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The Influence of a Nature of Raw Materials and Applied Temperature on a Change in Make-Up and Characteristics of Fuel Shales in Baltic Area

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Abstract

In this paper the chemical composition and properties of briquettes from combustible slates is studied during the heat treatment, made of waste of a slate field of the Leningrad region. Formation of a large amount of ashes is the main problem connected with processing and use of combustible slates. The component structure of mineral part of slate is revealed. Change of mass of combustible slate at heat treatment in the range of temperatures 25-950°C is defined. Reduction of mass of slates happens during five cycles about change of structure and physical and chemical properties. The analysis of allocations of gas components condensed in water solution during heat treatment showed that at increase in temperature pH environment decreases with 6,72 to 6,31 and P_2O_5, SO_3 are allocated. Also in the form of a suspension at solution there are Al_2O_3, SiO_2, CuO, ZnO, MgO. Studying of structure and physical and chemical properties of briquettes from combustible slates during heat treatment gives the chance to define the periods of devolatilization of coal and coking of samples.

Keywords: Combustible slate; Processing; Mineral part; Weight change

Introduction

At present, coal and fuel shales are the most common and reliable energy sources. The wide applicability of fuel shales calls for study of their physicochemical properties to permit their effective use in industry as an energy source and a raw material for the production of graphite components [1].

World reserves of fuel shales (fuel tar and gas) significantly exceed reserves of oil and natural gas. Russia has extensive reserves of fuel shales, exceeded only by those of the United States and Brazil. At present, with rising oil costs, the processing of fuel shales is of increasing interest.

Fuel shale may be regarded as an organic rock, whose practical value is due primarily to the presence of transformed plant and microbial matter (kerogens) [2]. As a rule, the mineral component of fuel shales is greater than the organic component. The mineral composition is extremely variable, with components such as SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO, as well as rare and trace elements. The processing of fuel shales must take account of factors such as the content of fusible ash; the presence of carbonates, whose decomposition consumes considerable heat; the conversion of up to 65% of the organic mass of the kerogens to liquid products; and the active bituminization in the range 300°C/400°C [3].

The major utilization of fuel shales is to use it as a heat-transfer medium, but fuel shales while burning tend to produce less heat than coal or oil, that is why it is important to use not only the organic, but also the mineral part of shales at high as possible. In order to solve this problem one has to explore physical and chemical profile of fuel shales and also a performance of its organic and mineral parts while heating. This knowledge will provide the effective way of its utilization in various fields of industry [1,2].

The aim of this paper is to explore the physical and chemical profile of fuel shales ant its performance while heating by the temperature from 200°C/950°C for complex utilization of organic and mineral parts of shales.

In order to reach this aim, the following tasks were solved in this work:

- to determination of the composition of oil shales mineral part;
- to determination of optimal condition of briquettability of oil shale (composition, pressure of briquetting);
- to explore the influence of a temperature on a performance of briquets and shale's particles;

We investigate shale from the Pribaltiisk Basin (Leningrad field) extracted by the Slantsy plant (energy sample, ≤ 25 mm fraction) (Figure 1).

Methodology of the Experiment

The shale fines are classified on an AS Control granulometric unit.

Figure 1: A kind of fuel shales from the Pribaltiisk Basin of a Leningrad field.

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The moisture content of the sample is determined in a SNOL 420 300 LFNE; The ash content of the fuel shales is determined after heat treatment in a PM1.07; The porosity of the fuel shales is determined by analysis of the actual and apparent density. Element and component make-up of a mineral part of fuel shales is determined with the help of an energy-dispersive X-ray fluorescent spectrometer Epsilon-3 PANalitical.

Briquets are produced on a PVL laboratory hydraulic press from two shale fractions (<125 µm and from 125 µm to 2 mm) at 10 and 15 MPa, with and without preliminary wetting; in some cases, coal fines are added. The strength of the briquets is determined by the standard method: dropping from a height of 1 m until the briquet has completely disintegrated.

The research of an influence of a temperature on a physicochemical transformation of briquets was performed in a tube-type furnace PT-1,2-40 with unmonitored atmosphere (by temperature of 200°C and 400°C) and PTK-1,2-40 (Figure 2) with a monitored (nitrogen) atmosphere (by temperature of 400, 600, 800 and 950°C). The template weighs 3 gr, the heat rate 28°C/min, the material was motionless. The heat in a nitrogen atmosphere was studied more thoroughly. Gas discharge happened in a water environment, which chemical make-up was determined with the help of an energy-dispersive x-ray fluorescent spectrometer Epsilon-3 PANalitical.

The change of fuel shales' weight by heat treatment was studied in a calorimetric laboratory SETARAM Instrumentation within the range of a temperature of 25°C/950°C by the heat rate of hinge 18°C /min.

Experiment Results

The experimental results for the moisture content *W*, ash content *A*, actual and apparent density d, and porosity are consistent with the data obtained earlier at the shales plant for large shale fractions: (Table 1).

The findings are corresponding well with the ones in a literature. Historical: moisture content - 10 13%, ash content - 43 60%, actual and apparent density – 1860 and 1510 kg/m^3, porosity – 19% [2].

The findings of experimental research of a determination of an element make-up of a mineral part of shale with the help of energy-dispersive x-ray fluorescent analyzers are presented in a Table 2.

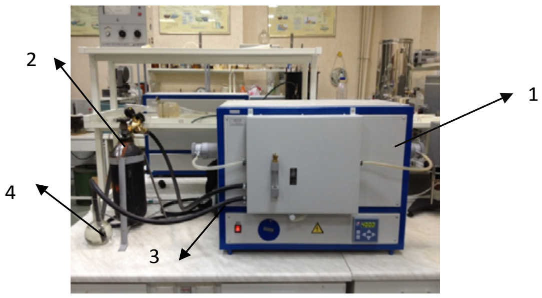

Figure 2: Electrical furnace with a monitories atmosphere (PTK-1,2-40): 1-electrical furnace; 2-nitrogen ballon; 3-gas outlet; 4-tube with water.

Moisture content, %	11.6
Ash content, %	50.5
Density, kg/m^3: actual apparent	1243
	1643
Porosity, %	24

Table 1: Characteristics of fuel shales in Baltic area.

Number	Element	Content	Number	Element	Content
1	**Ca**	45.322%	7	**Sr**	0.111%
2	**Al**	5.413%	8	**Mn**	0.156%
3	**Si**	19.588%	9	**Fe**	13.769%
4	**P**	0.300%	10	**Ti**	1.485%
5	**S**	2.671%	11	**Br**	0.191%
6	**K**	9.491%	12	**Mg**	1.503%

Table 2: Element make-up of a mineral part of fuel shale in Leningrad field (excluding the organic part).

Number	Component	Content	Number	Component	Number
1	Al_2O_3	7.691%	6	MnO	0.106%
2	SiO_2	30.220%	7	Fe_2O_3	10.258%
3	P_2O_5	0.470%	8	Br	0.191%
4	SO_3	4.499%	9	CaO	36.946 %
5	K_2O	7.147%	10	TiO_2	1.318%
6	MgO	1.154%			

Table 3: Characteristics of a mineral part of fuel shales in Leningrad field (excluded the organic part).

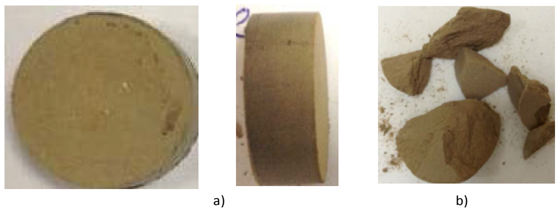

Figure 3: Shales briquette (2 mm-125 mkm and <125 mkm (1:1), Pbriquettting =15MPa). Experiment results of strength characteristics a) before dropping; b) after dropping. Has held 4 droppings.

It is clear, that dominant in a mineral part of shale are calcium Ca (45.322%), silicium Si (19.588%), aluminium Al (5.413%), ferrum Fe (13.769%). In a small amount there are such elements as Pb (316.9 ppm), Cr (420.3 ppm), Ni (511.9 ppm), Cu (271.6 ppm), Zn (407.7 ppm), Zr (596.0 ppm).

The findings of an experimental research of a determination of a component make-up of a mineral part of fuel shales showed, that all the elements of a mineral part of shales are present in a form of oxides: SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO (Table 3).

It is clear, that in a mineral part of fuel shales the most dominant are calcium oxide (CaO – 36,946%) and silicium oxide (SiO_2-30,220%).

After classification, the shale fines are pressed under different pressures (at 10 and 15 Mpa). On a Figure 3 there is an example of shale's briquett with a pressure of briquetting 15MPa and the results of an experiment to a determination of strength characteristics.

According to the findings of the experiment to define the influence of different factors on strength characteristics of briquetts: fractional composition (the fraction of 2 mm-125 mkm and less than 125mkm was used), humidity (from 2-27%) of shales, additive of coal particles (to 4% mass) and pressure of briquetting (from 10 to 15 Mpa), the appropriate conditions for briquetting of fuel shales were defined:

- Fractions less that 125 mkm, humidity of a material 27%, pressure of briquetting 15 Mpa, a briquett has held 6 falls.
- Fractions of 2 mm to 125 mkm and less 125 mkm (1:1),

perfect humidity of a material – 23%, pressure of briquetting 15 Mpa, a briquett has held 4 falls.

- It was discovered that: increasing of a pressure of briquetting (from 10 Mpa to 15 Mpa) and humidity of a material (from 2% to 27%) improves strength characteristics of the briquetts.

The experiment of a temperature influence on a performance of shales briquettes showed, that the form of a surface depends on an applied temperature of an experiment (Figure 4). The area of low-temperature carbonization decreases and with the increasing of a temperature a shift from the edge to the center happens, which can be explained as an increasing of a temperature gradient. It can be explained, that by a small index of thermal response (0,16-0,18 kl/(m hour °C)) while heating the separate parts of fuel its form heats to a higher temperature than the inner part [1]. The bigger the part of a fuel, the more is the difference of heating temperature. The thermal breakdown products of fuel, that appear in the inner part of a piece, have to go through an outer surface that is heated to a higher temperature [1].

The experimental findings of a definition of weight loss are presented on a Figure 5.

From the graphic above one can see, that the weight change of fuel shales happens in 5 steps. It is connected to a particularity of an organic and mineral make-up of shales particles. Let's go through each step individually.

Heating interval of 0/370°C corresponds with the part I. Affected by the temperature the organic material molecules of fuel shales (kerogen) at first start to produce some loosely bound gaseous substances – mostly carbon dioxide and hydrogen sulfide. By 270/290°C a so called pyrogenous water starts to detach.

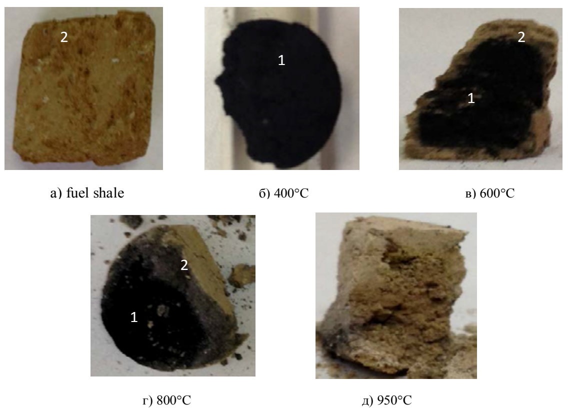

Figure 4: A shale briquett. a) initial (W=11,6%, A=50,5%); b) by 400°C, 1-semi-coke; c) by 800°C, 1- semi-coke, 2- a shale.

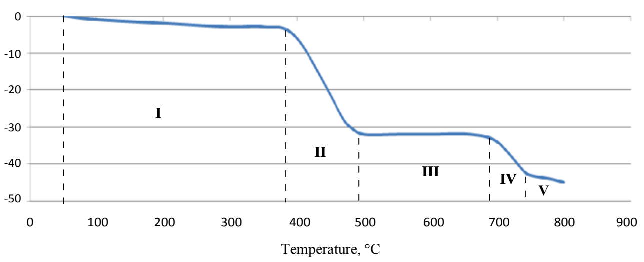

Figure 5: The change of weight of fuel shales by heating.

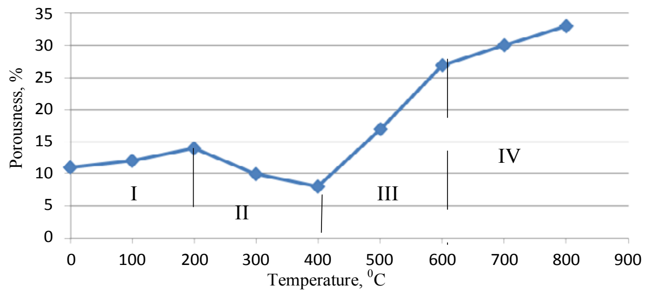

Figure 6: The change of porousness of Leningrad oil shale by heating.

The following heating of shales pieces drives to deeper changes. A sudden change in weight of shales on the part II by 370/500°C is explained as in this temperature interval the resin appears. A hard part of shale becomes semi-liquid by the temperature of 350 ÷ 380°C. This phenomenon is called butumisation. This process can be explained, that in the temperature interval of 320 ÷ 380°C the most part of shales' resin appears, but there isn't enough heat for it to vaporize. The most common control measure is to increase the heat rate. A very fast rise of temperature makes the resin vaporize; it goes away in form of steam that allows a part of shale not to become semi-liquid. By increasing the temperature till 400°C some amount of resin can appear, but by 450°C this process almost stops [1,2].

By further heating (more than 550°C) some amount of gas appears, because the number of oxygen and hydrogen in a semi-coke is small. A resin practically doesn't appear. That is why on a part III the out-gassing is inconsiderable. Also the additional amount of carbon dioxide in this temperature interval (500 ÷ 700°C) appears because of a dissociation of magnesite ($MgCO_3$). A dissociation of magnesite goes according to the equation 1 [1]:

$$MgCO_3 = MgO + CO_2 + 121\,kJ \tag{1}$$

A dissociation of magnesite starts by 400°C, but an active resolution starts by 640°C.

On th IV and V parts by temperature interval of 700/800°C one can see one more jump in weight loosing. It can be explained, that in this particular temperature interval an active resolution of dolomite ($CaMg(CO_3)_2$) happens, the content of which in a mineral part of shales reaches 50%. Resolution of dolomite happens in 2 endothermic effects [1]. The beginning of resolution happens in the temperature interval of 720/760°C according to the equation 2:

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2 \tag{2}$$

The second step of dolomite's resolution happens by the temperature interval of 895-910°C according to the equation 3:

$$CaCO_3 = CaO + CO_2 \tag{3}$$

The result of determination of porousness change of Leningrad oil shale under heating is shown on Figure 6.

The porousness change of oil shale is determined in the temperature range from 25°C to 90°C at heating rate of 28°C/min. From the figure it can be seen that porousness of oil shale changing in 4 stages. The reduction of porousness is connected with bitumisation process on the stages 2.

The output and a composition of gases by heat treating in a tube furnace PTK-1,2-40 was defined by its passing through aqueous solution. The change in pH sphere from the temperature is presented on Figure 7.

Decreasing of pH can be explained that by heating of fuel shales till the temperature of 20°/30°C such elements CO, CO_2, H_2S, SO_2 start to appear. By further heating of shales till 40°/50°C, when the active vaporisation of resin starts, that contains up to 25% of phenols, CO, CO_2 start to appear. By 50°/60°C the gas emission decreases, because the amount of oxygen and hydrogen in a semi-coke decreases too. Then, by the temperature more than 70°/80°C as a result of an active resolution of carbonates, which are contained in a mineral part of shale, carbon dioxide starts to appear, that leads to decreasing of pH. Also the amount of hydrogen, carbon oxide and light hydrocarbons (methane, ethane) rises, which are the final products of resolution of heavier hydrocarbons [2].

The study of a received aqueous solution showed that there are such components as Br, P_2O_5, SO_3 in it. As a suspended solid material there are such chemicals as Al_2O_3, SiO_2, CuO, ZnO, MgO. The change in sulfur oxides, phosphorus and bromine in a solution by heating shale is presented on a Figure 8.

From the Figure 7a one can see, that with a temperature rise the amount of phosphorus oxides (V) decreases from 28,2% to 30% in an analyzed water (a maximum concentration by the temperature of 800°C is 33,1%). On Figure 7b a bromine concentration rises is showed that happens because of a temperature rise. It is showed that with increasing the heating temperature, pH of an analyzed water decreases, which is also connected to the vaporisation of bromine from the mineral part of fuel shales and reacts with water that results in building-up a bromine water.

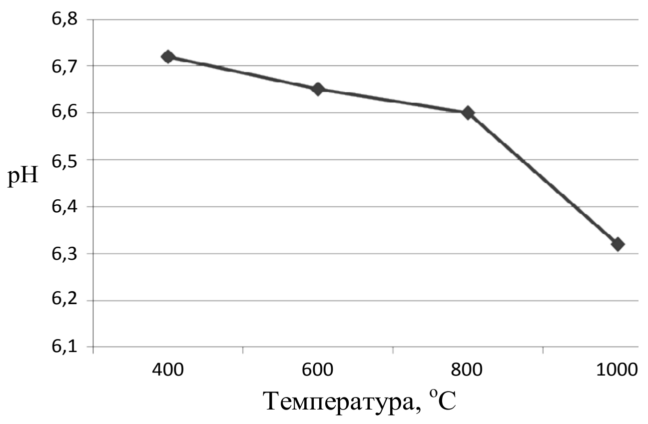

Figure 7: The influence of temperature of heat treatment on a change in pH of water sphere.

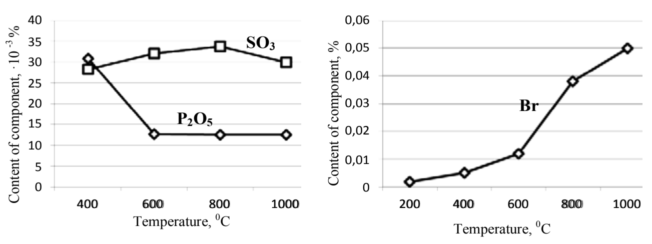

Figure 8: A change in composition in an analyzed water a), SO_3 b) Br.

Conclusions

In this paper the physical characteristics of initial fuel shale were defined, also an element and component composition of a mineral part of shale was determined. According to the experiment it was identified, that a mineral part of shale consists mostly of a calcium and silicium oxide. The influence of a briquetting pressure on strength characteristics of shale briquettes was also defined. According to the results of the experiment ideal for briquetting is the material, which consisted of oil shales of a fraction less than 125 mkm and water, while briquetting with a pressure of 15 Mpa, and held 6 falls. With a rise of briquetts' humidity and pressure strength characteristics of shales improve and when coal particles added (till 4% of weight) strength characteristics also improve. Ideal humidity of a material (fraction 2 mm-125 mkm and less than 125 mkm in the ratio 1:1) is 23-25%, while briquetting by pressure 15 Mpa a briquett held 4 falls.

The following was studied:

- The weight change of a fuel shale while heating in the temperature interval of 25°C/800°C, which showed, that the weight change of a shale happens in 5 stages: 1st stage-25°C/370°C; 2nd-370°C/500°C; 3rd-500°C/700°C; 4th and 5th-700°C/800°C;
- pH analysis of an a aqueous solution after heating in a tube furnace showed, that with a rise of a heating temperature pH decreases from 6,72 to 6,31 and such components as Br, P_2O_5, SO_3 appear;
- by evolution of dioxides and carbon oxides one can set the periods, that are strongly connected with a structure change in shales.

Finally, the conducted analysis of weight change and a change of chemical composition of briquettes from the fuel shales while heating gives a chance to define the periods of semi-coking and coking of the templates with account of transition in an organic and non-organic part.

The conducted research shows a need in a detailed examination of characteristics of fuel shales and its performance while heating.

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