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RESEARCH AND EXPERIMENTAL PROCESSING OF HIGH-SULPHUR OIL SHALES

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During the retorting process of oil shales in Fischer retorts sulphur is transferred to retorting products (to oil, gas or semicoke) in different proportions, depending on the content of organic sulphur (more precisely on the share of organic sulphur in total one) in the shales.

The conditions of retorting the shales do not influence the sulphur content in the retort oils.

High-sulphur oils obtained in the experimental retort are similar to each other in their chemical group composition. They are characterized by an increased content of aromatic hydrocarbons and a reduced content of phenols and alkenes.

The majority of oil shales of the world yield on retorting paraffinic oil which is similar to low-sulphur paraffinic petroleums in its physical and chemical properties. The second group of oil shales found throughout the world forms on retorting high-sulphur oil [1].

In order to learn about the physical, chemical and processing properties of the second group of oil shales the research of the corresponding samples has been carried out both in laboratory conditions and experimental retort. Samples were delivered to the Oil Shale Research Institute by various foreign organizations and geological expeditions at different times. These samples obviously do not reflect completely the average qualitative character of their deposits. Nevertheless, these samples give an idea about the physical and chemical properties and specific features of the oil shales originating from different deposits.

The present research has, in authors' opinion, a practical value for rating the oil shales as process raw materials for retorting, and the possibilities for their industrial use.

This paper generalizes the results of the investigation of oil shale samples obtained from the main shale deposits of the world, including the Volga Basin in Russia, and Uzbekistan (Table 1), the Ukraine, Morocco, Jordan, Syria and Brazil (Table 2). For a comparable study the corresponding data for the most common oil shales which yield paraffinic

Table 1. **Properties of Oil Shales from Russia and Uzbekistan Deposits**

Indices	Volga Basin						Sysol	Uzbekistan		
	Kasphir	Chagan	Perelyub, seam		Kotsebinsk	Rubezhinsk		Baisun	Urtabulak	Sangruntau
			1	4						
	Investigated shale sample number									
	1	2	3	4	5	6	7	8	9	10
Moisture of oil shale tested in experimental retort, %	20.0	5.8	–	9.4	4.9	12.5	13.6	2.6	7.2	8.7
Content (dry basis), %:										
Carbon dioxide $(CO_2)^d_M$	7.7	15.4	14.3	7.9	11.2	10.4	7.7	6.8	8.6	1.3
Ash A^d	65.3	52.4	43.6	46.1	51.7	40.2	66.2	63.2	60.3	74.8
Organic matter*	27.0	32.2	42.1	46.0	37.1	49.4	26.1	30.0	31.1	23.9
Total sulphur S^d_t	3.7	4.14	6.08	5.80	6.06	4.69	3.4	4.15	4.56	4.57
Including:										
Sulphate	0.2	0.23	0.12	0.08	0.33	0.08	0.12	0.05	–	0.79
Pyrite	1.7	1.13	1.11	0.59	1.51	0.67	1.43	3.28	–	2.26
Organic (by difference)	1.8	2.78	4.85	5.13	4.22	3.94	1.85	0.82	–	1.52
Heating value (bomb calorimeter), MJ/kg	8.54	10.76	14.25	16.37	12.18	16.66	8.37	10.93	10.55	6.32
Fischer assay product yield (standard retort), %:										
Shale oil	8.7	13.0	20.0	20.9	15.2	21.1	9.6	11.7	9.4	6.1
Pyrogenetic water	4.4	4.0	4.8	5.7	4.7	5.9	4.2	4.0	4.8	4.4
Semicoke	81.0	75.9	66.6	63.9	72.1	62.7	80.2	78.6	73.7	84.9
Gas and losses (by difference)	5.9	7.1	8.6	9.5	8.0	10.3	6.0	5.7	12.1	4.6
Fischer assay oil of organic matter, %	32.2	40.3	47.5	45.4	41.0	42.7	36.8	39.0	30.1	25.5

* Here and later on organic matter content is equal to: $100 - (CO_2)^d_M - A^d$.

Table 1. Properties of Oil Shales from Russia and Uzbekistan Deposits (end)

Indices	Volga Basin						Sysol	Uzbekistan		
	Kasphir	Chagan	Perelyub, seam		Kotsebinsk	Rubezhinsk		Baisun	Urtabulak	Sangruntau
			1	4						
	Investigated shale sample number									
	1	2	3	4	5	6	7	8	9	10
Fischer assay product yield (shale sample 200 g), %:										
Shale oil	–	12.1	18.3	19.6	13.6	19.5	8.4	–	–	–
Pyrogenetic water	–	3.6	4.3	5.3	4.3	5.3	3.6	–	–	–
Semicoke	–	76.2	67.7	64.6	72.1	64.2	78.6	–	–	–
Gas and losses (by difference)	–	8.1	9.7	10.5	10.0	11.0	9.4	–	–	–
Fischer assay oil of organic matter, %	–	37.6	43.5	42.6	36.7	39.5	32.2	–	–	–
Ash composition, %:										
SiO_2	38.0	29.9	24.6	40.5	32.4	31.9	46.1	45.5	34.7	55.0
Fe_2O_3	13.9	8.7	5.5	5.5	9.5	5.5	7.5	9.6	8.6	9.0
Al_2O_3	14.9	9.3	8.1	11.8	10.2	8.6	13.3	13.6	11.0	13.0
K_2O	2.8	1.6	1.4	2.3	1.6	1.9	4.0	}2.2	}7.1	}1.6
Na_2O	2.4	0.5	0.2	0.7	0.2	0.7	0.4			
MgO	0.7	3.0	2.1	1.8	1.8	2.3	2.6	3.6	3.1	3.2
CaO	20.4	34.1	43.7	22.8	28.0	33.2	17.5	19.2	23.6	12.4
SO_3	5.6	10.4	12.1	11.6	14.9	13.2	7.3	8.3	11.8	6.2
Total	98.7	97.5	97.7	97.0	98.6	97.3	98.7	102.0	99.9	100.4

Table 2. **Properties of Oil Shales from Various Deposits of the World**

Indices	Morocco, Timahdit			Syria, Senoman deposition	Jordan, El-Lajjun	Brazil, Irati	Ukraine: Verkhnesinevid	Ukraine: Boltysh	Estonia, Estonian (kukersite)
	Investigated shale sample number								
	11	12	13	14	15	16	17	18	19
Moisture of oil shale tested in experimental retort, %	5.66	4.36	5.8	–	–	–	3.0	4.4	5.1
Content (dry basis), %:									
Carbon dioxide $(CO_2)^d_M$	25.2	19.2	8.1	32.1	15.1	2.6	0.8	0.5	20.8
Ash A^d	62.2	62.5	68.8	53.1	63.0	79.8	76.6	57.5	46.2
Organic matter	12.6	18.3	23.1	14.8	23.9	17.6	22.6	42.0	33.0
Total sulphur S^d_t	1.77	2.37	3.07	2.03	3.23	4.20	2.68	1.40	1.90
Including:									
Sulphate	0.09	0.10	0.20	0.10	0.10	0.04	0.10	0.12	0.05
Pyrite	0.73	0.81	1.38	0.30	1.09	4.01	2.00	1.11	1.30
Organic (by difference)	0.95	1.46	1.49	1.63	2.04	0.15	0.58	0.17	0.55
Heating value (bomb calorimeter), MJ/kg	4.21	5.84	6.61	4.27	7.87	5.61	6.53	12.73	12.43
Fischer assay product yield (standard retort), %:									
Shale oil	5.5	7.2	8.7	6.5	12.7	7.0	–	17.5	21.8
Pyrogenetic water	0.8	2.0	2.7	1.9	1.1	1.3	–	3.9	2.4
Semicoke	90.6	87.7	84.3	88.2	82.1	88.2	–	72.9	70.2
Gas and losses (by difference)	3.1	3.1	4.3	3.4	4.1	3.5	–	5.7	5.6
Fischer assay oil of organic matter, %	43.6	39.3	37.9	44.0	53.1	39.8	–	41.7	66.1

Table 2. Properties of Oil Shales from Various Deposits of the World (end)

Indices	Morocco, Timahdit			Syria, Senoman deposition	Jordan, El-Lajjun	Brazil, Irati	Ukraine		Estonia, Estonian (kukersite)
							Verkhnesinevid	Boltysh	
	Investigated shale sample number								
	11	12	13	14	15	16	17	18	19
Fischer assay product yield (shale sample 200 g), %:									
Shale oil	4.6	7.0	7.6	–	–	–	3.4	–	–
Pyrogenetic water	0.5	0.9	2.9	–	–	–	1.5	–	–
Semicoke	90.2	86.5	84.6	–	–	–	92.2	–	–
Gas and losses (by difference)	4.7	5.6	4.9	–	–	–	2.9	–	–
Fischer assay oil of organic matter, %	36.5	38.2	32.9	–	–	–	15.0	–	–
Ash composition, %:									
SiO_2	29.5	36.1	48.3	10.4	38.5	60.3	73.8	65.8	28.5
Fe_2O_3	4.5	5.2	6.7	} 3.8	1.5	12.0	6.6	8.6	5.5
Al_2O_3	6.2	9.2	17.9		2.8	13.2	13.2	17.6	6.7
K_2O	1.9	1.3	1.2	–	–	4.8	1.1	2.6	2.1
Na_2O	0.2	0.1	0.1	–	–	2.1	0.8	1.7	0.4
MgO	3.9	6.8	2.7	–	3.2	3.1	0.7	1.5	4.4
CaO	47.0	33.9	15.5	79.8	38.9	2.8	1.1	2.1	44.8
SO_3	5.2	5.7	6.2	3.2	6.4	1.7	5.3	–	6.5
Total	98.4	98.3	98.6	97.2	91.3	100.0	102.6	99.9	98.9

Table 3. **Properties of Fischer Assay Products from Oil Shales of Russian and Uzbekistan Deposits**

Indices	Investigated shale sample number (see Table 1)									
	1	2	3	4	5	6	7	8	9	10
To obtain the semicoking products the Fischer retort was applied with oil shale sample, g	20	200	200	200	200	200	200	20	20	20
Shale Oil										
Density at 20 °C, kg/m^3	1027	1009	1009	943	1013	1010	973	962	972	973
Molecular mass	225	222	184	195	199	228	179	–	–	–
Heating value (bomb calorimeter), MJ/kg	39.10	38.60	38.98	38.60	38.77	38.81	38.90	40.95	40.49	40.82
Elemental composition (dry basis), %:										
C	80.0	78.92	77.56	79.10	78.41	78.16	79.8	80.8	82.0	80.7
H	9.6	8.96	9.43	9.00	9.38	8.90	9.5	10.2	10.1	10.0
S	7.4	7.12	7.39	7.50	8.50	6.69	4.8	4.2	6.0	7.8
N	0.7	1.20	0.47	0.74	0.60	0.68	0.7	1.9	} 1.9 (N+O)	} 1.5 (N+O)
O (by difference)	2.3	3.80	5.15	3.66	3.11	5.57	5.2	2.9		
Semicoke										
Content (dry basis), %:										
Carbon dioxide $(CO_2)^d{}_M$	9.9	19.4	20.4	11.6	15.2	16.6	8.7	8.3	8.5	1.8
Ash A^d	78.3	65.7	64.3	66.4	68.7	59.1	77.3	75.9	74.0	87.5
Carbon C^d	7.6	12.6	16.7	22.0	16.8	25.2	14.0	11.0	9.4	6.6
Total sulphur $S^d{}_t$	1.91	2.10	2.24	1.9	3.25	2.15	1.78	2.94	3.24	2.87
Heating value (bomb calorimeter), MJ/kg	4.48	5.35	6.15	8.75	6.07	8.96	4.40	5.74	6.36	3.35

Table 4. **Properties of Fischer Assay Products from Oil Shales of Various Deposits of the World**

Indices	Investigated shale sample number (see Table 2)							
	11	12	13	14	16	17	18	19
To obtain the semicoking products the Fischer retort was applied with oil shale sample, g	200	200	200	20	50	200	20	20
Shale Oil								
Density at 20 °C, kg/m^3	961	974	975	1010	918	983	898	968
Molecular mass	192	210	253	–	210	–	–	276
Heating value (bomb calorimeter), MJ/kg	40.50	40.26	40.19	38.39	42.16	39.9	42.7	40.19
Elemental composition (dry basis), %:								
C	79.64	79.00	80.62	76.5	84.4	78.9	84.66	83.12
H	9.99	10.02	10.23	9.0	11.0	9.3	11.95	10.13
S	7.14	7.02	7.10	10.6	1.3	5.6	0.82	0.84
N	2.54	2.34	1.43	} 3.9	0.6	1.0	0.64	0.20
O (by difference)	0.69	1.62	0.62		2.7	5.2	1.93	5.71
Semicoke								
Content (dry basis), %:								
Carbon dioxide $(CO_2)^d{}_M$	27.3	22.0	8.7	34.0	2.7	1.2	0.3	28.1
Ash A^d	67.8	70.2	80.7	58.8	90.0	82.0	81.6	64.8
Carbon C^d	4.9	6.8	9.4	5.8	6.2	16.8	10.5	7.6
Total sulphur $S^d{}_t$	0.8	1.0	1.6	0.66	3.1	1.9	1.3	1.5
Heating value (bomb calorimeter), MJ/kg	1.55	2.38	2.89	1.67	2.34	4.40	4.98	2.64

Table 5. **Yield and Characteristics of Gas* Obtained in the Fischer Retort from Oil Shales of Russian and Uzbekistan Deposits**

Indices	Investigated shale sample number (see Table 1)									
	1	2	3	4	5	6	7	8	9	10
Specific gas yield, m^3/t	41.1	56.2	65.9	74.5	68.2	75.2	45.4	47.7	60.8	40.4
Content of components, vol.%:										
CO_2	22.3	24.7	24.1	21.5	26.1	30.1	35.1	} 31.5	20.7	22.5
H_2S	27.7	24.7	36.6	29.7	35.1	25.0	19.9		19.3	21.4
H_2	17.7	10.0	5.7	6.5	7.1	5.4	13.1	33.3	23.7	27.3
CO	5.3	6.2	7.3	7.1	6.0	8.7	6.0	3.9	3.6	3.2
C_nH_{2n+2}	21.3	27.1	20.9	28.2	20.7	24.9	19.8	25.7	27.7	20.8
Including:										
CH_4	11.7	15.4	11.5	16.0	11.6	14.4	11.0	14.2	15.2	12.8
C_2H_6	6.4	6.5	5.4	7.0	5.2	6.2	5.0	7.6	9.1	5.5
C_3H_8	2.3	3.3	2.4	3.1	2.3	2.6	2.2	2.4	2.7	1.7
C_4H_{10}:										
n-butane	0.7	1.0	0.8	1.0	0.8	0.8	0.7	1.1	0.7	0.6
iso-butane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	–	–	–
C_5H_{12}:										
n-pentane	0.1	0.5	0.4	0.6	0.4	0.5	0.5	0.4	–	0.2
iso-pentane	–	0.1	0.1	0.1	0.1	0.1	0.1	–	–	–
C_6H_{14}:										
n-hexane	–	0.2	0.2	0.3	0.2	0.2	0.2	–	–	–

Here and later on all characteristics of gas are given at 20 °C and 760 mm Hg.

Table 5. Yield and Characteristics of Gas Obtained in the Fischer Retort from Oil Shales of Russian and Uzbekistan Deposits (end)

Indices	Investigated shale sample number (see Table 1)									
	1	2	3	4	5	6	7	8	9	10
C_nH_m	5.7	7.1	5.1	6.7	4.8	5.6	5.9	5.6	5.0	4.8
Including:										
C_2H_4	1.7	2.3	1.4	2.0	1.4	1.6	1.6	1.7	2.4	1.6
C_3H_6	2.0	2.5	1.9	2.4	1.7	2.0	2.1	2.1	1.7	2.0
C_4H_8:										
butene-1	1.0	1.1	0.9	1.1	0.8	0.9	1.1	1.0	0.9	0.9
trans-butene-2	0.2	0.3	0.2	0.3	0.2	0.3	0.3	0.2	–	0.1
cis-butene-2	0.8	0.2	0.1	0.2	0.2	0.2	0.2	0.3	–	0.2
C_5H_{10}:										
pentene-1	–	0.2	0.2	0.2	0.2	0.2	0.2	0.2	–	–
trans-pentene-2	–	0.2	0.1	0.1	0.1	0.1	0.1	0.1	–	–
cis-pentene-2	–	–	0.1	0.1	–	0.1	0.1	–	–	–
C_6H_{12}:										
2-methylbutene-1	–	0.1	0.1	0.1	0.1	0.1	0.1	–	–	–
3-methylbutene-1	–	0.1	–	–	–	–	–	–	–	–
hexene-1	–	0.1	0.1	0.2	0.1	0.1	0.1	–	–	–
Not identified	–	0.2	0.3	0.3	0.2	0.3	0.2	–	–	–
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Calculated heating value, MJ/m^3:										
high	22.4	30.27	27.72	31.57	26.71	27.42	24.37	24.37	26.80	23.78
low	20.5	27.84	25.58	29.10	24.62	25.29	22.40	22.10	24.40	21.44
Density, kg/m^3	1.271	1.313	1.389	1.347	1.378	1.395	1.345	1.022	1.079	1.068
Content of H_2S, g/m^3	391	349	517	420	454	353	281	-	273	302

Table 6. **Yield and Characteristics of Gas Obtained in the Fischer Retort from Oil Shales of Various Deposits of the World**

Indices	Investigated shale sample number (see Table 2)							
	11	12	13	14	16	17	18	19
Specific gas yield, m^3/t	24.1	32.5	33.0	26.0	27.0	18.3	51.0	38.2
Content of components, vol.%:								
CO_2	20.3	18.8	21.0	31.3	10.4	31.1	25.3	23.7
H_2S	24.7	21.1	24.6	22.4	28.6	11.9	4.3	14.6
H_2	12.6	13.2	17.9	12.8	13.6	10.9	24.4	5.3
CO	3.5	2.4	3.5	7.1	1.9	12.9	8.9	4.2
C_nH_{2n+2}	30.3	34.9	24.7	21.5	35.7	28.4	28.4	35.6
Including:								
CH_4	15.0	17.9	15.8	13.0	21.3	22.4	13.3	14.7
C_2H_6	8.3	9.6	6.0	5.7	6.9	4.0	10.1	8.6
C_3H_8	4.0	4.4	2.0	2.0	4.0	1.4	3.0	5.6
C_4H_{10}:								
n-butane	1.4	1.5	0.4	0.6	1.4	0.3	1.3	2.0
iso-butane	0.2	0.2	0.1	–	0.6	0.1	–	0.9
C_5H_{12}:								
n-pentane	0.9	0.8	0.2	0.2	0.8	0.2	0.7	3.0
iso-pentane	0.2	0.2	0.1	–	0.4	–	–	0.8
C_6H_{14}:								
n-hexane	0.3	0.3	0.1	–	0.3	–	–	–

Table 6. Yield and Characteristics of Gas Obtained in the Fischer Retort from Oil Shales of Various Deposits of the World (end)

Indices	Investigated shale sample number (see Table 2)							
	11	12	13	14	16	17	18	19
C_nH_m	8.3	9.0	8.1	4.9	9.8	4.8	8.7	16.6
Including:								
C_2H_4	2.1	2.1	2.0	1.5	2.3	1.3	2.9	3.3
C_3H_6	2.9	3.4	2.8	1.8	2.9	1.3	3.7	6.1
C_4H_8:								
butene-1	1.5	1.7	1.4	1.3	2.0	0.5	1.0	3.3
trans-butene-2	0.4	0.5	0.5	–	0.5	1.5	0.3	0.8
cis-butene-2	0.3	0.3	0.3	–	0.3	0.1	0.6	0.5
C_5H_{10}:								
pentene-1	0.4	0.4	0.4	0.3	0.3	0.1	0.2	2.6
trans-pentene-2	0.4	0.1	0.4	–	0.4	–	–	–
C_6H_{12}:								
2-methylbutene-1	0.1	0.2	0.1	–	0.2	–	–	–
3-methylbutene-1	0.1	0.1	0.1	–	0.1	–	–	–
hexene-1	0.1	0.2	0.1	–	0.2	–	–	–
Not identified	0.3	0.6	0.2	–	0.6	–	–	–
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Calculated heating value, MJ/m^3:								
high	34.96	37.30	24.97	23.53	39.27	23.03	29.26	46.51
low	32.15	34.29	22.77	21.56	36.09	21.10	26.75	42.92
Density, kg/m^3	1.291	1.264	1.106	1.285	1.224	1.225	1.117	1.481
Content of H_2S, g/m^3	349	296	346	317	405	168	61	206

Table 7. **Heat Balance of Retorting Russian and Uzbekistan Oil Shales in the Fischer Retort, %, and Sulphur Distribution between Retorting Products, %**

Indices	Investigated shale sample number (see Table 1)									
	1	2	3	4	5	6	7	8	9	10
Chemical heat of shale										
Shale oil	39.8	46.6	54.8	49.3	48.4	49.1	44.6	43.8	36.1	39.4
Gas	10.8	15.8	12.8	14.4	14.0	12.4	13.2	10.6	15.4	15.2
Gasoline, unregarded losses and analytical errors (by difference)	6.9	−0.2	3.6	2.2	1.7	4.8	0.1	4.3	4.0	0.4
Semicoke	42.5	37.8	28.8	34.1	35.9	33.7	42.1	41.3	44.5	45.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total sulphur of shale										
Shale oil	17.4	22.3	24.3	27.0	21.3	30.0	13.5	11.8	12.4	10.4
Gas (in the form of H_2S)	40.9	44.5	52.7	50.7	45.8	53.3	35.3	–	34.2	25.2
Semicoke	41.8	38.5	24.5	20.9	38.7	28.7	42.0	55.7	52.4	53.3
Other sulphur compounds in gas and analytical errors (by difference)	0.1	−5.3	−1.5	1.4	−5.8	−12.0	9.2	–	1.0	11.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	–	100.0	100.0

Table 8. **Heat Balance of Retorting Oil Shales from Various Deposits of the World in the Fischer Retort, %, and Sulphur Distribution between Retorting Products, %**

Indices	Investigated shale sample number (see Table 2)							
	11	12	13	14	16	17	18	19
Chemical heat of shale								
Shale oil	52.7	49.5	52.9	58.4	52.6	20.8	58.7	70.5
Gas	19.9	20.7	12.4	14.3	18.9	6.5	11.7	14.3
Gasoline, unregarded losses and analytical errors (by difference)	−5.8	−5.9	−2.1	−7.3	−8.3	10.2	1.1	0.3
Semicoke	33.2	35.7	36.8	34.6	36.8	62.5	28.5	14.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total sulphur of shale								
Shale oil	22.2	21.3	20.1	33.9	2.2	7.1	10.2	9.6
Gas (in the form of H_2S)	44.7	38.1	35.1	38.1	24.4	10.8	20.8	39.0
Semicoke	40.9	37.0	43.9	28.7	65.2	65.4	67.7	55.4
Other sulphur compounds in gas and analytical errors (by difference)	−7.8	3.6	0.9	−0.7	8.2	16.7	1.3	−4.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 9. **Distribution of Sulphur between Products during Retorting High-Sulphur Oil Shales from Various Deposits of the World, %**

Deposit (sample No.)	Share of organic sulphur in the total sulphur content of the initial shale, %	Content of sulphur, %			Percentage of sulphur transferred into, %		
		in shale		in oil			
		total S	organic S		oil	gas	semicoke
The first group							
Irati (16)	0.4	4.2	0.15	1.3	2.2	24.4	65.2
The second group							
Verkhnesinevid (17)	21.6	2.68	0.58	5.6	7.1	10.8	65.4
Baisun (8)	19.8	4.15	0.82	4.2	11.8	—	55.7
Urtabulak (9)	—	4.56	—	6.0	12.4	34.2	52.4
Sangruntau (10)	33.3	4.57	1.52	7.8	10.4	25.2	53.3
The third group							
Sysol (7)	54.4	3.40	1.85	4.8	13.5	35.3	42.0
Timahdit:							
(11)	53.7	1.77	0.95	7.14	22.2	44.7	40.9
(12)	61.6	2.37	1.46	7.02	21.3	38.1	37.0
(13)	48.5	3.07	1.49	7.10	20.1	35.1	43.9
Tchagansk (2)	67.2	4.14	2.78	7.12	22.3	44.5	38.5
Kashpir (1)	48.6	3.70	1.80	7.40	17.4	40.9	41.8
Kotsebinsk (5)	69.6	6.06	4.22	8.50	21.3	45.8	38.7
The fourth group							
Rubezhinsk (6)	84.0	4.69	3.94	6.69	30.0	53.3	28.7
Perelyub:							
Seam 1 (3)	80.0	6.08	4.85	7.39	24.3	52.7	24.5
Seam 4 (4)	88.4	5.80	5.13	7.50	27.0	50.7	20.9
Senoman deposition (14)	80.3	2.03	1.63	10.16	33.9	38.1	28.7

oil on retorting (Boltysh deposit) and kukersite with its very specific characteristics (Estonian deposit) are presented.

As can be seen from Tables 1 and 2, the sulphur content of oil shales, which form high-sulphur oils during retorting, varies considerably - from 1.77 to 6.0 %. The organic sulphur content of those shales also varies considerably - from 0.15 to 5.13 %. A rather high content of calcium carbonate is typical of the mineral part of oil shales from Morocco, Syria and Jordan. Silicon compounds prevail in the mineral part of oil shales from Brazil and the Ukraine.

Distillation of shale under laboratory conditions was carried out in a standard Fischer retort. The shale samples weighed 20 and 50 g and the final temperature reached 510 and 520 °C, respectively. We have established that both retorts give consistent results. A Fischer retort containing 200 g of shale was also applied for estimating the quality of the retorting products. This procedure was used primarily for oil shales low in organic matter.

During the retorting of the shale samples mentioned above, sulphur-rich oils (from 5 to 10 %) were formed irrespective of their initial sulphur content (Tables 3 and 4). Only the oil shales from the Irati deposit with their rather high original sulphur content of 4.2 %, yield an oil containing only 1.3 % of sulphur.

Sulphur content of the semicoke obtained from the oil shales of Russian and Uzbekistan deposits is moderate - 1.9-3.2 %. However, sulphur content of Moroccan, Syrian and Jordanian shale semicokes is rather low - 0.7-1.6 %. The content of hydrogen sulphide in retort gas is 20-30 % by volume for practically all the tested samples (Tables 5 and 6).

The most interesting aspect of the retorting process is the actual sulphur balance during the treating of oil shales in the Fischer retorts (Tables 7 and 8). The amount of sulphur of the original shale samples which passes on to the products during retorting, varies substantially. Thus, 2.2-33.9 % of the shale sulphur is transferred to the oil, 10.8-53.3 % - to the retort gas, and 20.9-65.4 % - to the semicoke.

Such diverse distribution of sulphur during the retorting process of oil shales is primarily due to the presence of organic sulphur in the shales. The greater the content of organic sulphur, the more of it passes on to oil and gas. In case of an elevated content of inorganic sulphur in oil shales, the quantity of sulphur in the semicoke rises.

According to the data generalized in Table 9, high-sulphur oil shales can be divided into four groups according to their share of organic sulphur in the total sulphur amount. The first group comprises oil shales with a low content of organic sulphur, not exceeding 5-10 % of the total sulphur in the shales. The share of organic sulphur in the second group is 20-35 %, in the third one - 50-70 %, and in the fourth group - 80-90 %. It is interesting to note that the transfer of sulphur from the initial shale to oil depends not so much on the content of organic sulphur in the shale as on its share of total sulphur.

Table 10. **Yield and Characteristics of Shale Oils Obtained in the Experimental Retort from Oil Shales of Russian and Uzbekistan Deposits**

Indices	Investigated shale sample number (see Table 1)								
	1*	2	4	5	6	7	8	9	10
Yield of shale oil, %:									
Plant yield (raw shale basis)	8.1	10.2	8.56	9.74	13.97	6.56	9.96	6.9	4.0
Yield of Fischer assay oil	81.8	83.1	45.2	67.4	75.6	78.8	87.7	67.7	60.7
Density at 20 °C, kg/m^3	1037	1033	996	1030	1030	1017	968	973	990
Water, %	2.0	29.1	67.3	40.4	20.0	40.0	32.0	–	–
Entrained solids, %	0.62	0.47	2.64	1.68	0.45	1.34	0.33	0.05	0.12
Ash, %	0.19	0.10	1.02	0.39	0.10	0.21	0.09	0.01	0.06
Viscosity at 75 °C, $10^{-6} \cdot m^2/s$	11.4	7.3	4.0	8.0	7.0	10.4	5.9	6.8	5.5
Flash point, °C	112	126	91	78	74	106	64	96	88
Pour point, °C	−7	12	5	−13	−14	7	–	–	–
Refraction index, n^{20}_D	1.571	1.572	1.548	–	–	–	1.495	1.548	1.549
Molecular mass	250	299	242	235	–	–	256	258	255
Phenolic compounds, %	1.8	1.5	–	6.6	–	–	2.5	3.4	3.1
Heating value (bomb calorimeter), MJ/kg	39.42	39.35	39.52	38.90	38.82	39.27	41.16	40.70	40.15

* Here and later on the data concerning commercial operation of vertical retorts in the Syzran oil shale processing plant (Volga Basin, Russian Federation) are presented (throughput rate of one retort is 60-70 tonnes of oil shale per day).

Table 10. Yield and Characteristics of Shale Oils Obtained in the Experimental Retort from Oil Shales of Russian and Uzbekistan Deposits (end)

Indices	Investigated shale sample number (see Table 1)								
	1*	2	4	5	6	7	8	9	10
Initial boiling point, °C	184	183	203	165	150	176	93	179	90
Distillation, vol.%, at:									
160 °C	–	–	–	–	1	–	4	–	2
180 °C	–	–	–	2	3	–	5	–	3
200 °C	2	1	–	4	5	2	7	3	4
220 °C	3	3	8	9	10	6	11	8	8
240 °C	5	9	18	14	15	9	15	15	14
260 °C	10	19	26	21	22	17	23	23	20
280 °C	14	25	36	29	30	23	29	31	28
300 °C	26	33	45	38	38	33	36	40	40
320 °C	33	54	56	50	49	48	45	49	46
340 °C	41	71	66	63	63	56	55	56	63
360 °C	69	–	75	80	88	83	69	70	76
Elemental composition (dry basis), %:									
C	79.6	79.44	77.59	78.82	78.99	79.92	84.9	81.5	79.8
H	9.8	9.20	9.51	9.62	8.75	9.50	10.3	10.0	10.8
S	7.2	6.19	6.49	6.81	7.19	4.27	4.2	4.7	6.4
N	}3.4	}5.17	0.62	0.03	0.76	0.87	}0.6	}3.8	}4.0
O (by difference)			5.79	4.72	4.31	5.44			

Table 11. **Yield and Characteristics of Shale Oils Obtained in the Experimental Retort from Oil Shales of Various Deposits of the World**

Indices	Investigated shale sample number (see Table 2)					
	11	12	13	17	18	19
Yield of shale oil, %:						
Plant yield (raw shale basis)	3.91	5.28	4.40	1.62	10.0	20.6
Yield of Fischer assay oil	75.3	76.7	53.7	49.2	60.0	99.5
Density at 20 °C, kg/m^3	982	981	994	994	908	988
Water, %	30.0	30.0	25.8	–	–	–
Entrained solids, %	0.55	0.45	0.86	1.26	0.80	0.50
Ash, %	0.09	0.09	0.35	0.20	0.10	0.24
Viscosity at 75 °C, $10^{-6} \cdot m^2/s$	6.4	5.7	7.6	7.3	5.2	11.4
Flash point, °C	91	88	88	90	84	65
Pour point, °C	3	0	5	–	–	–
Refraction index, $n^{20}{}_D$	–	–	1.552	1.535	1.517	1.549
Molecular mass	243	262	271	254	–	249
Phenolic compounds, %	1.6	2.0	1.9	14.8	3.7	26.1
Heating value (bomb calorimeter), MJ/kg	41.39	40.90	40.19	39.98	42.58	39.77

Table 11. Yield and Characteristics of Shale Oils Obtained in the Experimental Retort from Oil Shales of Various Deposits of the World (end)

Indices	Investigated shale sample number (see Table 2)					
	11	12	13	17	18	19
Initial boiling point, °C	182	178	160	125	135	116
Distillation, vol.%, at:						
160 °C	–	–	–	4	–	3
180 °C	–	–	2	6	2	4
200 °C	2	2	6	9	4	8
220 °C	3	4	11	12	6	12
240 °C	7	11	17	17	12	14
260 °C	16	17	23	28	17	18
280 °C	22	25	34	34	23	22
300 °C	30	33	44	44	29	26
320 °C	39	44	57	54	35	30
340 °C	51	54	78	61	43	35
360 °C	67	89	–	74	55	45
Elemental composition (dry basis), %:						
C	80.14	79.92	81.15	79.70	84.45	81.8
H	9.99	9.62	10.11	9.90	11.63	10.1
S	6.85	6.63	7.6	3.98	0.76	0.9
N	2.41	2.84	} 1.14	} 6.42	} 3.16	} 7.2
O (by difference)	0.61	0.99				

Table 12. **Chemical Group Composition of Light-Middle Fractions of Shale Oil Obtained in the Experimental Retort from Oil Shales of Various Deposits, wt.%**

Compounds	Investigated shale sample number (see Tables 1 and 2)							
	1	8	9	10	13	17	18	19
Fraction IBP-200 °C								
Alkanes and cycloalkanes	5	16	11	10	11	20	22	23
Alkenes	13	28	21	7	14	13	32	48
Aromatic hydrocarbons	52	33	49	62	56	41	27	20
Neutral heteroatomic compounds	28	22	16	18	15	14	16	5
Phenols	2	1	3	3	4	12	3	4
Fraction yield	2.6	7.48	11.5	7.2	5.5	8.27	8.7	7.6
Fraction 200-300 °C								
Alkanes and cycloalkanes	4	13	12	12	11	20	24	13
Alkenes	5	15	9	7	9	7	20	27
Aromatic hydrocarbons	52	44	51	57	58	44	33	28
Neutral heteroatomic compounds	32	22	21	17	18	15	15	17
Phenols	7	6	7	7	4	14	8	15
Fraction yield	20.9	27.8	21.2	25.2	24.8	27.17	19.9	16.5
Fraction 300-350 °C								
Alkanes and cycloalkanes	4	12	14	8	8	16	36	3
Alkenes	1	6	6	4	5	2	7	7
Aromatic hydrocarbons	48	43	48	58	59	45	31	27
Neutral heteroatomic compounds	40	32	27	23	23	19	21	36
Phenols	7	7	5	7	5	18	5	27
Fraction yield	18.5	14.24	14.3	16.9	14.4	14.89	15.6	11.8
Fraction IBP-350 °C								
Alkanes and cycloalkanes	4	13	13	11	10	19	28	12
Alkenes	4	14	11	6	8	7	18	25
Aromatic hydrocarbons	50	43	49	58	59	44	31	26
Neutral heteroatomic compounds	35	25	22	19	19	16	17	21
Phenols	7	5	5	6	4	14	6	16
Fraction yield	42.0	59.52	47.0	49.3	44.7	50.33	44.2	35.9

For a more thorough study of the physical and chemical properties of retort oil as the main product of thermal destruction of oil shales, some of the samples have been processed in an experimental retort under conditions for semicoke gasification. The retort had a throughput of 500-1000 kg of shale per day [2, 3]. As seen from Tables 10 and 11, processing in the experimental retort yields shale oil which ranges from 60 to 90 % of the Fischer assay oil, dropping to 45 % only in the case of Carpathian Menilitic shales. This experimental retort yielded high-sulphur oils which were virtually identical to the oils obtained in the Fisher retorts. However, condensation of oil and water vapours in the condensation apparatus resulted in the formation of a stable emulsion, and the separation of oil from water was troublesome.

At the beginning of the investigation of shale oil properties the group composition of light/middle fractions of shale oil was studied (Table 12), and later on the group composition of crude shale oil was determined (Table 13). The data presented in the tables show the resemblance between the light/middle fractions and the total high-sulphur oil. They are characterized by an increased content of aromatic hydrocarbons and a reduced content of alkenes and phenols (in comparison with paraffinic oil of oil shales from Boltysh deposit and with kukersite oil). The Carpathian Menilitic shale had an additional characteristic of a high content of phenols in its oil.

Table 13. **Chemical Group Composition of Crude Shale Oil Obtained in the Experimental Retort from Oil Shales of Various Deposits, wt.%**

Compounds	Investigated shale sample number (see Tables 1 and 2)					
	4	5	6	7	11	12
Alkanes and cycloalkanes	8.7	}5.1	}4.1	3.9	7.2	6.8
Alkenes	6.5			3.3	7.2	6.8
Aromatic hydrocarbons	46.8	54.5	50.4	44.9	58.3	58.5
Neutral heteroatomic compounds	34.8	34.7	40.8	43.7	22.7	22.7
Phenols and carboxylic acids	3.2	5.7	4.7	4.2	4.6	5.2

The Syzran oil shale processing plant in Russia where very small amounts of shale from the Kashpir deposit (60-70 thousand tonnes per year) are processed since 1932 is the only enterprise having any industrial experience in processing high-sulphur oil shales. This limited processing of Volga Basin shales is due to the high content of sulphur in the oil which makes it unusable as a liquid fuel. Only a limited assortment of products, including mainly medicinal such as sulphichton, albichtol, etc. is produced at this plant. Those medicinal compounds are extremely important in veterinary practic, but since they are needed only in negligible amounts, they cannot serve to justify their large scale production.

Table 14. **Characteristics of Shale Oils Obtained by Semicoking Oil Shale from Timahdit Deposit**

Indices	Bench-scale retort with ash solid heat carrier	Experimental vertical retort with gaseous heat carrier	Externally heated Fischer retort with shale sample 200 g
Yield of shale oil, %:			
Plant yield (raw shale basis)	6.64	5.28	7.0
Yield of Fischer assay oil	95.0	76.7	97.2
Density at 20 °C, kg/m^3	959	981	974
Flash point, °C	6	88	–
Pour point, °C	-21	0	–
Viscosity at 75 °C, $10^{-6} \cdot m^2/s$	2.0	5.7	–
Phenolic compounds, %	3.3	2.0	–
Molecular mass	180	262	210
Heating value (bomb calorimeter), MJ/kg	40.85	40.90	40.26
Initial boiling point, °C	117	178	–
Distillation, vol.%, at:			
150 °C	9	–	–
200 °C	24	2	–
250 °C	38	14	–
300 °C	55	33	–
350 °C	71	64	–
Elemental composition (dry basis), %:			
C	81.07	79.92	79.00
H	9.58	9.62	10.02
S	6.02	6.63	7.02
N	2.44	2.84	2.34
O (by difference)	0.89	0.99	1.62

The development of the Volga oil shale industry has been hindered by the lack of a simple and low-price desulphurization technology for high-sulphur oils. This is also the case in many countries of the world where oil shale resources have not been put to use. Therefore, the creation of such a technology is extremely important and pertinent to the development of thermal processing techniques for oil shales.

It is known that during the retorting of kukersite using a solid ash heat carrier which contains free calcium oxide, sorption of phenols occurs, resulting in an essential reduction of phenol content in the oil - from 25-30 to 10-12 % [4, 5]. Unfortunately, this kind of process does not affect sulphur compounds occurring in the oil. For example, on retorting the Moroccan shale on in enlarged laboratory unit with a solid ash heat carrier, the quantity of sulphur in the oil remained on the same level as it was in oils obtained from experimental and Fischer retorts. The experiment was carried out in the Moscow G. M. Krzhizhanovsky Institute of Energetics (Table 14).

A number of foreign organizations are engaged in development of desulphurization processes of shale oils and petroleums.Some of the identified projects seem to be of practical interest. These are being carried out at the Russian Fossil Fuel Institute [6] and the Saratov Polytechnical Institute [7]. In the first case the H-donor potential of oil shale organic matter is used for desulphurization of oils. The process proceeds by thermal liquefaction of the oil at a temperature of 400-430 °C without any hydrogen nor catalysts. In the second case, a pyrogasification of high-sulphur shale in the powdered state is proposed, which releases pure gaseous energy carrier and valuable chemical by-products (sulphur, aromatic hydrocarbons and thiophene). One can only regret that this work has not been developed to the stage of pilot-scale tests.

Conclusions

Oil shales which form on retorting high-sulphur oil with a sulphur content of 5-10 % have been studied. The total sulphur content of the studied shale samples is within a range of 1.77-6.0 % but the content of organic sulphur varies between 0.15-5.13 %. During processing in Fischer retorts, sulphur is transferred to the retorted products in the following proportions: to oil - 2.2-33.9 %, to gas - 10.8-53.3 %, and to semicoke - 20.9-65.4 % of the total content of sulphur in the original material. This diverse distribution of sulphur during the retorting process of oil shales is primarily a result of the presence of organic sulphur. In the case of a high organic sulphur content, most of the sulphur is transferred into the oil and gas. In the cases with high inorganic sulphur in the oil shales, the quantity of sulphur in the semicoke is high.

It is suitable to conditionally divide oil shales into four groups according to the relative share of organic sulphur in the total sulphur. The first group comprises the oil shales which have 5-10 % of the total sulphur in the organic form. The percentage of organic sulphur in the other groups is 20-35 %, 50-70 %, and 80-90 %, respectively. The transfer of sulphur from the original shale to the produced oil depends mainly on the share of its organic component in the total sulphur.

High-sulphur oils obtained in an experimental retort are quite similar to each other in their chemical group composition. These oils are characterized by an increased content of aromatic hydrocarbons and a reduced content of alkenes and phenols.

There exists no simple and low-price desulphurization technology for high-sulphur oils, and this has hindered the development of the oil shale industry in the Volga Basin as well as the exploitation of the industrial resources of oil shales in many other countries.The shale retorting method does not affect the sulphur content in the retort oils, whether it uses a solid heat carrier, a gaseous heat carrier or an external heat source.

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