justified the retreatment of low-grade residues, and the giant Ergo and Amururan schemes bear tribute to the success of this approach.

The process operated at Zandpan can be taken as the 'classical' prototype since it embodies most of the features incorporated in other processes. In essence, a bulk sulphide float is conducted and the concentrate is accepted for further treatment without further cleaning. As noted earlier, both gold and uranium are concentrated quite successfully by the use of reagents normally applied to pure sulphide flotation, so the fact that all three...
minerals can be concentrated simultaneously should come as no surprise.

Fig. 3 shows the flowsheet that was employed at Zandpan. The cyclone overflow (65 per cent minus 75 µm at a relative density of 1.21) was adjusted in pH to 10.1, and the following amounts of reagent per ton were added to the first conditioner: 0.06 kg of xanthate, 0.008 kg of Aerofloat 65, 0.013 kg of Aerofloat 25, and 0.063 kg of copper sulphate. From a feed averaging 1.05 per cent sulphur, and 7.2 g of gold and 0.25 kg of uranium per ton, a pyrite concentrate of 2.4 per cent by mass of the feed was produced containing 41.5 per cent sulphur and 255 g of gold and 3 kg of uranium per ton (recoveries of 91, 79 and 20 per cent respectively). In the scavenging step, 19.5 per cent of the feed was floated containing 4.3 g of gold and 0.45 kg of uranium per ton (recoveries, based on the feed, of 11 per cent gold and 35 per cent uranium). Thus, the total recovery was 90 per cent gold and 64 per cent uranium in 21.9 per cent of the feed. There was further slight scavenging of gold and uranium in the cyclone, giving a final tailing that averaged less than 0.7 g of gold and 0.14 kg of uranium per ton. The pyrite concentrate and the scavenger concentrate were pumped to Hartebeesfontein for separate treatment, and the final tailing was pumped to Ellaton.

Other successful applications of flotation ahead of cyanidation have been at Hartebeesfontein, Vogelstruisbult, Venterspost, and Libanon. In all cases, the aim of the process was to produce an acid-grade pyrite, so that the rougher concentrate was cleaned, reducing the gold and uranium recoveries.

Nevertheless, at Hartebeesfontein, a concentrate of 3.5 per cent by mass of the feed represented recoveries of 90 per cent sulphur, 79.4 per cent gold, and 28.9 per cent uranium. The feed to flotation was overflow from the secondary cyclone averaging 30 per cent minus 75 µm; the recovery of most of the gold at such a coarse grind permitted the average grind to be reduced from 83 to 68 per cent minus 75 µm with no drop in the overall recovery of gold but, of course, a significant increase in the total tonnage processed.

At Vogelstruisbult, primary ball-mill product averaging 37 per cent minus 75 µm was floated with xanthate to yield a pyrite concentrate containing nearly 350 g of gold per ton. The concentrate was milled before cyanidation to 90 per cent minus 75 µm, but the xanthate interfered with cyanidation and increased the overall plant residue by about 50 per cent. At Hartebeesfontein, the extraction of uranium before cyanidation destroyed the flotation reagents.

At both Venterspost and Libanon, however, primary ball-mill product at about 35 per cent minus 75 µm was floated with Aeromine 3037 (0.05 kg/t) and pine oil frother. The concentrate, averaging over 250 g of gold per ton (about 50 per cent recovery), was readily cyanided.
and no deleterious effects due to the flotation reagent were observed when the tailing was cyanided.

It should be noted that the Venterspost and Libanon experience could not be repeated at Western Areas, where the feed to flotation was final mill pulp rather than primary mill product. The finer grind required large quantities of amine, and the grade of the concentrate was poor. It was also noted that a disadvantage of floating gold and pyrite ahead of cyanidation was that any fault in the flotation plant could lead to a disastrous increase in the final tailings.

Reinforcing the general conclusion that high recoveries of gold and uranium can be achieved only at the expense of pyrite grade are the findings on the flotation of tailings. For instance, at Blyvooruitzicht, tailings after uranium leaching and cyanidation were conditioned with sulphuric acid at pH 5.0 to destroy residual cyanide and lime, and floated with 85 g of copper sulphate, 70 g of butyl...
xanthate, and 110 g of Dowfroth 250 per ton. The recoveries of gold and uranium are shown in Fig. 4.

Similarly, in attempts to recover pyrite, gold, and uranium simultaneously from Orange Free State residues, it was found extremely difficult to clean any simple rougher product without excessive loss of uranium. Even when a relatively low grade (33 per cent) of pyrite was accepted for acid production, the anticipated recoveries were only 85 per cent for pyrite, 51 per cent for gold, and 32 per cent for uranium (in a concentrate of about 2 per cent by mass of the feed) with mercapto- benzoiazole as collector and a dextrin gangue depressant. These recoveries may be optimistic in view of laboratory recoveries of 70 per cent pyrite, 38 per cent gold, and 20 per cent uranium for a typical low-grade residue.

The particular problem in the Free State appears to arise from easily floated gangue minerals, perhaps resulting from shales present in the area. The Ergo process is also based on the use of mercapto-benzoiazole and a frother at natural pH values between 4.5 and 7 but without a gangue depressant, and recoveries of 86 per cent sulphur, 54 per cent gold, and 20 per cent uranium were anticipated from a head grade of only 1 per cent sulphur, 0.63 g of gold, and 40 g of U₃O₈ per ton.

It should be mentioned that work was recently reported on a bulk flotation process designed to recover over 95 per cent of the gold and 80 per cent of the uranium in about 40 per cent of the mass of a coarse feed by means of a rougher float with relatively high concentrations (150 g/l) of longer-than-normal xanthates and frothers chosen to give a wet, fluid froth and so maximize the entrainment of fines into the product. In this way, it is hoped to deslime the feed to float out effectively, so that the flotation tailing, free of slimes, can be scavenged in a hydrocyclone operated to maximize the segregation on a density, rather than on a size, basis. Fig. 5 shows the recovery of gold and uranium as a function of size in this flotation step, and Fig. 6 shows the effectiveness of flotation as a grading step.

Conclusions

In conclusion, it appears that high recoveries of pyrite, gold, and uranium can be achieved only if a rougher concentrate of perhaps 20 per cent by mass of the feed is produced. It seems that reverse leaching (leaching before cyanidation) of this concentrate, followed by a cleaning flotation step to recover the pyrite, would permit significantly higher overall recoveries than the routes being employed at present.

References


