TR20_332_339

R.694. Production of a concentrate from oil shale at China Flat.

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The Endeavour Oil Company N.L. requested that an investigation be undertaken on a sample of oil shale from China Flat, near Latrobe, to evaluate the feasibility of producing an oil shale concentrate by means of grinding and flotation. The investigation aimed to produce a low ash oil spore concentrate, with a consequent high recovery.

The sample used in this investigation (registered number 742639) consisted entirely of large slabs of shale and was stated to have come from mined surface dumps at China Flat. The total sample was reduced to pass 6.37 mm (¼") screen in a laboratory jaw crusher and mixed, prior to commencement of test work. A head sample taken from the mixed -6.37 mm sample by riffling was found to contain 61.6% ash and gave the following sizing analysis and ash distribution.

Fraction	*% Mass*	*Cum. % Mass*	*% Ash*	*% Ash Distribution*	*Cum. % Ash Distribution*
+4.75 mm	1.9	1.9	57.5	1.8	1.8
+2.36 mm	35.2	37.1	58.6	33.7	35.5
+1.18 mm	20.9	58.0	59.2	20.2	55.7
+600 µm	9.8	67.8	59.7	9.5	65.2
+300 µm	8.1	75.9	55.7	7.4	72.6
+150 µm	6.2	82.1	48.6	4.9	77.5
+75 µm	4.2	86.3	58.8	4.0	81.5
+38 µm	1.4	87.7	70.5	1.6	83.1
-38 µm	12.3	100.0	84.1	16.9	100.0
Head	100.0	-	(61.3)	100.0	-

METHOD

Samples of the -6.37 mm shale were ball mill ground at 57% solids for periods of five, fifteen and thirty minutes; one further sample was ground in a laboratory hammer mill. Products from this treatment were sized and examined for ash distribution.

Samples of ball mill ground and hammer mill ground shale were subjected to froth flotation in a Denver laboratory flotation cell with the products being examined for ash distribution. The cleaner flotation concentrates resulting from two of the flotation tests were further ball mill ground prior to a final cleaner flotation stage.

Details of sizing analyses and ash distribution are given in Table 1.

Flotation

Test N1. -6.37 mm shale was ground for 15 minutes in a laboratory ball mill at 57% solids $^{W}/_{W}$, prior to flotation. One stage of concentrate cleaning was used and total reagent consumption was as follows.

Frother Teric 401	0.05 kg/tonne
fuel oil	0.10 kg/tonne

Table 1. SIZING ANALYSIS AND ASH DISTRIBUTION OF GROUND -6.37 mm SHALE

Particle Size	Laboratory Hammer Mill Discharge				Ball Mill Ground for 5 min (57% Solids w/w)				Ball Mill Ground for 15 min (57% Solids w/w)				Ball Mill Ground for 30 min (57% Solids w/w)			
	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn
+4.75 mm	-	-	-	-	0.5	54.1	0.4	0.4	-	-	-	-	-	-	-	-
+2.36 mm	-	-	-	-	9.4	53.0	8.1	8.5	-	-	-	-	-	-	-	-
+1.18 mm	-	-	-	-	8.9	50.6	7.3	15.8	0.1	45.7	0.1	0.1	-	-	-	-
+600 µm	-	-	-	-	8.3	49.8	6.7	22.5	12.3	24.6	4.8	4.9	-	-	-	-
+300 µm	2.2	17.4	0.6	0.6	11.4	46.0	8.5	31.0	17.9	28.6	8.2	13.1	0.2	14.8	0.1	0.1
+150 µm	20.2	29.2	9.6	10.2	11.9	38.7	7.5	38.5	7.1	50.3	5.7	18.8	6.3	13.0	1.3	1.4
+75 µm	20.7	47.2	15.9	26.1	9.2	48.3	7.2	45.7	2.8	53.7	2.4	21.2	16.1	13.6	3.6	5.0
+38 µm	10.3	67.5	11.3	37.4	5.7	76.0	7.0	52.7	9.8	73.5	11.5	32.7	7.1	34.8	4.0	9.0
-38 µm	46.6	82.5	62.6	100.0	34.7	84.1	47.3	100.0	50.0	84.1	67.3	100.0	70.3	79.1	91.0	100.0
Head	100.0	(61.4)	100.0	-	100.0	(61.7)	100.0	-	100.0	(62.5)	100.0	-	100.0	(61.1)	100.0	-

Fraction	*% Mass*	*% Ash*	*% Ash Distribution*
F2C	21.6	33.8	11.4
F2T	49.9	66.4	51.9
F1C	71.5	(56.6)	63.3
F1T	28.5	82.1	36.7
Head	100.0	(63.8)	100.0

Test N2. Flotation feed for this test was prepared by hammer mill grinding of the -6.37 mm shale. Three stages of flotation concentrate cleaning were adopted, followed by a fourth stage after the concentrate from the third cleaning operation had been ball mill ground for thirty minutes at approximately 30% solids W/w. Total reagent addition was as follows:

Calgon	3.4 kg/tonne
Frother Teric 401	0.08 kg/tonne
fuel oil	0.05 kg/tonne

Fraction	*% Mass*	*% Ash*	*% Ash Distribution*
F4C	33.7	27.0	15.1
F4T	12.5	64.4	13.4
F3C	46.2	(37.1)	28.5
F3T	5.3	69.8	6.1
F2C	51.5	(40.5)	34.6
F2T	16.3	72.9	19.8
F1C	67.8	(48.3)	54.4
F1T	32.2	85.3	45.6
Head	100.0	60.2	100.0

Test N3. Flotation feed in this test was prepared by ball mill grinding -6.37 mm shale for 15 minutes at 57% solids W/w. Four stages of concentrate cleaning were adopted, with the fourth stage occurring after the third cleaner concentrate had been ball mill ground for 30 minutes at 57% solids W/w. Total reagent consumption was:

Calgon	3.4 kg/tonne
Frother Teric 401	0.15 kg/tonne
fuel oil	0.05 kg/tonne

Fraction	*% Mass*	*% Ash*	*% Ash Distribution*
F4C	33.8	16.6	9.3
F4T	14.2	78.7	18.6
F3C	48.0	(35.0)	27.9
F3T	6.8	83.0	9.4
F2C	54.8	(40.9)	37.3
F2T	11.5	76.7	14.7
F1C	66.3	(47.1)	52.0
F1T	33.7	85.6	48.0
Head	100.0	60.1	100.0

Test N4. -6.37 mm shale was ground for 5 minutes at 57% solids w/w, prior to flotation. Three stages of flotation were used and the products of this test were sized and analysed for ash distribution. Total reagent consumption was as follows:

Calgon	3.4 kg/tonne
Frother Teric 401	0.10 kg/tonne
fuel oil	0.05 kg/tonne

Fraction	*% Mass*	*% Ash*	*% Ash Distribution*
F3C	36.0	(39.0)	23.4
F3T	9.4	(68.2)	10.7
F2C	45.4	(45.0)	34.1
F2T	8.2	(69.3)	9.5
F1C	53.6	(48.8)	43.6
F1T	46.4	(72.9)	56.4
Head	100.0	(60.0)	100.0

Details of size analysis and ash distribution are given in Table 2.

DISCUSSION

Flotation Test No.	*Stage of Flotation Cleaning*	*% Mass of Final Cleaner Concentrate*	*% Ash in CFC*	*% Ash Distn in CFC*	Method and grinding time
N1	2	21.6	33.8	11.4	15 min B/M
N2	4	33.7	27.0	15.1	H/M + F3C 30 min B/M
N3	4	33.8	16.6	9.3	15 min B/M + F3C 30 min B/M
N4	3	36.0	39.0	23.4	5 min B/M

H/M = hammer mill

From the results obtained it can be seen that it is possible to reduce the percentage ash (and consequently increase the hydrocarbon quantity) of the sample as supplied quite significantly by grinding and flotation of the oil shale. The oil shale floated quite readily but in all tests the percentage ash of the flotation concentrate was increased by the presence of slime material.

An ash examination of the final concentrate (F3C) of test N4 revealed that as the size of the oil shale particle decreased the percentage ash increased. This is thought to have occurred due to the impingement of barren siliceous particles into the oil spore cavities as well as the presence of some slime in the finer fractions.

The ash examination of the various methods of grinding the head sample shows that all material should be ground to at least -600 μm prior to flotation. No grinding of oil shale material through a definite particle size has been attempted in this investigation.

To enable an evaluation of the oil recovery in each flotation test to

Table 2. TEST N4 - SIZE ANALYSIS AND ASH DISTRIBUTION

Fraction	F3C				F3T				F2T				F1T			
	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn	Mass %	Ash %	% Ash Distn	Cum. % Ash Distn
+2.36 mm	-	-	-	-	-	-	-	-	-	-	-	-	1.1	42.9	0.6	0.6
+1.18 mm	-	-	-	-	-	-	-	-	trace	-	trace	trace	10.7	46.0	6.8	7.4
+600 µm	0.1	25.2	9.4	9.4	0.5	34.6	6.2	6.2	3.1	37.1	1.6	1.6	14.8	46.6	9.5	16.9
+300 µm	14.4				11.8				16.9	41.4	10.1	11.7	10.6	51.5	7.5	24.4
+150 µm	29.4	28.0	21.1	30.5	7.5	39.6	4.4	10.6	6.1	54.2	4.8	16.5	3.5	65.1	3.1	27.5
+75 µm	21.2	36.3	19.7	50.2	3.5	59.7	3.1	13.7	2.2	72.0	2.3	18.8	2.9	82.2	3.3	30.8
+38 µm	12.8	52.4	17.2	67.4	6.1	86.1	7.7	21.4	5.7	91.7	7.5	26.3	10.7	94.8	13.9	44.7
-38 µm	22.1	57.4	32.6	100.0	70.6	75.9	78.6	100.0	66.0	77.4	73.7	100.0	45.7	88.2	55.3	100.0
Head	100.0	(39.0)	100.0	-	100.0	(68.2)	100.0	-	100.0	(69.3)	100.0	-	100.0	(72.9)	100.0	-

be made, an approximate relationship between contained oil volume and percent ash was obtained and its details are appended. An approximate comparison of the oil recovery in the four flotation tests performed is detailed below:

Test	*Fraction*	*% Mass*	*% Ash*	*Oil (litres/tonne)*	*% Oil Distribution*
N1	F2C	21.6	33.8	410	41.3
	F2T	49.9	66.4	197	45.9
	F1T	28.5	82.1	96	12.8
	Head	100.0	(63.8)	(214)	100.0
N2	F4C	33.7	27.0	455	67.2
	F4T	12.5	64.4	210	11.5
	F3T	5.3	69.8	178	4.1
	F2T	16.3	72.9	158	5.2
	F1T	32.2	85.3	76	12.0
	Head	100.0	(60.2)	(228)	100.0
N3	F4C	33.8	16.6	522	73.7
	F4T	14.2	78.7	120	7.1
	F3T	6.8	83.0	90	2.6
	F2T	11.5	76.7	130	6.2
	F1T	33.7	85.6	74	10.4
	Head	100.0	(60.1)	(240)	100.0
N4	F3C	36.0	39.0	375	56.2
	F3T	9.4	68.2	188	7.4
	F2T	8.2	69.3	180	6.1
	F1T	46.4	72.9	157	30.3
	Head	100.0	(60.0)	(240)	100.0

From a comparison of approximate oil distribution it can be seen that the conditions used in test N3 provided an oil recovery of approximately 74%.

CONCLUSIONS

(1) The oil shale sample can be readily concentrated by flotation but the flotation feed should be at least -600 µm in particle size to enable a high kerogen recovery.

(2) Grinding of primary cleaner flotation concentrates is essential for maximum rejection of barren material.

(3) The oil shale sample was found to contain approximately 230 litres/tonne of oil and had an ash content of 61.6%.

APPENDIX 1

To enable an assessment of the recovery of oil and gas in a certain shale after a particular concentration process it is necessary to know the relationship between percentage ash and the percentage hydrocarbon. Products from investigation R.694 were therefore distilled in a cast iron retort, and the volumes of gas and oil measured.

The method used was based on that given in U.S. Bureau of Mines Bulletin 415 (Studies of certain properties of oil shale and shale oil). Thirty, 50 or 100 g (depending upon grade) of the shale products were separately placed in a cast iron retort; the cast iron retort was then sealed and heated slowly in a gas furnace at such a rate as to achieve a temperature of 650°C in approximately one and a half hours. The temperature of the retort was then increased rapidly to between 950°C and 1000°C to complete the distillation. The distilled gas was cooled in a water cooled condenser and its volume measured by use of inverted measuring cylinders at atmospheric pressure and temperature. The distilled oil was collected in a glass separating flask; oil was removed at the end of each test and its volume measured.

RESULTS

It was found impossible to obtain repetitive measures of gas volumes on similar samples. This is thought to have occurred through

(a) break down of oil into gas;
(b) problems with sealing of the cast iron retort and consequent leaks; and
(c) lack of complete control of furnace temperature.

Gas volume results will therefore not be quoted.

Some duplication of results were obtained in oil quantity and the relationship between oil quantity (litres per tonne) and percentage ash is shown on the accompanying graph (fig. 108).

CONCLUSION

The apparatus used enabled an approximate relationship between percentage ash and oil volume from various oil shale samples to be achieved. However, due to the nature of the results it should be noted that the graph supplied is for use as a guide only particularly when it is considered that oil and gas are co-ordinate in any one oil shale sample.

[23 December 1975]

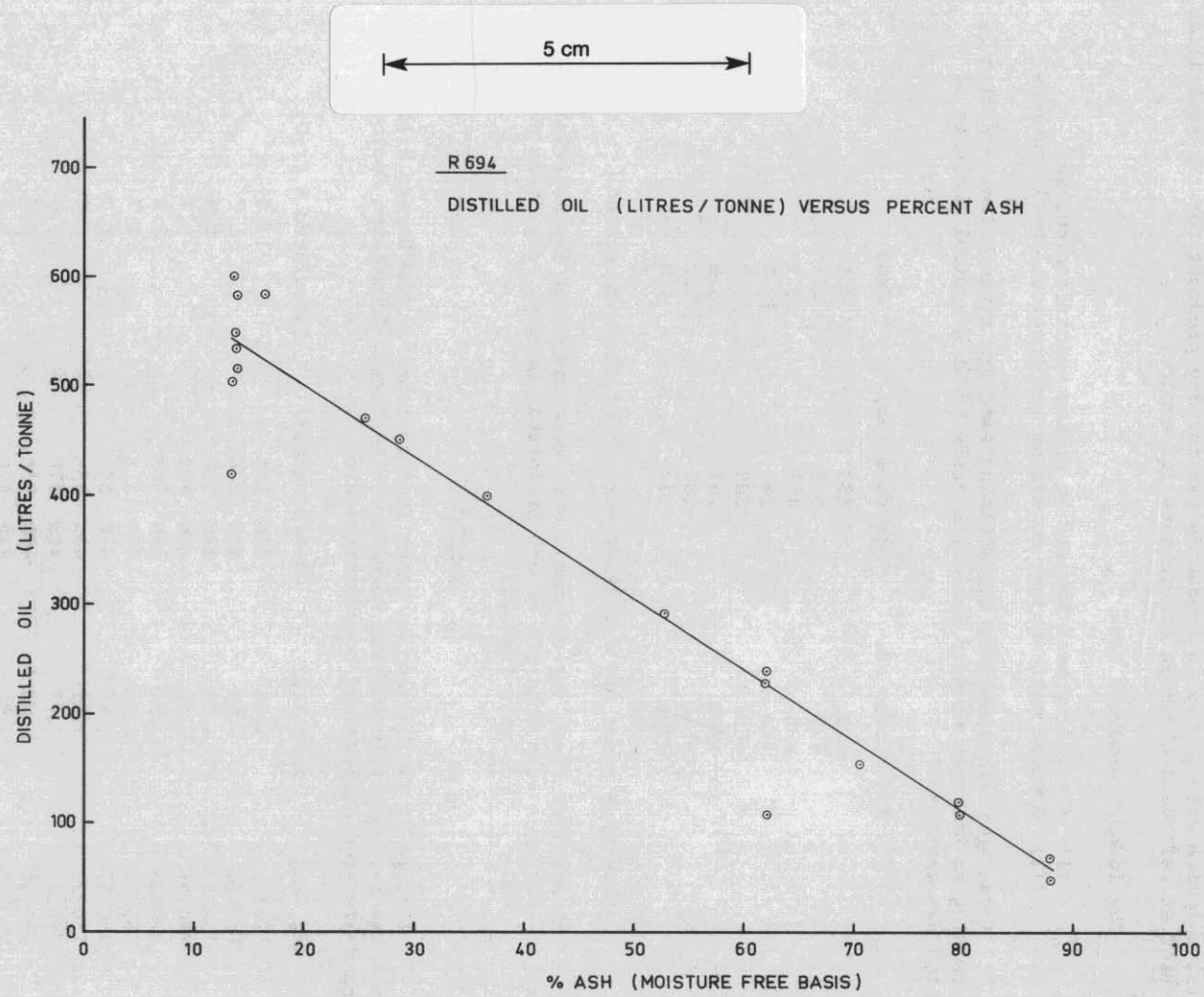
5 cm
R 694
DISTILLED OIL (LITRES / TONNE) VERSUS PERCENT ASH
DISTILLED OIL (LITRES / TONNE)
0
100
200
300
400
500
600
700
0
10
20
30
40
50
60
70
80
90
100
% ASH (MOISTURE FREE BASIS)

Figure 108.