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Sorptional Properties of Fuel Shale and Spent Shale

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Abstract—The sorptional properties of fuel shales and spent shales in removing organic compounds (petroleum and its derivatives) from water are studied. The basic benefit of spent shale as a sorbent is that it is available at no expense as the processing waste of fuel shale. After sorption, the fuel shale or spent shale saturated with petroleum or its derivatives may expediently be used as a fuel, on account of their high calorific value.

Keywords: fuel shale, spent shale, organic pollutants, petroleum, petroleum derivatives, sorption, sorptional capacity

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Fuel shales contain kerogen—that is, transformed organic matter from higher plants and simple organisms. They differ from coal in that they form a large quantity of tar on semicoking (20–70%, in terms of the organic component) [1, 2]. After processing fuel shales, a large quantity of spent shale remains (up to 50 wt % of the initial shale); its storage consumes enormous areas [3, 4]. Fuel shales also provide less energy, mass for mass, than other fossil fuels, including petroleum and natural gas. Nevertheless, interest in processing fuel shales has risen sharply in the last decade. Researchers assert that effective industrial use of fuel shales demands the use of not only the organic component but also the mineral component, so as to reduce the waste generation [5–9].

The composition and surface reactivity of fuel shales and spent shales were studied in [9, 10]. On that basis, it seems that fuel shales and spent shales may be used as sorbents, since they resemble materials such as sand and zeolite in terms of their composition (content of calcium, silicon, an aluminum oxides) and properties (porosity, density, etc.), as we see in Table 1.

The main benefit of spent shale as a sorbent is that it is available at no expense as the processing waste of fuel shale. In the present work, we assess the prospects for using fuel shale and spent shale in removing organic pollutants (petroleum and its derivatives) from water. That involves the following steps.

(1) Determination of the granulometric composition of spent shale from shale gasification.

(2) Study of the sorptional properties of fuel shale and spent shale in removing petroleum and its derivatives of different density and viscosity from water.

(3) Comparison of the sorptional properties of fuel shale and spent shale with those of sand and zeolite.

EXPERIMENTAL METHOD

We consider fuel shales from the Baltic Basin of the Leningrad field and the spent shales from their gasification. They are compared with sand and zeolite. The following materials are used to determine the sorptional capacity: light raw petroleum (density 0.867 g/cm^3, viscosity 11 mm^2/s); heavy viscous petroleum (density 0.940 g/cm^3, viscosity 570 mm^2/s); diesel fuel (density 0.854 g/cm^3, viscosity 3.21 mm^2/s); light catalytic-cracking gas-oil (density 0.963 g/cm^3, viscosity 2.42 mm^2/s); and heavy catalytic-cracking gas-oil (density 1.061 g/cm^3, viscosity 44.66 mm^2/s).

The granulometric composition of the spent shale is determined by means of an AS Control 200 analyzer, with grids ranging from 4 mm to <125 μm. The sample mass is 1 kg; its amplitude is 2 mm/g; and the classification time is 10 min. We analyze 10 kg of spent shale.

Table 1. Content of potassium, aluminum, and silicon oxides (wt %) in various sorbents [11]

Sorbent	Porosity, %	SiO_2, %	Al_2O_3, %	CaO, %
Sand	40	49.7	7.0	3.0
Zeolite	34	71.5	13.1	2.1
Fuel shale	24	33.2	7.6	39.9
Spent shale	38	40.3	9.2	41.2

The sorptional capacity is investigated for fractions from <0.125 to 4 mm at 25°C; the sample mass is 3 g. A weighed portion of material is placed in a chamber with petroleum or a petroleum derivative for 5, 10, 15, and 20 min, and then the sample is weighed. Comparison of the mass of the material before and after the experiment permits determination of its sorptional capacity.

DISCUSSION OF THE RESULTS

The granulometric composition of the spent shales from shale gasification is shown in Fig. 1.

We see that, for more than half of the material studied, the grain size is 4 mm or more.

The dependence of the shale's sorptional capacity on the grain size, density, and viscosity is shown in Tables 2–6.

On the basis of Tables 2–6, we conclude that the 1–2 mm fraction of the fuel shale has the best sorptional capacity. Therefore, we choose the 1–2 mm fraction in comparing the sorptional capacity of fuel shale with that of spent shales (Table 7).

The sorptional capacity of the 1–2 mm fraction of the spent shales exceeds that of the fuel shale by a factor of 1.7 for light raw petroleum and diesel fuel; 2.1 for heavy viscous petroleum and heavy catalytic-cracking gas-oil; and 2.2 for light catalytic-cracking gas-oil.

In Table 8, we compare these results with the sorptional capacity of sand and zeolite The minimum and maximum values are shown for fractions from 4 mm to <125 μm.

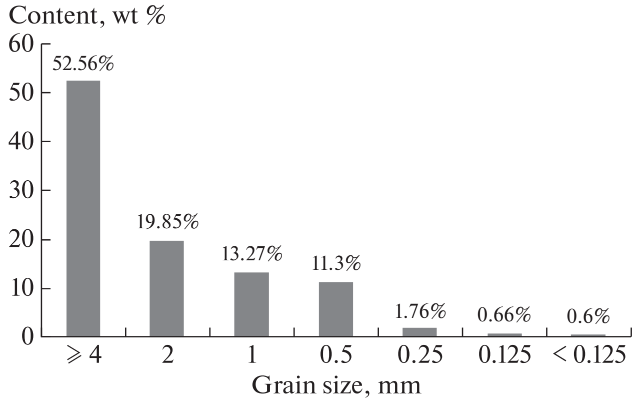

Fig. 1. Granulometric composition of spent shales.

The sorptional capacity of fuel shale is broadly comparable with that of sand and zeolite. For spent shales, the sorptional capacity is higher. That may be attributed to its greater porosity: 38%, as against 24% for fuel shale.

The spent shale may have a small content of residual carbon. Accordingly, we also study the sorptional capacity of spent shale with different carbon contents (0, 3.5, and 7.4 wt %) for various organic pollutants: light petroleum, diesel fuel, and light gas-oil (Fig. 2). The sorptional capacity is higher for the spent shale

Table 2. Sorptional capacity of fuel shale for light raw petroleum (density 0.867 g/cm^3, viscosity 11 mm^2/s)

Fraction, mm	Sorptional capacity, mL/cm^3			
	5 min	10 min	15 min	20 min
<0.125	0.67	0.72	0.73	0.74
0.125–0.500	0.62	0.68	0.69	0.70
0.5–1.0	0.53	0.67	0.68	0.69
1–2	0.67	0.72	0.77	0.74
2–4	0.42	0.46	0.47	0.48

Table 3. Sorptional capacity of fuel shale for heavy viscous petroleum (density 0.640 g/cm^3, viscosity 570 mm^2/s)

Fraction, mm	Sorptional capacity, mL/cm^3			
	5 min	10 min	15 min	20 min
<0.125	0.87	0.89	0.92	0.94
0.125–0.500	0.84	0.86	0.89	0.90
0.5–1.0	0.84	0.86	0.90	0.90
1–2	0.86	0.89	0.93	0.94
2–4	0.80	0.83	0.85	0.86

Table 4. Sorptional capacity of fuel shale for diesel fuel (density 0.854 g/cm^3, viscosity 3.21 mm^2/s)

Fraction, mm	Sorptional capacity, mL/cm^3			
	5 min	10 min	15 min	20 min
<0.125	0.53	0.59	0.60	0.62
0.125–0.500	0.53	0.58	0.60	0.61
0.5–1.0	0.53	0.58	0.59	0.60
1–2	0.53	0.67	0.68	0.69
2–4	0.40	0.45	0.46	0.47

Table 5. Sorptional capacity of fuel shale for light catalytic-cracking gas-oil (density 0.963 g/cm^3, viscosity 2.42 mm^2/s)

Fraction, mm	Sorptional capacity, mL/cm^3			
	5 min	10 min	15 min	20 min
<0.125	0.64	0.70	0.72	0.73
0.125–0.500	0.52	0.57	0.59	0.60
0.5–1.0	0.48	0.52	0.53	0.53
1–2	0.64	0.71	0.73	0.74
2–4	0.40	0.44	0.46	0.47

Table 6. Sorptional capacity of fuel shale for heavy catalytic-cracking gas-oil (density 1.061 g/cm^3, viscosity 44.66 mm^2/s)

Fraction, mm	Sorptional capacity, mL/cm^3			
	5 min	10 min	15 min	20 min
<0.125	0.87	0.90	0.91	0.93
0.125–0.500	0.82	0.85	0.88	0.90
0.5–1.0	0.82	0.83	0.83	0.84
1–2	0.87	0.91	0.92	0.93
2–4	0.80	0.83	0.85	0.85

Table 7. Sorptional capacity of spent shale 1–2 mm fraction)

Sorbed material	Sorptional capacity, mL/cm^3			
	5 min	10 min	15 min	20 min
Light raw petroleum	1.07	1.20	1.22	1.23
Heavy viscous petroleum	1.89	1.92	2.00	2.01
Diesel fuel	1.06	1.12	1.15	1.16
Heavy catalytic-cracking gas-oil	1.76	1.94	1.96	1.99
Light catalytic-cracking gas-oil	1.52	1.59	1.61	1.61

Table 8. Sorptional capacity of various materials, mL/cm^3

Sorbed material	Sorbent			
	sand	zeolite	fuel shale	spent shale
Light raw petroleum	0.39–0.48	0.52–0.79	0.42–0.74	1.07–1.23
Heavy viscous petroleum	0.78–0.85	0.86–0.94	0.80–0.94	1.72–2.01
Heavy catalytic-cracking gas-oil	0.70–0.78	0.85–0.99	0.80–0.93	1.76–1.99
Light catalytic-cracking gas-oil	0.32–0.40	0.64–0.82	0.40–0.73	1.28–1.61
Diesel fuel	0.37–0.42	0.47–0.51	0.40–0.62	1.06–1.16

with no carbon than for that with 7.4% carbon. The improvement in sorptional capacity with decrease in carbon content may be explained in that the increase in total surface porosity is due to the opening of pores previously closed by carbon.

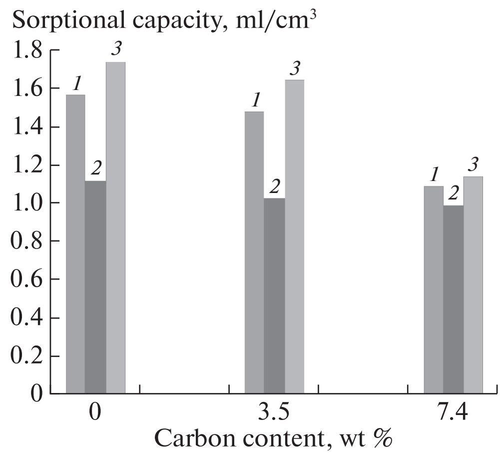

Fig. 2. Dependence of the sorptional capacity of spent shale for light petroleum (*1*), diesel fuel (*2*), and light gas-oil (*3*) on its carbon content.

Regardless of its carbon content, the spent shale outperforms the fuel shale: the sorptional capacity with respect to light petroleum is 0.74 mL/cm^3 for fuel shale and 1.15 mL/cm^3 for spent shale with 7.4% carbon; in the case of diesel fuel, the corresponding figures are 0.62 and 0.95 mL/cm^3; and in the case of light gas-oil, they are 0.73 and 1.18 mL/cm^3.

CONCLUSIONS

(1) According to our results (Table 5), the sorptional capacity of spent shale (1.07–2.01 mL/cm^3) is greater than that of fuel shale (0.42–0.94 mL/cm^3), sand (0.39–0.85 mL/cm^3), and zeolite (0.47–0.99 mL/cm^3). The higher sorptional capacity of spent shale than of fuel shale may be attributed to its greater porosity: 38%, as against 24% for fuel shale.

(2) The sorptional capacity of spent shale depends on its carbon content: it is higher for spent shale with no carbon than for that with 7.4% carbon. Regardless of its carbon content, the spent shale outperforms the fuel shale in terms of sorption.

(3) After sorption, the fuel shale or spent shale saturated with petroleum or its derivatives may expedi-

ently be used as a fuel, on account of their high calorific value.

REFERENCES

1. Yudovich, Ya.E., *Goryuchie slantsy Respubliki Komi. Problemy osvoeniya* (Utilization of Fuel Shales from Komi Republic), Syktyvkar: Geoprint, 2013.
2. Wang, Q., Bai, J., Ge, J., and Wie, Y.Z., Geochemistry of rare earth and other trace elements in Chinese oil shale, *Oil Shale*, 2014, vol. 31, no. 3, pp. 266–277.
3. *Spravochnik slantsepererabotchika* (Shale-Processing Handbook), Rudin, M.G. and Serebryannikov, N.D., Eds., Leningrad: Khimiya, 1988.
4. Xie, F.F., Wang, Z., Lin, W.G., and Song, W.L., Study on thermal conversion of Huadian oil shale under N_2 and CO_2 atmospheres, *Oil Shale*, 2010, vol. 27, no. 4, pp. 309–320.
5. Raado, L.-M., Rein, K., and Hain, T., Oil shale ash based stone formation—hydration, hardening dynamics and phase transformations, *Oil Shale*, 2014, vol. 31, no. 1, pp. 91–101.
6. Swift, T. and Mayer, S., Study of thermal conversion of oil shale under N_2 and CO_2 atmospheres, *Oil Shale*, 2010, vol. 27, no. 4, pp. 309–320.
7. Bityukova, L. and Motler, R., Composition of oil shale ashes from pulverized firing and circulating fluidized-bed boiler in Narva thermal power plants, *Oil Shale*, 2010, vol. 27, no. 4, pp. 339–353.
8. Leimbi Merike, R., Tiina, H., Eneli, L., and Rein, K., Composition and properties of oil shale ash concrete, *Oil Shale*, 2014, vol. 31, no. 2, pp. 147–160.
9. Vatin, N.I., Petrosov, D.V., and Kalachev, A.I., Use of ash and ash-slage wastes in construction, *Inzh. Zh.*, 2011, no. 4, pp. 16–21.
10. Nazarenko, M.Yu., Bazhin, V.Yu., Saltykova, S.N., and Sharikov, F.Yu., Change in composition and properties of fuel shales during heat treatment, *Coke Chem.*, 2014, vol. 57, no. 10, pp. 413–416.
11. M.Yu. Nazarenko, N.K. Kondrasheva, and S.N. Saltykova, Surface reactivity of fuel shales from the Baltic basin, *Coke Chem.*, 2016, vol. 59, no. 5, pp. 196–199.

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