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HISTORICAL REVIEWS

BENEFICIATION OF ESTONIAN (KUKERSITE) OIL SHALE

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The beneficiation of oil shales and separation of organic matter (OM) enables expansion of fields of their industrial application. For example the concentrate of OM may be used for separation of dicarboxylic acids for further production of plastics, plasticizers and other chemical products. Due to enrichment in OM in the beneficiation process, oil shales may be used more effectively in both power engineering and oil production. Besides, the separation of calcite allows to reduce emission of carbon dioxide at processing oil shales.

To choose the optimum grinding method to enable most selective separation of OM, different possibilities were tested. The best results, related to further separation of OM in the hydrocycling process, were obtained by using a centrifugal-rebound mill for grinding oil shale. The three-stage hydrocycling of the ground oil shale makes it possible to upgrade the concentrate up to 50.2% OM at high recovery – 91.5% from the feed ore.

Separation of OM was carried out by using the flotation process, and the effect of different parameters was investigated. These included reagent conditions, particle size, pH level and flotation time. After five cleaner flotation of the rough concentrate the product containing 85.7% OM at the recovery of 81.3% from the feed oil shale was obtained.

In this report the general flow sheet involving combined hydrocycling and flotation processes is described. This flow sheet enables to produce a concentrate containing 90% OM at the recovery of 90.9% from the feed oil shale.

Introduction

Working at the former Institute of Chemistry of the Estonian Academy of Sciences both authors under the supervision of Dr. R. Koch investigated benefication of Estonian oil shale. The materials were not published and now the authors hope that this paper may be of interest for readers nowadays.

Separation of organic matter by beneficiation of oil shales can significiantly extend their industrial applications. The concentrate of kerogen was used in the former Institute of Chemistry of the Estonian Academy of

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Sciences [1] for separation of dicarboxylic acids – from adipic to sebacic acid – for further production of plastics, platicizers and other chemical products. Besides, upgraded oil shales may be used more effectively and economically in power engineering or for oil production. There are big reserves of low-grade oil shales which up to now have not been of particular interest for industrial utilization [2].

It can be pointed out that the main features that influence technological characteristics of the oil shale upgrading and predetermine possible methods for their beneficiation are chemical and mineral composition of oil shales, their structural specific features, and hence, different approaches may be required.

Experimental setup

Oil shale –25 + 0 mm from the Käva mine was used for carrying out the beneficiation. Gravimetric composition of the feed oil shale is presented in Table 1. Main constituents of oil shale were: organic matter (OM) – 35%, carbonate component (calcite) – 35% and terrigenic part (quartz, feldspars, kaolinite, alumina) – 30% [3].

The method of kerogen analysis in ground samples and flotation products is based on the dependence between density and OM content of oil shale. Samples were vacuum filtered, washed and dried in an oven at 105 °C. Dried samples (3 g) were subjected to determination of apparent density (relation of oil shale mass to its volume without pore volume) by pycnometric method [3 pp. 48–50, 4].

Grinding

To choose the optimum grinding method in respect to further selective separation of OM we tested different possibilities for grinding, such as roller mill, hammer mill and centrifugal-rebound mill. The flow sheet for three-stage grinding of oil shale in the roller mill (dimensions of plates 300×200 mm, power 7 kW) is presented in Fig. 1, and the data obtained in Table 1.

The feed oil shale was ground in the roller mill to less than 1.25 mm. The results show the increasing of yield of classes –1.25 + 0.63 (from 3.8% to 11.82%) and –0.63 + 0.315 mm (from 17.95% to 25.45%) after the third stage of grinding. That means that harder pieces (calcite) remain unbroken in the three-stage grinding process. The data about the distribution of OM show that it is mostly concentrated in fine classes: 73.74% of OM in the feed belongs to the size range of –0.16 + 0.0 mm. In the grinding process OM percentage in the fraction –0.63 + 0.315 mm increases from 20.30% in the first stage to 24.37% in the third stage, in correlation with increasing yield of this fraction, and decreases in the fine fraction –0.16 + 0.0 from 66.54% to 53.95% in the third stage.

Table 1. **Distribution of OM in different fractions obtained at grinding in roller mill**

Grain size, mm	Feed –1.25 mm			After the first grinding			After the second grinding			After the third grinding		
	Yield, %	OM content, %	OM recovery, %	Yield, %	OM content, %	OM recovery, %	Yield, %	OM content, %	OM recovery, %	Yield, %	OM content, %	OM recovery, %
–1.25 + 0.63	3.80	33.1	3.27	4.78	33.6	4.30	89.65	34.8	8.42	11.82	33.8	11.17
–0.63 + 0.315	17.95	31.4	14.65	22.35	34.1	20.30	23.58	34.3	22.63	25.45	34.3	24.37
–0.315 + 0.16	10.95	29.3	8.34	10.64	31.1	8.83	10.50	32.8	9.62	70.97	34.0	10.41
–0.16 + 0.074	12.39	45.8	14.73	12.32	45.3	14.89	10.50	45.4	13.34	9.96	45.1	12.54
–0.074 +0.045	11.12	64.9	18.75	9.90	59.8	15.80	9.28	59.6	15.47	8.57	59.9	14.32
-0.045 + 0.0	43.79	35.4	40.26	40.11	33.5	35.85	37.5	29.1	30.52	33.23	29.3	27.19
Total	100.00	38.5	100.00	100.00	37.5	100.00	100.00	35.8	100.00	100.00	35.8	100.00
–0.16 + 0.0	67.30	42.2	73.74	62.33	40.0	66.54	57.28	37.0	59.33	51.76	37.4	53.95

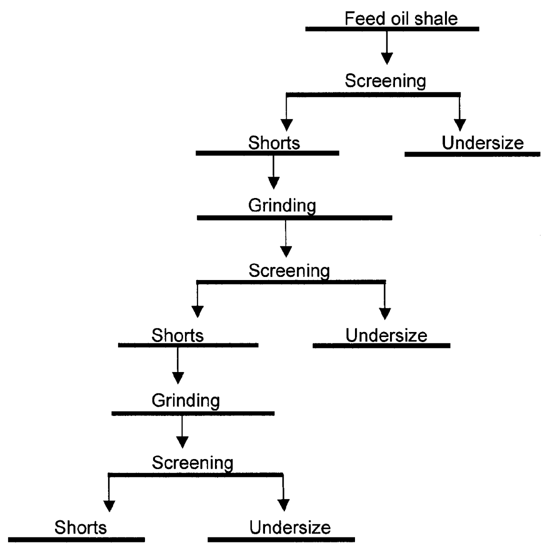

Fig. 1. Scheme of multi-stage grinding.

The results of grinding in the roller mill compared with those obtained in the hammer mill (diameter of rotor 400 mm, rotational speed 1450 rev/min) are presented in Table 2.

Table 2. **Comparison of OM distribution in different fractions obtained at grinding using roller mill and hammer mill**

Size, mm	Roller mill			Hammer mill		
	Yield, %	OM content, %	Recovery, %	Yield, %	OM content, %	Recovery, %
–3.0 +1.25	0.00	0.00	0.00	3.20	30.80	2.78
–1.25 + 0.63	7.70	37.10	7.84	12.00	31.10	10.48
–0.63 + 0.315	29.62	34.10	27.69	14.40	28.90	11.69
–0.315 + 0.16	15.47	26.00	11.02	11.40	28.00	8.96
–0.16 + 0.074	14.54	43.10	17.19	11.80	44.20	14.66
–0.074 + 0.045	9.67	52.60	13.95	8.70	63.10	15.42
–0.045 + 0.00	23.00	35.40	22.31	38.50	33.30	36.01
Total	100.00	36.51	100.00	100.00	35.60	100.00
–0.16 + 0.00	47.21	42.50	53.45	59.00	39.50	66.09
–0.16 + 0.045	24.21	46.90	31.14	20.50	52.20	30.08

At grinding in the hammer mill the yield of the fine fraction –0.045 + 0.00 mm is higher than in the roller mill (38.5% and 23.0%, respectively). As for OM distribution, the recovery of OM in the fine class (36.1%) at grinding in the hammer mill is higher (36.01%) in comparison with the data for the roller mill (22.31%).

The above presented methods of grinding were tested more completely by the following separation of OM from the mineral part by using centrifugation of the products ground in different mills. As a medium calcium chloride (density 1200/m^3) was used. The data obtained (Table 3) indicate the increase in the yield of the heavy fraction during the third stage of grinding in the roller mill (from 79.2 to 85.8%), while OM content remains about 27%. OM percentage in the heavy fraction increased from 58.5 to 67.4%, what indicates the increase in the share of heavy minerals intergrown with OM.

Table 3. **Characteristics of products of centrifugation in calcium chloride medium at density 1.2 t/m^3**

	Multi-stage grinding in roller mill					
	Light fraction			Heavy fraction		
	Yield, %	OM content, %	Recovery, %	Yield, %	OM content, %	Recovery, %
Feed –1.25 + 0 mm	20.8	80.1	42.9	79.2	28.0	57.1
After 1st grinding	18.9	81.3	41.5	81.1	26.7	58.5
After 2nd grinding	16.1	80.9	35.4	83.9	28.1	64.6
After 3rd grinding	14.2	81.5	32.6	85.8	27.8	67.4
	Comparative grinding in roller mill and hammer mill					
Fraction –0.16 + 0 mm						
Roller mill	23.2	90.1	49.0	76.8	30.7	51.0
Hammer mill	32.0	82.2	65.2	68.0	22.5	34.8

The increase in OM recovery in the light fraction at using the hammer mill is significant, but the increase in the fraction yield and decrease in OM content in the light fraction indicate overgrinding in the hammer mill. Considering the results presented for grinding oil shales roller mill should be preferred.

Next the grinding of oil shales was tested using centrifugal-rebound mill constructed by Kitsnik and Ahelik [5]. The scheme of the mill is presented in Fig. 2. Operation principle of the centrifugal-rebound mill bases on the rebound of particles against the plate by the agency of centrifugal power.

The data about grinding in the centrifugal-rebound mill of oil shales previously ground to –3.0 mm in the roller mill (Table 4) show that 83% of the ground material after the first grinding belong to the size range of –0.16 – 0.0 mm, after the second stage the percentage is 90%. However, during the grinding process OM content of fractions decreases. The main components of oil shale are OM, limestone and terrigenic material (quartz, feldspars, alumina). Hardest are limestone particles and they are found after grinding in coarse fractions together with intergrown OM. As for OM, its recovery after the first grinding in fine fractions (–0.16 mm) is up to 69.2%

and after the two stage grinding 94.31%. Fine fractions (–0.074 + 0.045 mm) contain maximally up to 60% OM. To liberate OM particles from terrigenic minerals ground as well, care must be taken not to produce excessive fine particles. That means that the particles must made only one rebound to liberate OM. The data given show that using the centrifugal-rebound mill, overgrinding of the material may be avoided while particles are removed after rebound.

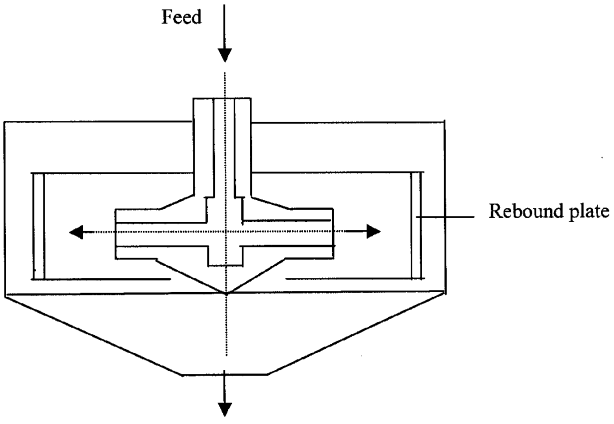

Fig. 2. Basic scheme of the centrifugal-rebound mill.

Table 4. **Distribution of OM in the grinding processes by using centrifugal mill**

Feed –3.0 mm	One-stage grinding			Two-stage grinding		
Size, mm	Yield, %	OM content, %	Recovery, %	Yield, %	OM content, %	Recovery, %
–1.00 + 0.315	6.47	35.00	5.80	2.62	18.20	1.33
–0,315 + 0.16	10.31	31.40	8.32	7.36	19.60	4.00
–0.16 + 0.074	14.12	46.00	16.68	14.82	39.30	16.17
–0.074 + 0.045	13.10	61.30	20.61	14.32	58.30	23.19
–0.045 +0	56.00	33.80	48.59	60.88	32.70	55.31
Total	100.00	38.96	100.00	100.00	36.00	100.00

In the work [6] the dependence of grain size distribution and heating value on mining conditions of oil shale is studied. The increase in heating value by the separation of fine classes is established.

Taking into consideration the results obtained we have developed a flow sheet involving the combined process of grinding in the centrifugal-rebound mill and hydrocycling (Fig. 3).

The flow sheet presented involves mat hydrocycling and two cleaning hydrocyclings of heavy and light fractions. The tests were carried out in the closed circuit with recirculation of hydrocycling products. By hydrocycling

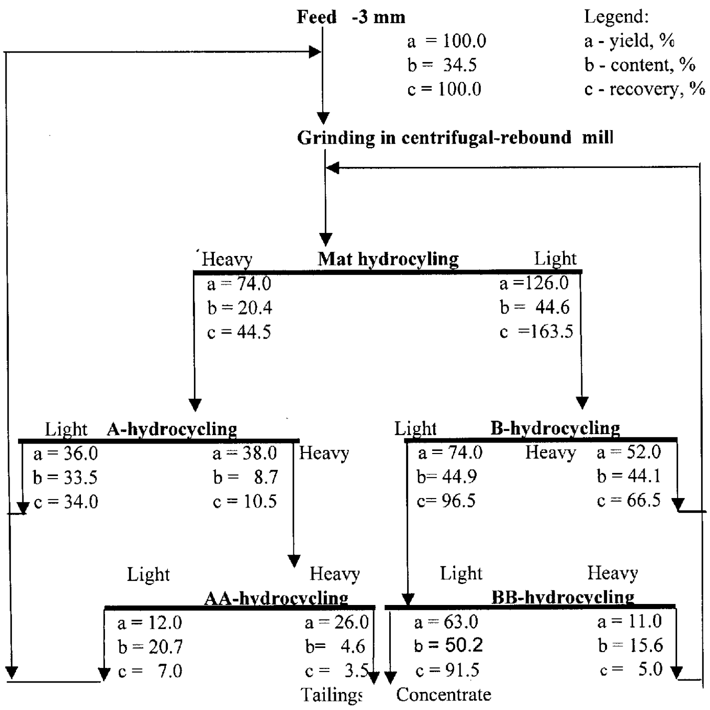

Fig. 3. Flow sheet of upgrading oil shale ground in the centrifugal-rebound mill by using multi-stage hydrocycling. Recycling of products is considered.

of the light fraction of mat hydrocycling, heavy fractions were recirculated to mat hydrocycling and by hydrocycling of the heavy fraction of mat hydrocycling, light fractions were directed back to grinding.

As for hydrocycling of the heavy fraction of mat hydrocycling, in the process of three-stage hydrocycling a considerable decrease in the yield of heavy fractions (74.0, 38.0 and 26.0%), a decrease in OM content (20.4, 8.7 and 4.6%), and, respectively, a decrease in OM recovery (44.5, 10.5 and 3.5%) take place. As for the light fraction of mat hydrocycling, the data obtained show the decrease in the yield of light fractions at three-stage hydrocycling (126, 74.0 and 63.0%), while OM content slightly increases at the third stage of hydrocycling (from 44.9 to 50.2%).

Granulometric analysis shows that in the light fraction of the second hydrocycling 83.04% of the material falls into the size range –0.045 + 0.0 mm. By hydrocycling of the heavy fraction of mat hydrocycling the share of the fine fraction (–0.045 + 0.0 mm) in light fractions increases from 47.5 to 54.0%.

The flow sheet presented enables to produce a concentrate containing 50.2% OM at recovery of 91.5%, while OM content of tailings is only 3.5%. It must be pointed out that in this process about 30% of the feed is removed from the further treatment.

Flotation

For more upgraded OM, concentrate flotation was carried out. The reagents recommended in [7] to be used for flotation of OM were kerosine as collector for OM and turpentine oil as frothing agent in the ratio 1:1. The reagents were added into the pulp in 2% emulsion of water. Laboratory flotation machine with cell volume 900 ml was used at rotation speed of the impeller 1800 and 2300 rev/min. We have established the main working conditions, such as solid-to-liquid ratio, particle size and reagent conditions.

Solid-to-liquid ratio may have a significant effect on the recovery of OM by flotation. Mat flotation (prime operation to separate concentrate and residue) was carried out at the following solid-to-liquid ratios: 1:1, 1:2, 1:2:5, 1:3, 1:4 (Table 5).

Table 5. **Dependence of flotation efficiency on pulp density**

Solid-to-liquid ratio	Product	Yield, %	OM content, %	OM recovery, %
1:4 (20% of solid)	Concentrate Tailings	73.3 26.4	48.2 2.0	98.5 1.5
1:3 (25% of solid)	Concentrate Tailings	68.1 31.9	56.5 4.4	96.5 3.5
1:2.5 (28.6% of solid)	Concentrate Tailings	67.0 33.0	57.9 3.4	97.2 2.8
1:2 (33.3% of solid)	Concentrate Tailings	75.0 25.0	52.0 3.2	98.0 2.0
1:1.5 (40% of solid)	Concentrate Tailings	67.6 32.4	53.6 12.0	90.3 9.7

Feed oil shale was ground to less than 0.16 mm. Data given in Table 5 show increasing efficiency of flotation when 40-% pulp is diluted to contain 28.6% solid matter. The highest recovery and OM content were obtained by flotation at the solid-to-liquid ratio 1:2.5.

Further the impact of collector-to-frother ratio on the efficiency of OM flotation was investigated. The data presented in Table 6 show a very significant increase in OM recovery at the ratio 80:20 and slight improvement in OM recovery further up to the ratio 50:50, while OM content in concentrate is decreasing. Basing on the presented data, the ratio 80:20 would be best at rougher flotation and 60:40 at scavenger flotation.

The effect of concentration of reagents (from 0.5 kg/t to 3.0 kg/t) on separation of OM was also tested (Table 7). By increasing concentration of reagents from 0.5 to 1.0 kg/t, recovery of OM becomes significantly higher, but continuing increase in reagent concentration lowers OM content in concentrate. In further tests reagent concentration 1.5 kg/t was used.

The kinetics of flotation processes has also been studied. Data presented in Table 8 show that optimum retention time per flotation cell is between 3 and 4 minutes at reagent concentration 1.5 kg/t. For improving OM recovery retention time 4 min is required. The tests have shown that good results could be obtained when feeding the reagents in three equal portions.

Table 6. **Dependence of flotation efficiency on collector to frother ratio**

Collector to frother ratio	Yield, %	OM content, %		Recovery, %
		Concentrate	Tailings	
100 : 00	19.1	62.0	34.9	29.5
90 : 10	47.4	66.2	17.5	77.3
80 : 20	59.6	62.2	8.5	91.5
70 : 30	68.2	57.6	3.7	97.1
60 : 40	70.2	54.2	2.8	97.9
50 : 50	71.5	53.8	2.1	98.5
40 : 60	73.1	54.2	2.2	98.5
30 : 70	73.4	52.3	3.2	97.8
20 : 80	74.6	53.2	3.1	98.1
10 : 90	77.4	52.8	2.3	98.7
0 : 100	75.4	53.7	2.7	98.4

Table 7. **Dependance of efficiency of flotation on reagents concentration**

Concentration of reagents	Product	Yield, %	OM content, %	Recovery, %
0.5 kg/t	Concentrate	68.0	55.4	94.5
	Tailings	32.0	6.6	5.5
1.0 kg/t	Concentrate	73.6	50.6	97.6
	Tailings	26/4/10	3.1	2.4
1.5 kg/t	Concentrate	76.9	50.9	98.9
	Tailings	23.1	2.1	1.1
2.0 kg/t	Concentrate	81.3	49.1	98.9
	Tailings	18.7	2.3	1.1
3.0 kg/t	Concentrate	80.8	49.2	99.1
	Tailings	19.2	1.9	0.9

Table 8. **Test results of shale oil flotation for determination of retention time**

Flotation period, min	Yield, %	OM content, %	Recovery, %
0.5	6.7	51.9	8.8
0.5	9.8	53.9	13.3
1.0	21.7	54.3	29.8
1.0	23.1	58.7	34.2
1.0	8.0	44.3	9.0
2.0	4.6	25.3	2.9
2.0	2.1	13.2	0.7
2.0	0.9	6.5	0.2
Total concentrate	76.9	50.9	98.9

Flow sheet

Basing on the laboratory test results a flow sheet involving screening, crushing and fine grinding of oil shale in the centrifugal-rebound mill, two-stage hydrocycling with further treatment of the ground oil shale by roughing, five cleanings of the concentrate and scavenging of the tailings has been developed [8]. The recirculation of the middlings from the first cleaning and scavenger flotation to the hydrocycling was used. The flow sheet is presented in Fig. 4.

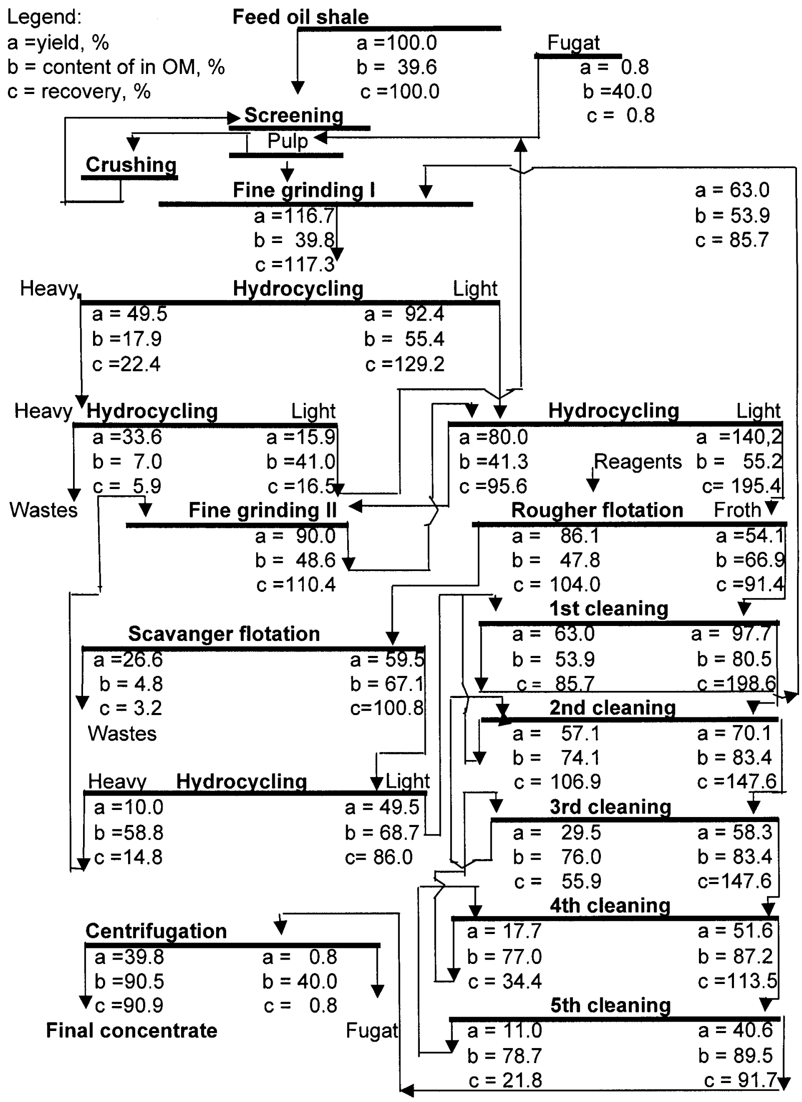

Fig. 4. Flow sheet of beneficiation of oil shale. Recycling of products is considered.

Oil shale –25 + 0 mm was fed into the roll crusher combined with screening, and ground product (–3 + 0 mm) was directed after producing the pulp (50% in solid) into the centrifugal-rebound mill (diameter of rotor 0.800 m, rotational speed – 1660 rev/min, the feed was charged at the pressure of up to 2.5 kg/cm^2). Thereafter the ground product was treated by two-stage hydrocycling. The hydrocyclone diameter was 0.100 m, the overflow nozzle diameter – 0.025 m, and nozzle for heavy fraction – 0.012 m. The heavy fraction of hydrocycling (the yield 33.3% and OM content about 7.0%) was led into wastes, middlings of hydrocycling were recirculated to fine grinding in the centrifugal-rebound mill, and the light fraction –0.16 + 0 mm with OM content 55.2% was directed to rough flotation.

The rougher flotation was carried out on a 12-l flotation machine worked out in the experimental plant of Institute "Mehanobr" in St.-Petersburg. The reagents turpentine and kerosine at ratio 1:4 were added to the pulp in 1-% emulsion at concentration of 1.0–1.3 kg/t. The froth product of rougher flotation with kerogen content 66.9% was subjected to cleaning flotation, middling with 47.8% kerogen was directed to scavenger flotation. Tailings from scavenger flotation 4.8% kerogen were removed to disposal. The froth product was treated by hydrocycling and the products obtained were circulated back to the beneficiation process – the heavy fraction to the centrifugal-rebound mill for fine grinding and the light fraction to the first cleaning flotation.

At cleaning flotation counter-current circulation of the flotation products was used. Kerogen content increased from 80.5% in the first froth product to 89.5% in the final product which was then subjected to centrifugation for dewatering. The final concentrate of centrifugation contained 90.5% kerogen at recovery 90.9%. The overflow was directed back to the head of the scheme for preparing the pulp.

When a lower-grade concentrate is desired, a shorter and simpler flow sheet should be applied, involving combined screening – crushing, fine grinding in the centrifugal-rebound mill, hydrocycling and flotocycling (Fig. 5).

The pulp of ground to 3.0 mm oil shale was fed to mat hydrocycling (diameter of hydrocyclon 0.100 m) for classification. The heavy product with kerogen content 28.2% was directed to fine grinding in the centrifugal-rebound mill and thereafter sent to two-stage cleaning hydrocycling. The heavy product of the last hydrocycling (8.5% kerogen) was sent to disposal, and the light one back to the first cleaning hydrocycling. The light product of mat hydrocyling (48.7% kerogen) was directed to the mixer into which flotoreagents were added (kerosine and turpentine at ratio 1:4) and the pulp was saturated with air. The prepared pulp was sent to flotocyclon constructed by R. Koch, A. Kitsnik and V. Ahelik [9] (Fig. 6).

In the flotocyclon the feed pulp was split into three fractions: the heavy fraction of hydrocycling (42.4% OM) was directed to cleaning hydrocycling, overflow (13.5% OM) was sent to disposal, and froth fraction subjected to centrifugation for dewatering. Kerogen content of the concentrate obtained was 78.9% at recovery 40.0%.

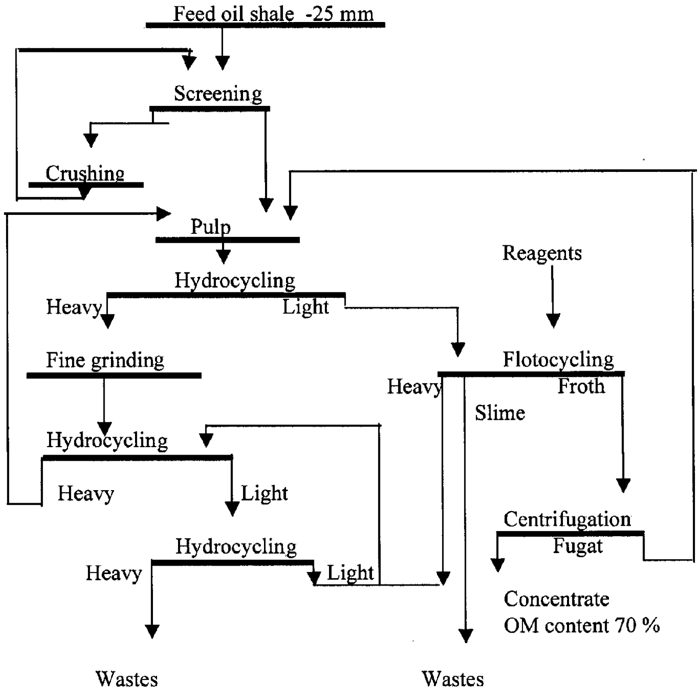

Fig. 5. Flow sheet involving multi-stage hydrocycling and flotocycling for producing concentrate containing more than 70% OM.

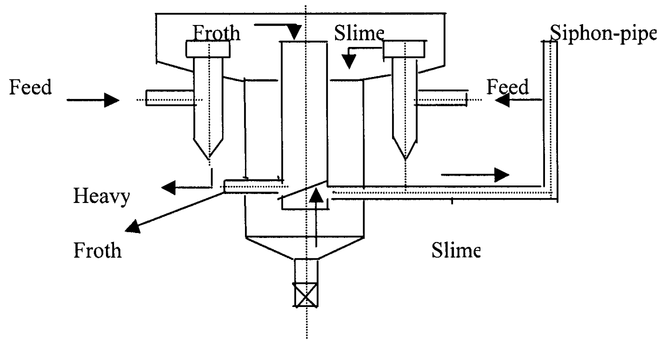

Fig. 6. Scheme of flotocyclone.

Conclusions

Basing on the laboratory test results, the optimum grinding method was estimated. Good results of oil shale upgrading were achieved by using the centrifugal-rebound mill for grinding. The effect of different parameters such as reagent conditions, retention time, solid-to-liquid ratio, concentration of reagents has been investigated.

Taking into consideration laboratory results, we have developed a combined flow sheet involving hydrocycling and flotation and have produced a concentrate containing about 90% kerogen at the recovery of about 91% from the feed oil shale. When concentrates of lower grade are needed, a simplified flow sheet involving multistage hydrocycling and flotocycling may be used providing the concentrate with kerogen content more than 70%.

The flow sheet presented for upgrading oil shales was proved by testing at a pilot plant producing about 60 t concentrate containing more than 90% kerogen.

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