

# The separation of kerogen from pyrophyllite by flotation

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## SYNOPSIS

Tests were carried out in a Hallimond microflotation cell and a Denver D12 cell on typical residue material from a gold mine in the Orange Free State (South Africa), in which 50 per cent of the kerogen was larger than 100  $\mu\text{m}$  in size. Although kerogen is naturally hydrophobic, the observed unexpectedly poor flotation response may be due to occlusion of the kerogen by a slime coating and subsequent depression of the slime by guar gums.

The recovery of gold from samples spiked with kerogen increased, with no significant reduction in grades, when a petroleum-based collector and tetrasodiumpyrophosphate (a dispersant) were used.

## SAMEVATTING

Daar is toetse in 'n Hallimond-mikroflotasiesel en 'n Denver D12-sel uitgevoer op tipiese residumateriaal afkomstig van 'n goudmyn in die Oranje-Vrystaat (Suid-Afrika), waarin 50 persent van die kerogeen groter as 100  $\mu\text{m}$  was. Hoewel kerogeen van natuur hidrofobies is, kan die waargenome onverwags swak flottasiereaksie toe te skryf wees aan die okklusie van die kerogeen deur 'n slikslag en die daaropvolgende onderdrukking van die slik deur guargom.

Die herwinning van goud uit monsters wat met kerogeen gesout is, het toegeneem, met geen beduidende daling in die graad nie, toe 'n versamelaar met 'n petroleumbasis en tetranatriumpirofosfaat ('n disperseermiddel) gebruik is.

## Introduction

Kerogen is a carbonaceous mineral occurring widely in South Africa, in the gold-bearing reefs of the Transvaal and the Orange Free State. It usually contains<sup>1</sup> thorium, uranium, carbon, hydrogen, and oxygen, often in concentrations of up to 2 kg per ton of gold and more than 50 kg per ton of uranium. It is thought to have originated from primitive microbial matter that served as a collecting matrix for the uranium and gold<sup>2</sup>. In the Witwatersrand reefs it occurs as individual seams that are several millimetres thick and up to a few metres in length<sup>3</sup>. According to its mode of occurrence it can be classified as either columnar or flyspeck<sup>4</sup>, and is often associated with pyrophyllite, particularly in the basal reefs of the Orange Free State goldfields<sup>5</sup>. Although the monitoring of kerogen is difficult in material balances, it is accepted that, notwithstanding its natural hydrophobicity, significant quantities are lost during the flotation of pyrite<sup>6</sup>.

The purpose of the study described here was to investigate the flotation characteristics of kerogen, and to compare its floatability with that of pyrophyllite, so that its selective flotation in the presence of the latter could be improved.

Four reasons have been proposed for the poor recovery of kerogen. Firstly, it is thought that, as a result of its extreme friability, it may be present in a very finely divided form and hence be difficult to float. Secondly, as a result of its normally low density, it may pass through the cyclone overflow of a milling circuit and thus report to the flotation cells in a coarsely divided state<sup>7</sup>. Third-

ly, it has been proposed that the standard depressants used in the flotation process to prevent the flotation of the gangue mineral pyrophyllite may also depress the kerogen. Fourthly, a slime coating of pyrophyllite round a kerogen particle may occlude the mineral and render it unfloatable.

Such coatings are known to interfere with interactions between mineral particles and bubbles<sup>8,9</sup>. Jowett<sup>9</sup> investigated the effect of a coating of slime from clays on coal. Slime particles coated the hydrophobic non-polar surface of the coal, rendering it hydrophilic. The edges of the clay particles were positively charged in a manner not dissimilar to that of pyrophyllite, and the slime coating was largely a result of an electrostatic attraction between the gangue and the mineral. Jowett observed that this effect could be reduced by the use of a dispersant that neutralizes the positively charged end sites of the clay particles.

Leach<sup>10</sup> showed that flotation and conditioning times have little effect on the recovery of kerogen, and that the addition of pine oil and kerosene do not significantly improve the recovery of the mineral. Gordon<sup>8</sup>, however, achieved high recoveries of kerogen (88 to 98 per cent) using 1000 to 2000 p.p.m. of kerosene. Lagendijk<sup>11</sup> showed that the stagewise addition of frother increased the recovery of kerogen, but this may have been largely due to the increased mass of concentrate.

## Experimental Procedure

Samples of kerogen were hand-picked underground at the Western Deep Levels Gold Mine, and, after having been crushed into pieces smaller than 5 mm, they were separated by hand-sorting from any associated quartzitic material. This almost pure sample was then ground to produce a size fraction of 38 to 90  $\mu\text{m}$ . The pyrophyllite used in this study was obtained from Free State Geduld

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Gold Mine, and was screened to produce a size fraction of 38 to 90  $\mu\text{m}$ .

The zeta potentials of the pyrophyllite and kerogen were determined at 22°C by the use of a zetameter. The accuracy of the measurement technique was confirmed with silica, which was found to have a zeta potential of 27,6 mV (reported<sup>12</sup> value 29,0 mV). The size distribution of the kerogen in the feed sample was determined by use of a 10 kg sample of residue material split into six size fractions. Each fraction was mixed well with bromoform (relative density 2,5) in an ultrasonic bath, and the float was filtered, washed with acetone, dried, and weighed. The bromoform test was also used in the determination of the kerogen concentrations in the flotation studies.

Microflotation studies were carried out with a Hallimond microflotation cell<sup>12</sup>. In all the microflotation studies, 2 g of the ore were mixed with 20 ml of deionized water. An aeration rate of 4 cm<sup>3</sup>/min and a conditioning time of 2 minutes were used.

Flotation was carried out for 3 minutes, which was found to be adequate for reproducibility (Fig. 1). The ore that floated and the tailings were filtered, dried, and weighed. The recovery was calculated by differences, and mass balances were checked in all cases. Considerable effort was taken to ensure that adequate reproducibility was obtained. Bottled air was used, and all the runs were repeated at least three times. In some instances, the recovery data were normalized with respect to the natural floatability performance.

The conventional batch work was carried out in a laboratory-scale Denver D12 cell on residue material from President Steyn Gold Mine.

In the standard flotation procedure, the reagent dosages were as follows: Senkol (100 p.p.m.), Acrol J2P350 (60 p.p.m.), and triethoxybutane (TEB) (10 p.p.m.).

In addition to these reagents, a petroleum collector, Accoal, and a dispersant, tetrasodiumpyrophosphate, were investigated. In some tests material containing 0,33 per cent kerogen by mass was added to the residue material. Sulphur, gold, and uranium assays were carried out on all the concentrate, feed, and tailing samples.

### Results

An analysis of the kerogen used in this study showed that it contained the following: uranium (58 500 p.p.m.), thorium (4240 p.p.m.), gold (1250 p.p.m.), silver (250 p.p.m.), and carbon (57,05 per cent), in addition to significant amounts of lead, aluminium, and iron.

Fig. 1 shows the cumulative size distribution of the feed used in the batch tests; 50 per cent of this material is finer than 74  $\mu\text{m}$ . The same diagram shows the size distribution of the kerogen in this feed, 50 per cent being coarser than 100  $\mu\text{m}$  and 5 per cent smaller than 38  $\mu\text{m}$ . Table I gives the zeta potentials of the kerogen and pyrophyllite at various pH values.

Fig. 2 shows the reproducibility obtained for the recovery of pyrophyllite in the Hallimond-tube flotation cell, and Fig. 3 the natural floatability of the pyrophyllite and kerogen. It is clearly seen that, as expected, both minerals are readily floatable.

Figs. 4 and 5 show the effects of carboxymethyl cellulose

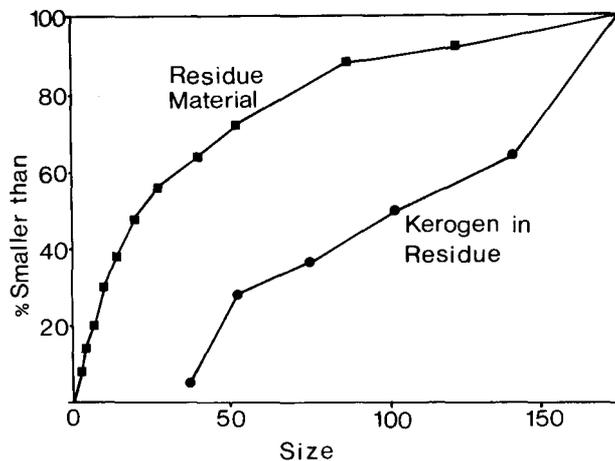


Fig. 1—Cumulative size distribution (in  $\mu\text{m}$ ) of residue material and kerogen in the residue

TABLE I  
ZETA POTENTIALS OF KEROGEN AND PYROPHYLLITE

Kerogen mV	Pyrophyllite mV	pH
-2,6	-12,8	4
-18,8	-24,0	5,5
-36,0	-24,0	7

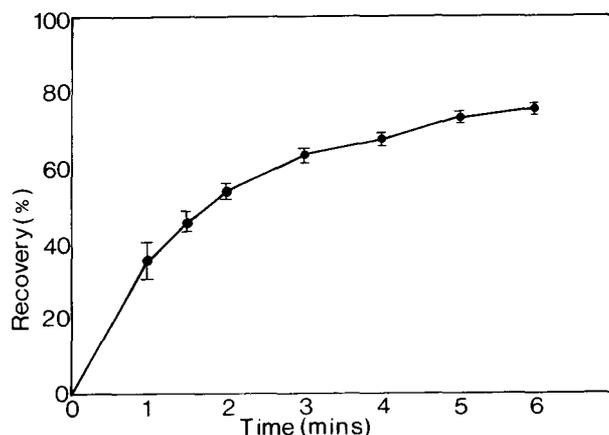


Fig. 2—Reproducibility obtained in the flotation of pyrophyllite (Hallimond tube)

(CMC) and the substituted guar gums, Jaguar M700 and Acrol J2P350, on the floatability of pyrophyllite and kerogen at a pH value of 4. It is clear that these reagents depress the kerogen but have a greater depressive effect on the pyrophyllite than on the kerogen. Moreover, addition rates of more than approximately 50 g/t have little further effect on the recoveries. At pH values of 6 and 8, similar but less significant trends were observed. No increase in the depressive action of a guar-gum depressant was observed when the tests were carried out in the presence of Ca<sup>2+</sup> ions. Neither the collector sodium mercaptobenzothiazole (SMBT) nor the frother TEB has any significant effect on the action of these depressants.

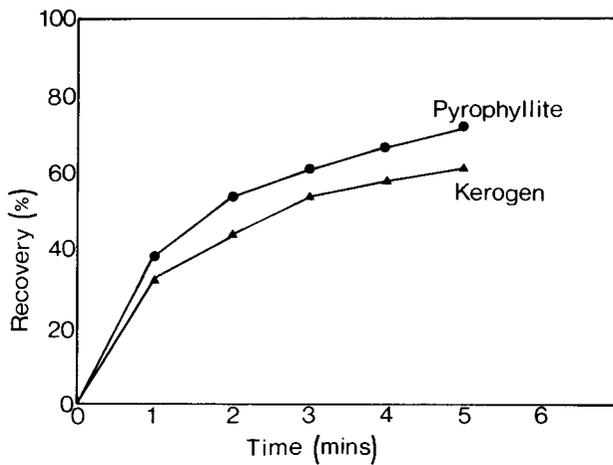


Fig. 3—Natural floatability of pyrophyllite and kerogen

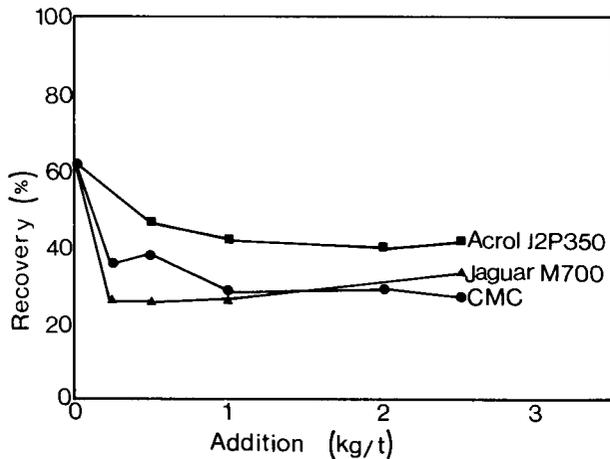


Fig. 4—Effect of depressants on the flotation of kerogen

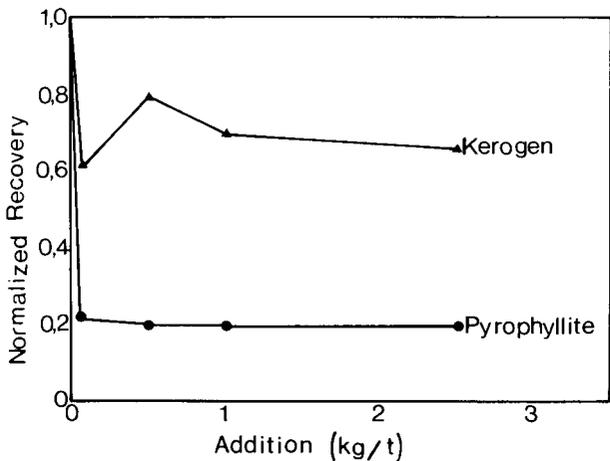


Fig. 5—Normalized recoveries when Acrol J2P350 was used

Fig. 6 shows the flotation of kerogen in a Hallimond tube from a mixture of pyrophyllite and kerogen in the proportions 95:5 in the presence of Acrol J2P350 at a pH value of 4. Plot A1 shows clearly that the addition of the dispersant tetrasodiumpyrophosphate (TSPP) at dosages of more than 200 p.p.m. caused an increase in

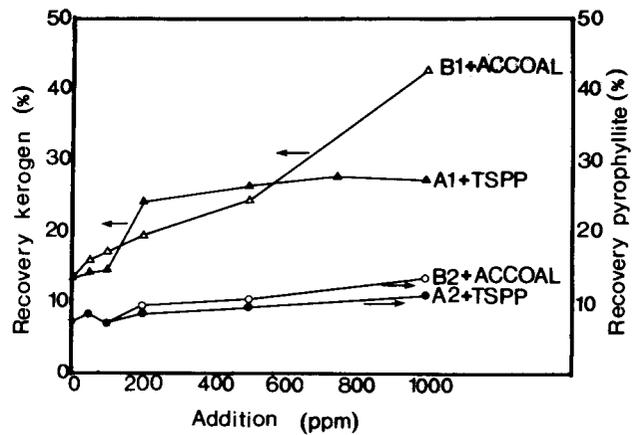


Fig. 6.—Flotation from a mixture of pyrophyllite and kerogen in the proportions 95:5 in a Hallimond tube (A1 and B1 = recovery of kerogen; A2 and B2 = recovery of pyrophyllite)

the recovery of kerogen from 13 to 27 per cent. Plot A2 shows the effect of the same treatment on the recovery of the pure pyrophyllite. The dispersant did not merely cause an increase in the mass of concentrate but is clearly playing a role in enhancing the selective recovery of kerogen. Plot B1 shows the effect when a petroleum-based collector, Accoal, was added to the kerogen-pyrophyllite mixture dosed with Acrol J2P350, and plot B2 shows the effect of the same treatment on the recovery of pure pyrophyllite. The petroleum collector caused the expected increase in mass of concentrate, together with an increase in the selective recovery of kerogen.

Conventional batch-scale tests were carried out on the effect of the TSPP dispersant and the Accoal collector on the flotation of kerogen from the residue material obtained from President Steyn. The petroleum collector was added after 6 minutes of flotation to ensure that it did not cause a totally unselective float of the fine gangue material. It was thus intended to act partially as a scavenger of residual kerogen.

Table II shows the results of these tests. The dispersant had little effect on the flotation, causing only very slight increases in the recovery of gold and uranium. The petroleum collector, as expected, caused an increase in mass of concentrate, with a consequent decrease in grades. In the tests in which the ore was spiked with kerogen (0,33 per cent), dispersant was added at  $t = 0$  minutes and Accoal was added at  $t = 6$  minutes. As shown in Table II, the dispersant caused significant increases in the recovery of gold and uranium—more than would be expected from the results on the standard ore. Moreover, the grades did not decrease, indicating that the dispersant was playing a role in increasing the recovery of kerogen. The addition of the petroleum-based collector at  $t = 6$  minutes resulted in increased recoveries owing to an increase in mass of concentrate, but the grades were consequently lower. In all the batch tests, the maximum standard deviation for the final recoveries was less than 1,5 per cent.

### Discussion

The size distribution of the kerogen in the President Steyn feed used in this study is consistent with the results obtained by Feather<sup>7</sup>: 50 per cent of the kerogen was

TABLE II  
CONVENTIONAL BATCH-SCALE TESTS

Flotation test	Time min	Recovery, %			Grade		
		S*	Au	U	S* %	Au g/t	U g/t
Head assays		—	—	—	0,83	0,77	121
Standard (Senkol, Acrol, TEB)		90	52	32	15	8,5	750
Standard + dispersant (TSPP)		90	53	33	14	8,6	750
Standard + petroleum collector (Accoal)		92	65	40	10,6	6,2	600
Sample spiked with kerogen + standard reagents	6	80	71	68	19,8	108	6400
	18	92	79	73	12,6	63	3700
Sample spiked with kerogen + standard reagents + TSPP ( <i>t</i> = 0 min)	6	82	76	72	20,4	113	6450
Sample spiked with kerogen + standard reagents + TSPP ( <i>t</i> = 0 min) + Accoal ( <i>t</i> = 6 min)	18	95	86	77	8,8	56	3100

\*Sulphide sulphur

greater than 100  $\mu\text{m}$ , which indicates that the loss of kerogen in flotation processes is probably not due to ultrafines of the material. Where the size distribution of the kerogen particles differs from that of the feed, this may be due to the larger kerogen particles passing through the cyclone overflow as a result of their generally low relative density<sup>12</sup>. The results obtained in this investigation with the Hallimond tube show clearly that kerogen is depressed by the standard pyrophyllite depressants used on flotation plants. Fig. 6, which shows that a dispersant tends to increase the recovery of kerogen, indicates that the depression of kerogen may be a result of its being occluded by coatings of slime from the pyrophyllite.

It was shown that the addition of TSPP and a petroleum-based collector to a sample of feed spiked with kerogen caused no change in the grade of pyrite, but increased the gold and uranium grade and recoveries. This was notwithstanding the fact that the dispersant and petroleum collector resulted in an increase in the mass of concentrate, as would be expected. It can thus be

reasonably concluded that the dispersant and petroleum collector played an important role in recovering the kerogen added to the sample. This is consistent with the theory that a dispersant prevents the occlusion of kerogen by coatings of slime arising from the pyrophyllite, allowing the petroleum collector to play its role as a kerogen collector. Cabassi *et al.*<sup>6</sup> showed recently that the use of a mixture of MIBC and paraffin in addition to the suite of reagents normally used increased the gold recovery substantially on kerogen-rich flotation plants in the Orange Free State. However, the sulphur grades were lower, implying an increased mass of concentrate. The recovery of kerogen increased considerably, but the proportion of uranium associated with this mineral was small.

### Conclusions

This work indicated that the depressive action of standard guar-gum depressants acting on the coatings of slime formed on kerogen particles may be the main reason for the poor flotation response of kerogen. The recovery of kerogen can be improved by the use of a dispersant, such as tetrasodiumpyrophosphate, and a petroleum-based collector. As 50 per cent of the kerogen was greater than 100  $\mu\text{m}$ , its low recovery cannot be explained in terms of its fineness.

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