Estonian oil shale properties and utilization in power plants

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Oil shale is a sedimentary rock containing organic matter and belongs to the sapropel fuel group. Estonia has significant oil shale recourses. Estonia is the only country in the world that uses oil shale fired power plants to supply most of its electricity to domestic customers and can export it to neighboring countries. Estonian oil shale is a carbonaceous fuel which contains a complicated composition of organic and mineral matter. The complicated compositio offers numerous sophisticated problems that can influence power plant equipment operation and reliability. We have examined oil shale as a power fuel and its utilization problems.

Key words: organic matter, mineral matter, combustion characteristics, pulverized firing, fluidized bed combustion, environmental protection

1. INTRODUCTION

Oil shale is a sedimentary rock containing organic matter, kerogen, and belongs to the group of sapropel fuels. A significant feature of oil shale organic matter is its low solubility in strong solvents.

Oil shale differs from humus fuels by its high content of organic matter. The atomic ratio of hydrogen to carbon (H/C) is about 1.5, which is approximately the same as for crude oil, for coals being only about 0.3 to 0.4. The high hydrogen-to-carbon ratio is the main reason for the high yield of volatile matter and condensable oil during the thermal decomposition of kerogen.

Oil shale deposits have been discovered on all continents. More than 600 oil shale basins are known. The world oil shale resources are estimated to about 11.5 Tt.

The largest oil shale resources belong to the Middle Cambrian, Early and Middle Ordovician, Later Devonian, Late Jurassic, and Paleogene periods. The formation oil shale took place mostly in marine conditions and less often in lakes. Therefore, the geotectonic structure of oil shale deposits is predominantly of the platform type.

Estonia has significant oil shale resources; they are estimated to more than 7 Gt. Estonia is the only country in the world that operates oil shale fired power plants to supply most of its electricity to domestic customers and can export power to neighboring countries. In addition to thermal power plants, Estonia has also oil shale thermal processing plants for shale oil production. Power plants and processing factories in Estonia are supplied with oil shale from two underground mines and two opencast mines.

Estonian oil shale as a power fuel undoubtedly belongs to the fuel class with the most complicated organic and mineral matter composition in the world. The composition of oil shale offers numerous complicated and interrelated problems that can influence power plant equipment operation and reliability.

Various aspects of Estonian oil shale and its characteristics as well as energy use are presented in [1–4].

Below, we present Estonian oil shale as a power fuel and its utilization problems in power plants.

2. ESTONIAN OIL SHALE GEOLOGY AND RESERVES

The oil shale body lies at a depth of between 30 to 60 m, but in the center of the Pandivere upland its depth of occurrence is 100 to 120 meters. The total area is about 3000 km². The mined area covers a total of 425 km².

Oil shale beds have a stratified structure, with oil shale seams alternating with mineral interbeds.

Figure 1 shows a cross-section of an Estonian oil shale deposit.

In an oil shale seam, organic matter is tightly bound with sandy-clay minerals and forms a uniform mixture. Oil shale is a yellow-brownish, relatively soft material. The main substances in the interbeds are carbonate minerals – mainly calcium carbonate, to a lesser extent dolomite.

A commercial bed consists of seven indexed oil shale seams counted from bottom to top. The majority of oil shale seams contain lens-like concretions of kerogenous limestone. They are present in different layers and in various proportions. The thickness of oil shale seams varies from 0.05 to 0.6 m.

There are four oil shale seams in the Leningrad oil shale basin, and they are marked with Roman numbers from top to bottom.

Considering oil shale as a fuel, its dry matter consists of three parts: organic – R, sandy-clay (terrigenous) – T, and carbonate – K. Consequently,

$$R^d + T^d + K^d = 100\%.$$

The values of R, T, and K differ for different oil shale seams.

Figure 2 shows the dynamics of Estonian oil shale production over time and also the operation time of opencast and underground mines.
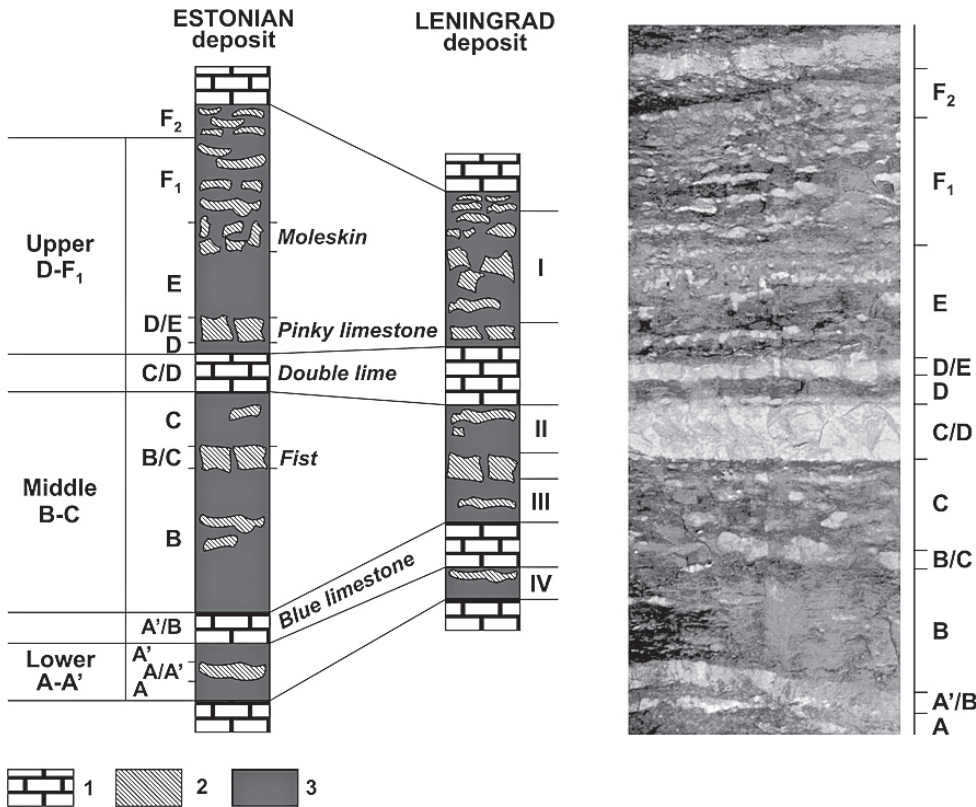
Fig. 1. Cross-section of oil shale deposit: 1 – limestone, 2 – kerogenous limestone, 3 – oil shale
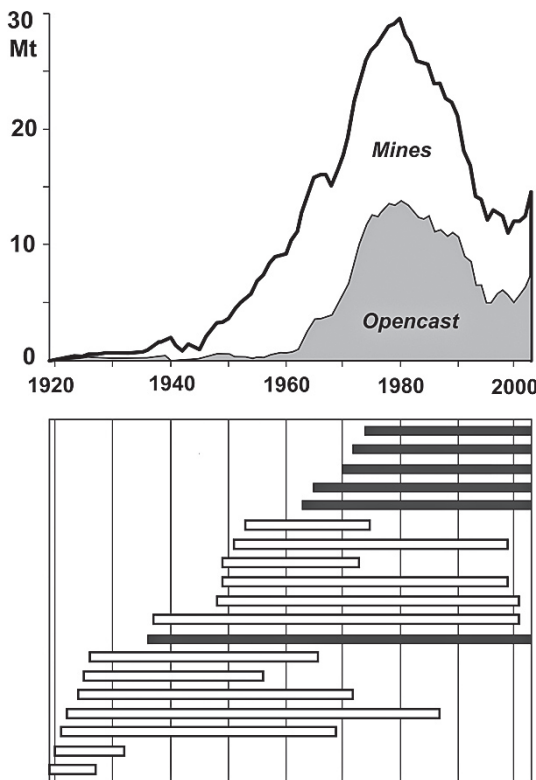

Fig. 2. Estonian oil shale production and operation time of mines

The largest consumers of oil shale in Estonia are thermal power plants. Today power plants consume about 12 Mt/y. The shale oil production industry consumes the second highest amount – about 2 Mt/y.

3. OIL SHALE PROPERTIES

3.1. Organic and combustible matter

The elemental composition of the organic matter of oil shale is given in Table 1.

The main characteristics of the organic matter of oil shale are a high hydrogen and oxygen content and a low nitrogen percentage. Oil shale organic matter contains on average about 1.8% of organic sulfur. An important characteristic of the organic matter is a high chlorine content.

One of the combustible components of oil shale is marcasite (pyrite) with the general chemical formula FeS_2 (Tables 2 and 3). The sum of organic and pyretic sulfur is called combustible or volatile sulfur:

$$S_V = S_o + S_p.$$

Organic matter together with pyretic sulfur is considered a combustible matter of oil shale.

Figure 3 presents the thermal decomposition characteristics of oil shale as the release of different components during devolatilization.

The first signs of the thermal decomposition of organic matter appear at 150 °C. Visible decomposition starts at 200–250 °C.
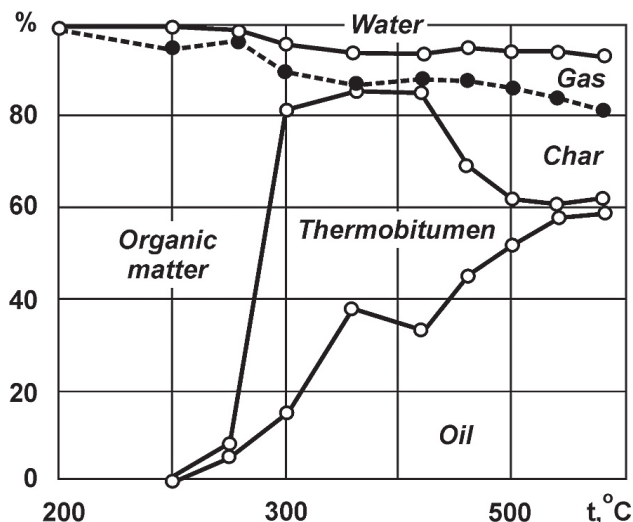
Table 1. **Elemental composition of organic matter of Estonian oil shale, %**

Element	C	H	O	N	S	Cl
Range	77.11–77.80	9.49–9.82	9.68–10.22	0.30–0.44	1.68–1.95	0.60–0.96
Average	77.45	9.70	10.01	0.33	1.76	0.75

Fig. 3. Material balance of Estonian oil shale organic matter as a function of temperature

One feature in the decomposition process of oil shale organic matter is thermobitumen formation at temperatures between 250–425 °C. It is also notable that the proportion of the condensing phase in volatile matter decreases with temperature and the decrease is accompanied by an increase in the gaseous phase.

Due to the high H/C ratio, oil shale has a very high volatile matter content. Its standard value is 85–90%.

The higher heating value (HHV) of oil shale organic matter is 36.68 MJ/kg and the lower heating value (LHV) is 34.56 MJ/kg. The LHV of volatile matter is approximately 34 MJ/kg.

3.2. Mineral matter

The mineral matter of oil shale can be divided into two large groups: sandy-clay or terrigenous part and carbonate matter. The sandy-clay part is densely intertwined with organic matter. Carbonate minerals in the Estonian oil shale deposit occur as separate layers or are distributed as limestone concretions in oil shale seams. Table 2 presents the chemical composition of the sandy-clay and carbonate parts of oil shale.

The main component of the oil shale carbonate matter is calcium oxide (48.1%), followed by magnesium oxide (6.6%).

Table 2. **Chemical composition of Estonian oil shale mineral matter, %**

Sandy-clay part		Carbonate part	
Component	**Content**	**Component**	**Content**
SiO_2	59.8	CaO	48.1
CaO	0.7	MgO	6.6
Al_2O_3	16.1	FeO	0.2
Fe_2O_3	2.8	CO_2	45.1
TiO_2	0.7		
MgO	0.4		
Na_2O	0.8		
K_2O	6.3		
FeS_2	9.3		
SO_3	0.5		
H_2O	2.6		
Total	100.0	**Total**	100.0

Their ratio corresponds to the average oil shale carbonate part CaO/MgO = 7.3.

The average ratio of oxides and CO_2 in the oil shale carbonate part is $MO_c/CO_2 = 1.217$, where MO_c and CO_2 denote the content of oxides in carbonate minerals and mineral CO_2 content in mineral matter, respectively.

Table 3. **Mineralogical composition of Estonian oil shale mineral matter, %**

Group of minerals	Mineral	Formula	Content
Carbonate minerals	Calcite	$CaCO_3$	69.1
	Dolomite	$CaMg(CO_3)_2$	30.6
	Siderite	$FeCO_3$	0.3
		Total	100.0
Sandy-clay minerals	Quartz	SiO_2	23.9
	Rutile	TiO_2	0.7
	Orthoclase	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	29.0
	Albite	$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	6.0
	Anorthite	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	1.4
	Muskovite	$[K_{1-x}(H_2O)_x \cdot Al_3Si_3O_{10}(OH)_2]_2$	23.7
	Amphipole	$[NaCa_2Mg_4)Fe,Al)Si_8O_{22}(OH)_2]$	2.1
	Markasite	FeS_2	9.3
	Limonite	$Fe_2O_3 \cdot H_2O$	2.9
	Gypsum	$CaSO_4 \cdot 2H_2O$	1.0
		Total	100.0

The main components in the sandy-clay part are SiO_2, Al_2O_3 and K_2O. The content of potassium (given as K_2O) exceeds that of Na_2O by about 8 to 12 times.

Table 3 gives the mineralogical composition of Estonian oil shale mineral matter.

The main minerals in the carbonate part are calcite and dolomite.
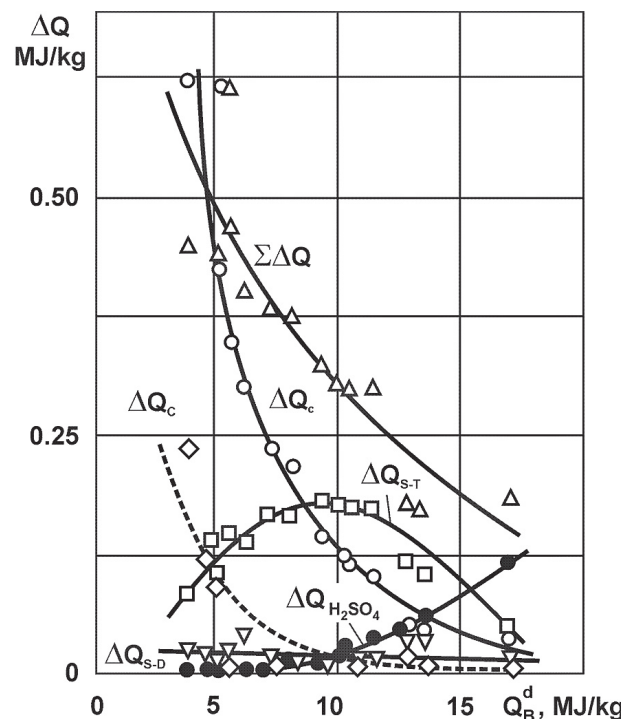

Fig. 4. Thermal effects occurring during combustion of oil shale in a calorimetric bomb

The main minerals in the oil shale sandy-clay part are quartz, feldspars (mainly as orthoclase), and micas (mainly as muscovite). Iron present in the oil shale sandy-clay part is bound mainly to marcasite sulfur, but, to a limited extent, also to siderite.

3.3. Heating value

The heating value of oil shale as a fuel with a complicated composition of organic and mineral matter determined in a calorimetric bomb does not coincide with the actual amount of heat released during the combustion of fuel in the combustion chamber because of differences in the combustion processes in a calorimetric bomb and in the furnace, which are greatly influenced by the behavior of fuel mineral matter. Therefore, one should know the phenomena influencing thermal effects in a calorimetric bomb and in the combustion chamber.

The relationships between thermal effects and the heating value measured in a calorimetric bomb, as well as the sum of thermal effects $\Sigma \Delta Q$ are presented in Fig. 4. There are:

ΔQ_C – thermal effect due to incomplete combustion of carbon, ΔQ_c – thermal effect due to incomplete decomposition of carbonaceous minerals, ΔQ_{S-D} – thermal effect due to incomplete oxidation of sulfides, $\Delta Q_{H_2SO_4}$ – thermal effect due to formation of sulfuric acid, ΔQ_{S-T} – thermal effect due to formation of sulfate.

Heat released during oil shale combustion is dependent on the combustion technology used. The most important factor is the influence on the behavior of carbonate minerals. The behavior of carbonate minerals is expressed as the extent of carbonate decomposition k_{CO_2}. This is the ratio of the amount of CO_2 released from carbonate minerals in the combustion process to the total content of mineral CO_2 in the initial material.

The average extent of decomposition of carbonate minerals during high-temperature pulverized firing (PF) of oil shale is 0.97. However, in the case of low-temperature fluidized combustion (FBC), the extent of decomposition of carbonates remains in the range of 0.7 to 0.8.
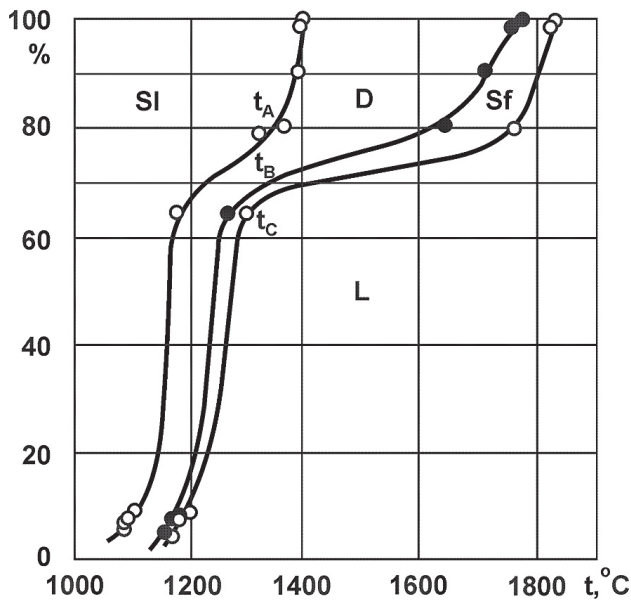
3.4. Ash fusion characteristics

The fusion characteristics of ash at three temperatures are as follows: t_A (or t_1) – the initial deformation temperature, t_B (or t_2) – the softening temperature, and t_C (or t_3) – the fusion temperature.

The fusion temperatures of ash depend on the chemical and mineralogical composition of the ash. The main components in oil shale ash that influence ash fusibility are CaO, SiO_2, and Al_2O_3.

Oil shale mineral matter is a heterogeneous system containing minerals of carbonate and sandy-clay parts. Therefore, different ash particles have different fusion temperatures depending on the proportions of the mentioned components. Consequently, ash as a whole consists of a mixture of particles of different phase state. Integral fusion characteristics of oil shale ash as a function of temperature are shown in Fig. 5. The vertical axis represents the share of the corresponding phase in ash.

The curves show the proportion of ash components in different states. The first signs of deformation of oil shale ash appear at about 1050 °C; the fusion temperature is close to 1150 °C. At higher temperatures, the amount of the liquid phase in the system increases rapidly.
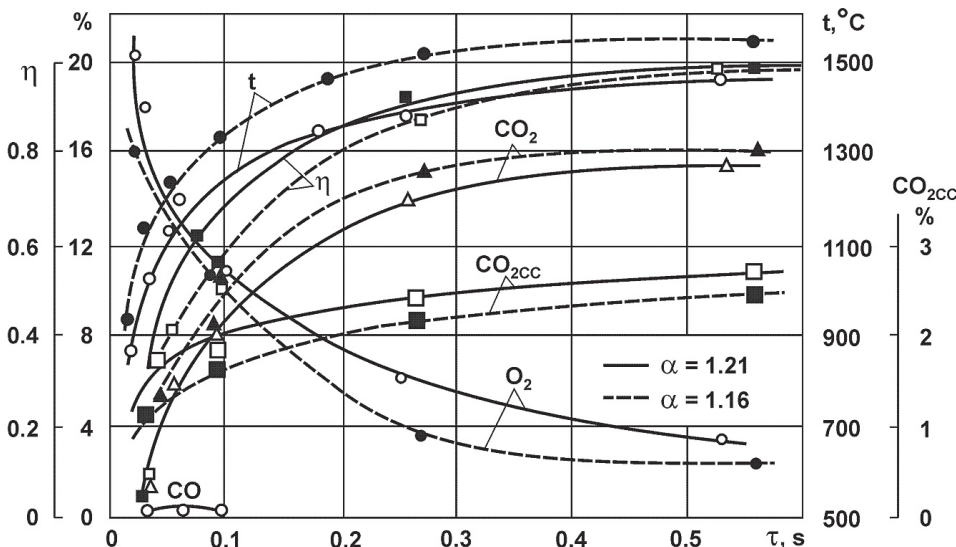

Fig. 5. Integral fusion characteristics of oil shale ash. SI – solid state, D – deformed state, Sf – softend state, L – liquid state

Fig. 6. Combustion characteristics of polyfractional pulverized oil shale

4. COMBUSTION AND MINERAL MATTER BEHAVIOUR CHARACTERISTICS

Figure 6 shows the dynamics of the combustion of polyfractional pulverized oil shale at two different excess air factors. The vertical axis represents the temperature and volumetric concentration of flue gas components along the axis of the combustion chamber. The horizontal axis represents time. The figure also expresses the extent of fuel combustion η.

An intensive heat release (combustion) and a rapid rise in temperature start after a short period of 0.02 to 0.04 s. Intensive combustion demonstrated a rapid decrease in oxygen concentration and an increase in CO_2 concentration. Particles burn with a particular intensity within 0.25 to 0.35 s.

The value of combustion extent 0.8 (zone of combustion of volatile matter), depending upon the combustion regime, corresponds to the combustion time 0.12 to 0.20 s. The volumetric heat release rate in the zone of combustion of volatile matter is high and can reach 1.5 to 2.5 MW/m^3. Beginning from the value 0.8, slower char burning dominates, and heat release diminishes rapidly. The extent of combustion starts to approach asymptotically the unity. The time required for a complete combustion of pulverized oil shale is in the range of 1.0 to 1.5 s.

Carbon dioxide released during oil shale combustion forms both from organic carbon (CO_{2C}) and through the thermal decomposition of carbonate minerals (CO_{2CC}). The ratio $\theta = CO_{2CC} / (CO_{2C} + CO_{2CC})$ indicates the share of mineral CO_2 in the amount of total CO_2 formed. Dissociation of carbonate minerals is a dynamic process, and θ increases over time. The maximum possible ratio is $\theta = 0.18$–0.22. One can see in Fig. 6 that the amount of mineral CO_2 increases the absolute concentration of CO_2 in flue gas by 2.5 to 3.0%; the total concentration of CO_2 in the flue gas is 15 to 16%.

Oil shale ash is characterized by the ability to react with gaseous sulfur compounds present in flue gas. This phenomenon is known as ash sulfation.

Sulfation takes place when the boiler gas passes through reactions between fly ash components and sulfur containing gaseous compounds, either in the space of the boiler gas pass or on the heat exchange surfaces during formation of the ash deposit. In the first case, the concentration of SO_2 in the flue gas and SO_2 emissions into the atmosphere diminish. In the second case, a sulfate ash deposit forms on boiler heat transfer surfaces, and SO_2 concentration in the flue gas also somewhat decreases.

Oil shale ash sulfation intensity depends on temperature, partial pressures of SO_2 and oxygen, and particle sizes. The dynamics of the sulfation of oil shale fly ash at two different temperatures and values of $p_{SO_2}\sqrt{p_{O_2}}$ is shown in Fig. 7. Value of m on the vertical axis denotes mass increase, and the horizontal axis denotes time.

Sulfation of oil shale ash is possible at relatively low partial pressures of SO_2, as proved by a significant increase in the ash mass during the sulfation process, even at a low concentration of SO_2 in the surrounding medium. Fig. 7 also shows that at the same temperature (1000 °C), but at lower values of $p_{SO_2}\sqrt{p_{O_2}}$ sulfation proceeds slower.

5. OIL SHALE FIRING POWER PLANTS

Initially, Estonian oil shale was used as a fuel in locomotives. Thereafter, more and more lump oil shale was burned in industrial boilers [2, 4].

An important milestone in the history of the oil shale power industry was the switch to oil shale firing at the Tallinn Power Plant in 1924. The electrical capacity of the Tallinn power plant was 23 MW. This year can be considered the start of the oil shale power industry. Thereafter, many oil shale-fired power plants were built in north Estonia (Püssi, Kohtla, Kunda, and Kiviõli).

At that time, a steam boiler with a grate-firing furnace was typical. The key problem with firing oil shale rich in volatile matter is ensuring soot-free combustion. This issue was successfully solved.

The next stage was introducing oil shale PF technology. The first power plants using oil shale PF technology were the Kohtla-Järve Power Plant, which began operation in 1949 and had the designed electrical capacity of 48 MW, and the Ahtme Power Plant, which began operation in 1951 and had an electrical capacity of 75.5 MW. Steam boilers at these power plants were slightly modified medium-pressure boilers initially designed for PF of coal or brown coal. Operational experience showed that these boilers on oil shale could be operated only at loads considerably below the design value, because ash deposits caused fouling of the radiant and convection heat transfer surfaces and a high-temperature corrosive-erosive wear of the boiler tubes. This experience indicated for the first time specific problems with fouling of heat transfer surfaces, high-temperature corrosion and wear of boiler tubes, cleaning of heating surfaces from ash deposits, and heat transfer. It became evident that boilers designed for burning coal or brown coal cannot work satisfactorily with oil shale due to the very specific and complex composition of oil shale mineral and organic matter. Systematic application of the results of scientific studies allowed the operational capacity of medium-pressure boilers to increase, which formed a basis for designing an original construction of oil shale boilers.

The next stages in the development of oil shale power engineering industry started in 1959 when the first high-pressure PF boilers, specially designed for firing oil shale, were launched
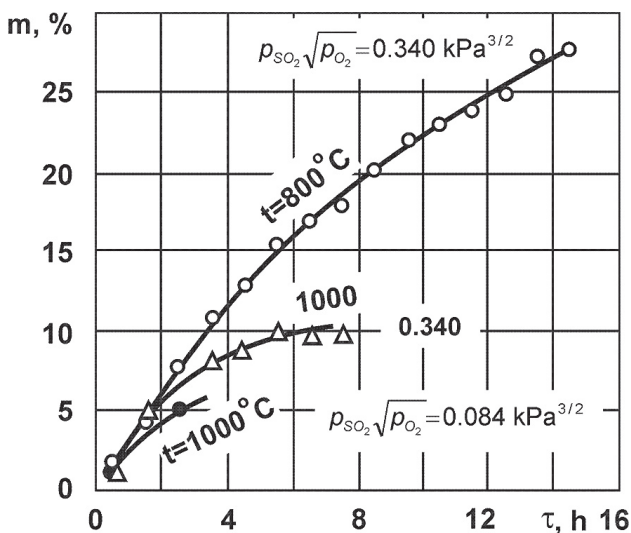

Fig. 7. Dynamics of sulfation of oil shale ash

at the Balti Power Plant. The designed electrical capacity of the Balti Power Plant was 1624 MW.

The first power unit at the Eesti Power Plant was inaugurated in 1969. The design capacity of the power plant was 1610 MW.

At the beginning of 2004, a power unit of electrical capacity of 215 MW with two circulating fluidized bed combustion (CFBC) boilers, was put into operation at the Eesti Power Plant. Some months later, a power unit of the same type was put into operation at the Balti Power Plant.

Oil shale burned in power plants has the following proximate characteristics W^r = 11–13%, A^r = 45–57%, $(CO_2)^r_c$ = 16–19%, and Q^r_L = 8.3–8.7 MJ/kg.

6. OIL SHALE FIRING TECHNOLOGIES

6.1. Pulverized firing

Today, PF is the most widely used combustion technology for solid fuels. This is true in oil shale fired-power plants by installed power.

PF of solid fuels is a high-temperature combustion technology. The maximum flame temperature in the furnace chamber when burning pulverized oil shale reaches 1400–1500 °C.

The conceptual solutions of the boilers designed in cooperation with the Thermal Engineering Department of Tallinn University of Technology (STI TUT) and built at the Taganrog

Boiler Factory for the Balti and Eesti power plants differ from those of typical PF boilers. The designers have taken into account the experience gained from the operation and reconstruction of medium-pressure boilers for PF of oil shale and also research results.

The main issues that must be accounted for when designing oil shale firing boilers are the following:

1. The ash fouling mechanism and ash deposits formation dynamics on boiler heat transfer surfaces.

2. Arrangement of boiler gas passes and heat exchange surfaces according to the ash fouling mechanism.

3. The influence of the ash fouling mechanism on heat transfer on boiler heat exchange surfaces.

4. Heat transfer in heat exchange surfaces as a transient process due to an unlimited growth of ash deposits.

5. Boiler heat exchange surface ash deposit cleaning technology.

6. The influence of boiler heat exchange surface cleaning technology on heat transfer conditions.

7. High-temperature corrosion of boiler tube metal under the influence of ash deposits.

8. The influence of heat exchange surface cleaning technology on the corrosive-erosive wear intensity of boiler tubes.

The longitudinal section of the high-pressure pulverized oil shale firing TP-101 boiler mounted at the Eesti Power Plant is shown in Fig. 8.

TP-101 is a balanced-draft, natural-circulation, single-drum boiler with a superheater and reheater. The steam capacity of the
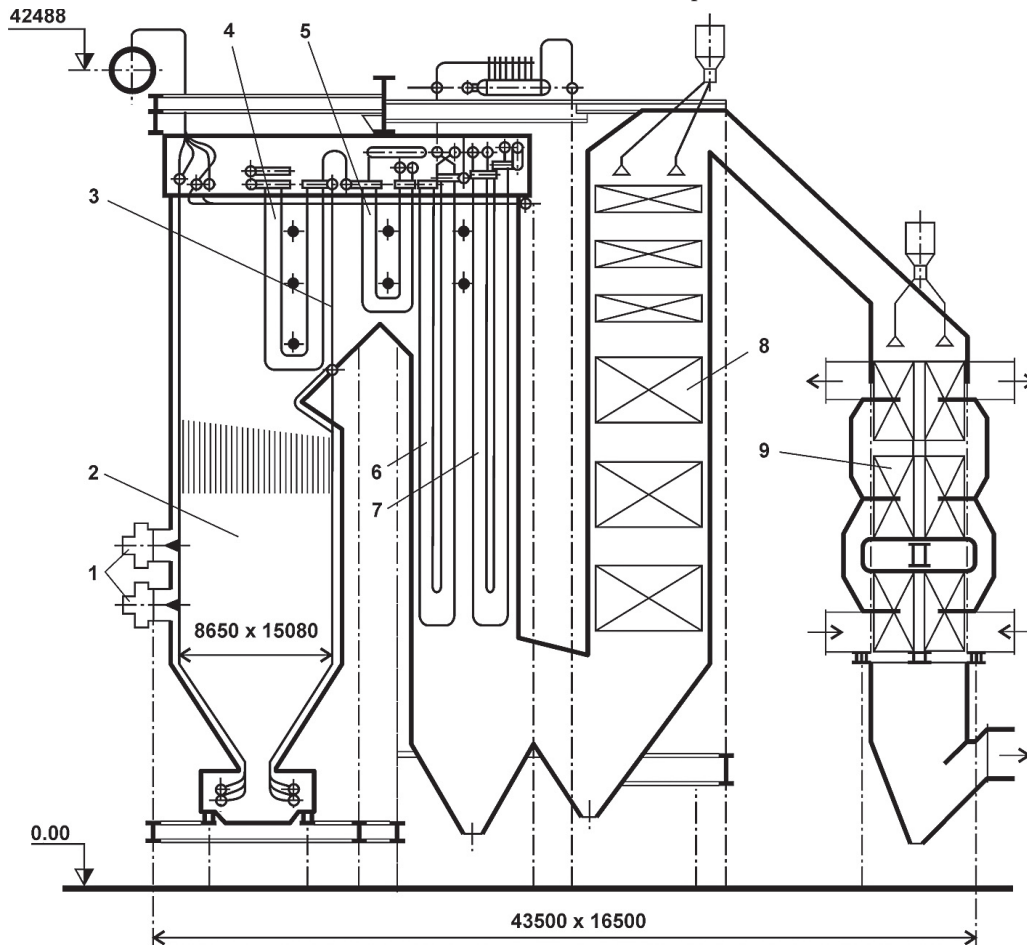

Fig. 8. Boiler TP-101: 1 – burners, 2 – furnace, 3 – outlet screen, 4 – furnace platen superheater, 5 – intermediate platen superheater, 6 – hanging platens of primary superheater, 7 – hanging platens of reheater, 8 – economizer, 9 – air preheater

boiler is 320 t/h. The pressure in the drum is 15.3 MPa. The pressure and temperature of superheated steam after the boiler are 13.8 MPa and 520 °C. Steam pressure and temperature at the reheater inlet and outlet are 2.5 MPa/330 °C and 2.2 MPa/525 °C, respectively.

The boiler has four vertical gas passes. The first (rising) gas pass is the furnace chamber. In the second (downflow) gas pass, there are hanging platen-type superheaters. In the third (rising) gas pass, there is an economizer and in the fourth (downflow) gas pass an air preheater.

The rear and side walls of the furnace are screened by water tubes. Radiant superheater panels cover the front wall.

In the front wall of the furnace, two rows of eight turbulent burners are placed. Oil shale fed into the boiler is pulverized in four hammer mills with an inertial classifier. The particle size distribution of the pulverized oil shale is characterized by the following residues in the sieves: $R_{90} = 25$–35% and $R_{200} = 17$–22%. The median size of pulverized fuel $\Delta_M^* = 45$–55 μm.

6.2. Fluidized combustion

FBC of solid fuels, a technology that is still in the development stage, is the newest trend in thermal power plants. It is very promising also for firing oil shale [4].

A fluidized bed is a floating aerodynamic system of fine inert solid particles in a gas flow. If fuel particles are fed into the fluidized bed where the temperature is at least equal to the ignition temperature, continuous combustion without the need for a high temperature takes place. The combustion temperature is typically between 800–900 °C. FBC is a low-temperature firing technology.

Estonian power plants have more than three years of experience in burning oil shale in circulating fluidized combustion (CFBC) boilers.

Figure 9 shows the CFBC oil shale boiler designed by Foster Wheeler for burning oil shale in the Eesti and Balti power plants. The circulating loop corresponds to the Foster Wheeler compact boiler design concept, but the heat exchange surfaces design and placement after the separator is similar to concept used in PF boilers. The power unit with the electrical capacity 215 MW has two boilers. The main parameters of the boiler are as follows: steam capacity 342/272 t/h; primary/reheated steam pressure 12.7/2.4 MPa; and primary/reheated steam temperature 535/535 °C.

The circulating fluidized bed loop consists of the following items making up the solid particles recirculation system: furnace, gas-solid separator, loop-seal and internal heat exchanger. The back-pass consists of a superteater, reheater, economizer and air preheater.

The inert bed material is usually sand. However, if high mineral matter content oil shale is burned, the bed material forms ash during the fuel combustion process.

The concentration of fuel in a CFBC is very small (usually 0.5 to 2%); heat release is dissipated over the entire combustion chamber and balanced by the uniform energy absorption of the heat exchange surfaces on the furnace wall. Therefore, flue gas temperature is not dramatically changed along the furnace height, and there is no need to add tube bundles into the bed.
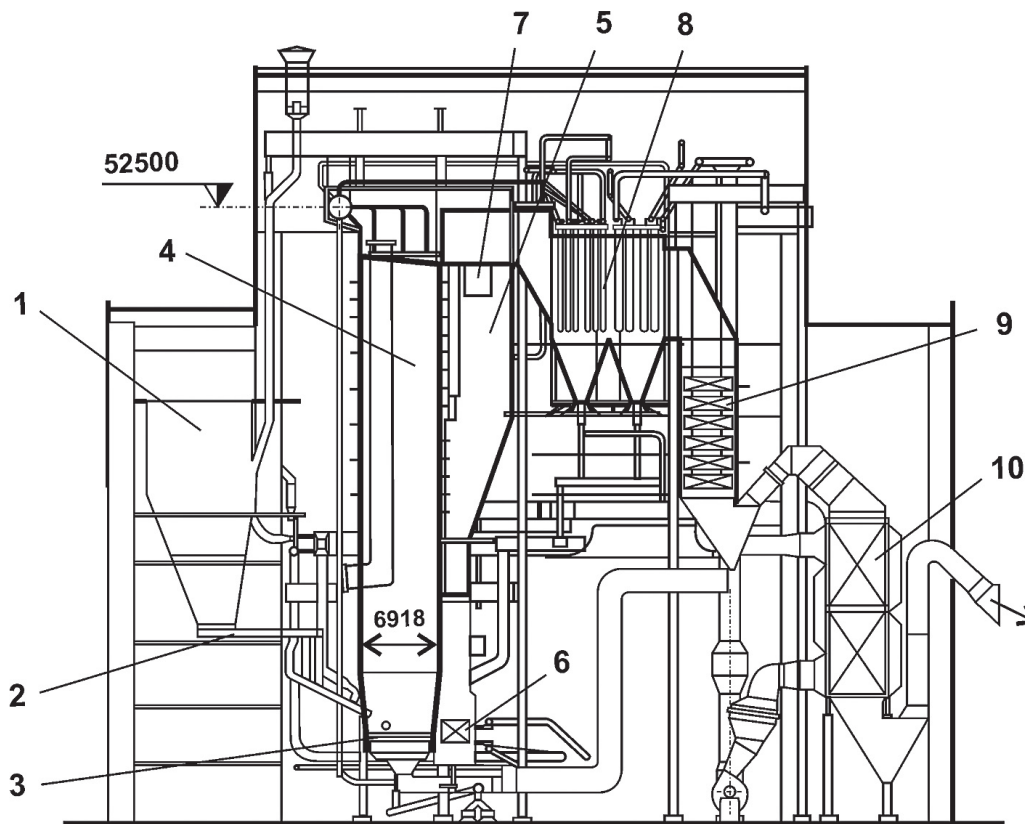

Fig. 9. Oil-shale-fired CFB boiler. 1 – raw fuel bunker, 2 – fuel feeder, 3 – grate, 4 – furnace chamber, 5 – separating chamber, 6 – fluidized bed internal heat exchanger, 7 – separator, 8 – superheater, 9 – economizer, 10 – air preheater
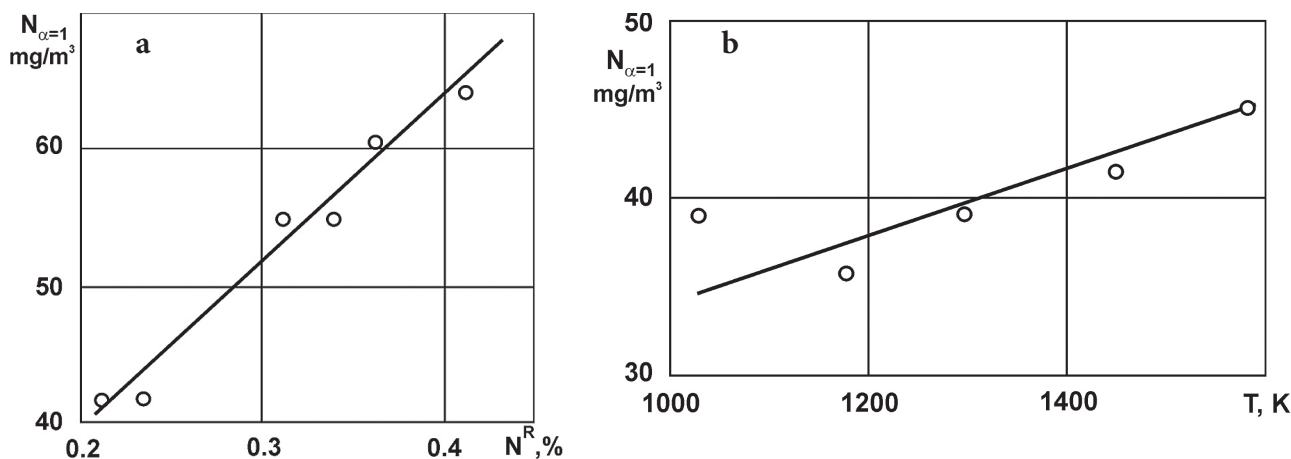
Fig. 10. Content of bound nitrogen in flue gas as a function of nitrogen content of organic matter of oil shale and flue gas temperature. Excess air factor $a = 1.25$
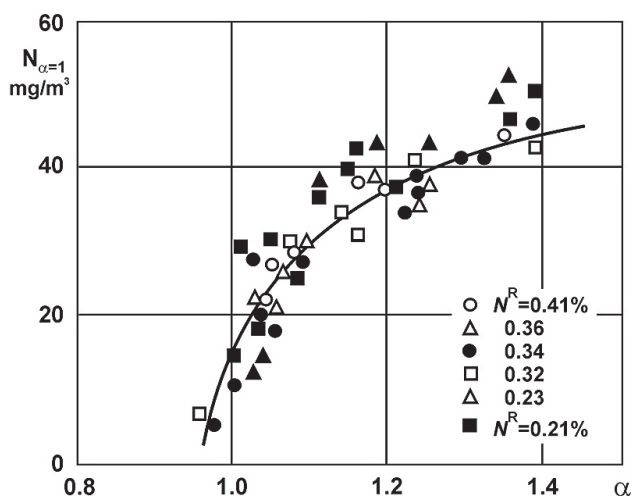

Fig. 11. Concentration of bound nitrogen in flue gas as a function of excess air factor. Results are reduced to nitrogen content of fuel N = 0.33% and temperature t = 1300 °C

7. FORMATION AND EMISSION OF AIR POLLUTANTS

The main air pollutants formed during the combustion are nitrogen oxides, sulfur dioxide, hydrogen chlorine, and solid particles. The most substantial greenhouse gas emitted is CO_2. The concentration of air pollutants in oil shale flue gas depends primarily on the combustion technology and burning regime, while the emissions of solid particles are determined by the efficiency of fly ash-capturing devices.

With regard to emissions of air pollutants, the characteristics of oil shale include the low nitrogen content of organic matter (0.3%), a large amount of organic and marcasite sulfur (1.6–1.8% in as-received fuel), a high Ca/S molar ratio (8–10), and an abundance of carbonate minerals (16–19% of mineral CO_2 content in as-received fuel).

7.1. Nitrogen oxides emission

During fuel combustion, NO_x can be formed in the following ways: in a reaction between nitrogen and oxygen from the air (thermal NO_x), in a reaction between hydrocarbon radicals and molecular nitrogen (prompt or fast NO_x), and from fuel nitrogen (fuel NO_x).

Most of NO_x forms from fuel nitrogen during both PF and FBC.

The influence of the nitrogen content of oil shale on the total concentration of nitrogen oxides (as bound in NO_x nitrogen) in flue gas is explained in Fig. 10a. In the first approximation, the NO_x concentration in flue gas as a function of the nitrogen content of oil shale organic matter can be treated as linear. By extrapolating the experimental line to the value $N = 0$, one can estimate the concentration of nitrogen oxides formed from nitrogen in the air; at 1300 °C it is approximately 12 mg/m³.

The effect of combustion temperature on the formation of NO_x from fuel nitrogen is weak. Figure 10b shows the concentration of NO_x formed from oil shale nitrogen as a function of combustion temperature. An increase in combustion temperature by 100 K increases the amount of bound nitrogen in flue gas by approximately 4 mg/m³.

The most important parameter that influences the nitrogen oxide content of flue gas is oxygen concentration (excess air factor). To determine the influence of the excess air factor on NO_x concentration formed from fuel nitrogen in flue gas, experimental results are reduced to an average nitrogen content of oil shale organic matter of 0.33% and a temperature of 1300 °C. Results obtained in this way are presented in Fig. 11.

The average concentrations of NO_x in flue gas leaving the industrial PF oil shale boiler (flue gas contained 6% of O_2) depending on the type of boiler are in the range 220 to 270 mg/m³. Measurements in an industrial oil shale CFBC boiler showed that the NO_x concentration was in the range 140 to 160 mg/m³.

During oil shale PF in industrial boilers, the portion of thermal nitrogen oxides in the total NO_x is 35 to 40% (maximum combustion temperature of 1400 to 1500 °C). Since the concentration of thermal NO_x is highly dependent on the combustion temperature, the amount of NO_x formed from air nitrogen in FBC, where the combustion temperature remains about 800 to 900 °C is very small. Therefore, during FBC nitrogen oxides form primarily from fuel nitrogen.

During oil shale FBC, the distribution of bound nitrogen between various individual oxides is different compared to PF. The N_2O emissions at PF are almost negligible because of the

high combustion temperature; however, the emissions of nitrous oxide from an industrial oil shale CFBC boiler does not exceed 10 mg/m³.

7.2. Sulfur dioxide emission

The processes occurring during oil shale combustion in a PF boiler furnace and gas passes yield sulfur compounds (mainly SO_2) in amounts much less than would be expected based on the sulfur content of oil shale. The ability of oil shale ash to bind sulfur and is the reason why sulfur mainly is removed from the boiler along with ash.

The main sulfur-binding component in oil shale is calcium. Therefore, to characterize the potential of sulfur capture, the molar ratio Ca/S is used.

Because oil shale contains alkali metals, part of the sulfur is bound with those compounds, usually in the form of sulfates. However, not all alkali metals present in fuel are converted into sulfates; the portion depends primarily on the extent of alkali metals volatilized from mineral matter during combustion.

The emissions of sulfur dioxide and the extent of volatilization of combustible sulfur during oil shale combustion are influenced by many factors. The most important ones are as follows.

Sulfur content in fuel. The effects of the content of combustible sulfur in fuel dry matter on the total sulfur amount in slag, in ash from the reversing chamber between the superheater and the economizer, and in fly ash of oil shale PF boiler are shown in Fig. 12. This result clearly indicates that the amount of sulfur in fly ash, in ash from the reversing chamber, and in slag increases with an increase in the sulfur content of oil shale.

Grinding rate of fuel. The effect of fuel particle size can be indirectly deduced from the relationship between the total sulfur content of the ash particles and the particle size distribution. The finest fractions are characterized by the highest sulfur content, whereas coarser particles contain less sulfur (Fig. 13).

Finer ash particles have a higher potential of binding sulfur oxides because of their greater specific surface area, which favours contact between sulfur oxides in flue gas and active ash components, mainly free lime. One can assert that the finer crushing of oil shale will increase the specific surface area of ash particles containing CaO and, therefore, their ability to capture sulfur oxides from flue gas.
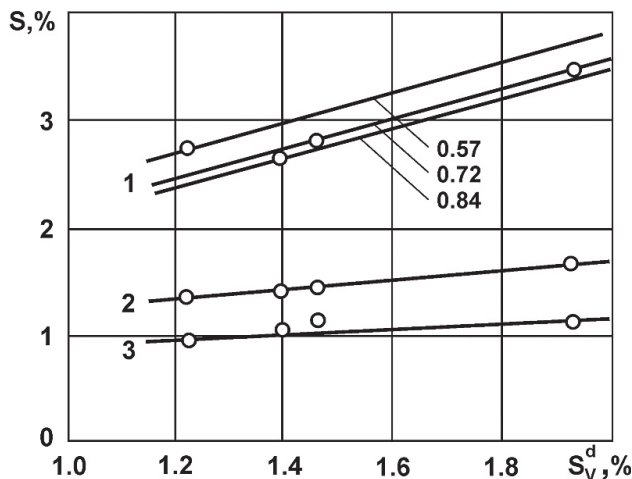

Fig. 12. Total sulfur content of ash as a function of the content of combustible sulfur in dry oil shale. 1 – fly ash, 2 – ash from reversing chamber, 3 – slag. Numbers by the curves 1 denote the relative load of boiler

Oxygen concentration in flue gas. As already mentioned, calcium oxide is the main component of oil shale ash that reacts with SO_2. The sulfation rate of CaO is proportional to $\sqrt{p_{O_2}}$, where p_{O_2} is oxygen partial pressure in flue gas (Fig. 7). Oxygen concentration in flue gas in practice is expressed by the excess air factor.

The SO_2 concentration in flue gas leaving the PF boiler (flue gas contained 6% of O_2) ranged within 1750 to 2700 mg/m³, and he extent of sulfur capture by ash k_S = 0.72 to 0.81.

The sulfur dioxide emissions in an industrial CFBC device is very low (<15 mg/m³).

The possibility of capturing sulfur dioxide by oil shale ash strongly depends on the behavior of calcium oxide in the combustion process. Important is the form of calcium in the ash.

One parameter that influences the extent of sulfur capture by ash is the molar ratio Ca/S.

In oil shale, the Ca/S ratio is 8 to 10. During the high-temperature PF of oil shale and the formation of novel minerals in the boiler, about 70 to 80% of CaO combines with the sandy-clay minerals. The calcium oxide bound within novel minerals is chemically less active toward SO_2 compared to active free CaO. Therefore, it is not always sufficient to characterize the fuel by the Ca/S ratio.
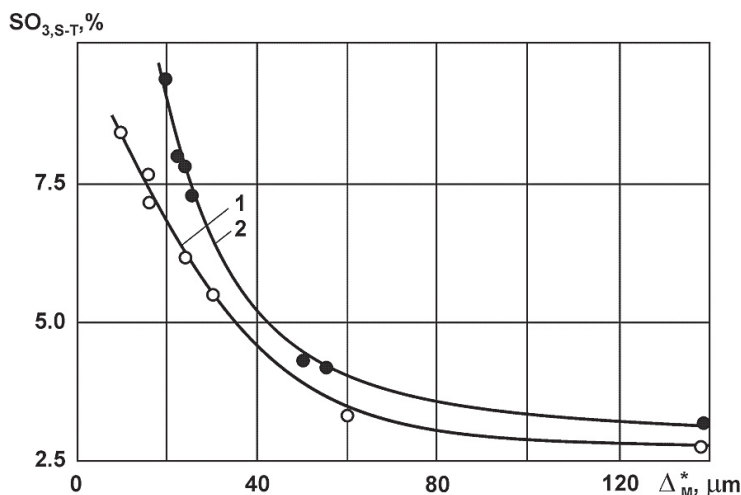

Fig. 13. Content of sulfur in ash precipitated in gas passes of an oil shale boiler as a function of median particle size. Relative boiler load: 1 – 0.94, 2 – 0.69
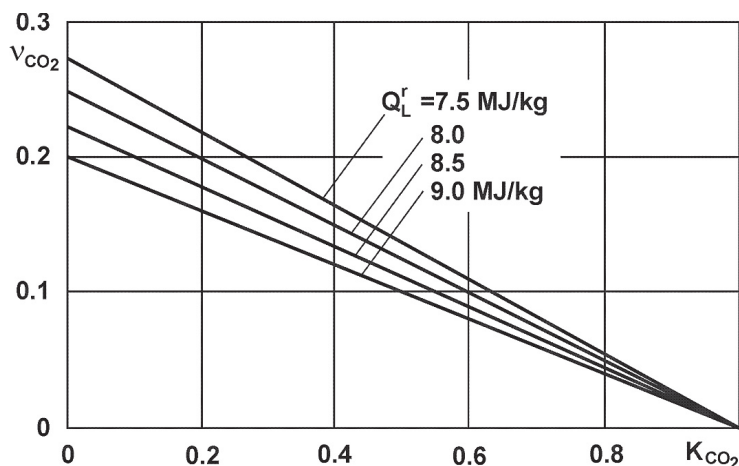
Fig. 14. Changes in carbon dioxide concentration in flue gas depending on the extent of carbonates decomposition at different heating values

The Ca/S ratio by active (free) CaO is only 1.5 to 2.5, which is not for sufficient sulfur capture. This is why, during PF of oil shale, the extent of SO_2 capture by ash is approximately 0.72 to 0.81.

During fluidized combustion, the formation of novel minerals containing calcium oxide is slow because of the low combustion temperature, and CaO released from carbonate minerals stays mainly in the active free form.

7.3. Carbon dioxide emission

Carbon dioxide belongs to the group of greenhouse gases.

Carbon dioxide is formed in combustion reactions of organic carbon and from minerals present in fuels as carbonates. Full conversion of organic carbon to CO_2 is possible only at complete combustion. The release of carbon dioxide from carbonate minerals is determined by the behavior of fuel mineral matter during the combustion process.

The combustion technology used to burn the fuel does not significantly affect the amount of CO_2 formed from organic carbon. However, the combustion technology may strongly influence the emissions of mineral CO_2. The concentration of mineral CO_2 formed from carbonate compounds is determined by the conditions of the thermal decomposition of minerals and also by the direct combination of gaseous components present in flue gas and CO_2-containing minerals.

The total volume of CO_2 released for each mass unit of oil shale depends on the amount of organic matter, the content of mineral CO_2, and the decomposition degree of carbonates. The influence of the degree of carbonate decomposition on CO_2 concentration in flue gas can be expressed by the following formula:

$$\nu_{CO_2} = 1 - \frac{(V_{CO_2})_{k_{CO_2}}}{(V_{CO_2})_{k_{CO_2}=1}},$$

where $(V_{CO_2})_{k_{CO_2}=1}$ is the highest possible concentration of CO_2 in flue gas, which corresponds to complete decomposition of carbonate minerals ($k_{CO_2} = 1$), m^3/kg, and $(V_{CO_2})_{k_{CO_2}}$ is CO_2 concentration in flue gas, which corresponds to the arbitrary decomposition degree of carbonates, m^3/kg.

Based on the relationship between the composition of oil shale and its heating value, Fig. 14 presents the relationship between the factor ν_{CO_2} and the extent of carbonate decomposition

at four different lower heating values. If carbonate minerals do not decompose ($k_{CO_2} = 0$), CO_2 emissions from oil shale, whose heating value is 8.5 MJ/kg, are by about 22% lower compared to the conditions when $k_{CO_2} = 1$.

CONCLUSIONS

Oil shale is a fuel with a very complicate composition of organic and mineral matter.

Oil shale can be successfully utilized in power plants. It needs for this purpose specific firing equipment – boilers.

The scientific and practical results of studying oil shale combustion have a much wider value and applications for firing other kinds of fuels with a complicated composition of organic and mineral matter.

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Arvo Ots

ESTIJOS SKALŪNŲ SAVYBĖS IR JŲ PANAUDOJIMAS ELEKTRINĖSE

S a n t r a u k a

Skalūnas yra nuosėdinė uoliena, sudaryta iš organinės medžiagos, kuri priklauso sapropelių kuro grupei. Estijoje yra dideli skalūnų ištekliai. Ji yra vienintelė šalis pasaulyje, naudojanti skalūnų kurą elektrinėms, kurios užtikrina elektros tiekimą saviesiems vartotojams ir gali eksportuoti elektrą į kaimynines šalis. Estijos skalūnai yra karbonatinės klasės kuras, kurį sudaro sudėtingos struktūros organinės ir mineralinės medžiagos.

Sudėtinga kuro sudėtis sukelia daug problemų, kurios gali turėti įtakos elektrinių įrangos darbui ir patikimumui. Straipsnyje nagrinėjamos skalūnų kaip energetinio kuro savybės ir jo panaudojimo problemos.

Raktažodžiai: organinė ir mineralinė medžiaga, degimo charakteristikos, dulkinio kuro deginimas, degimas verdančiame sluoksnyje, aplinkosauga

Арво Отс

СВОЙСТВА ЭСТОНСКИХ СЛАНЦЕВ И ИХ ИСПОЛЬЗОВАНИЕ НА ЭЛЕКТРОСТАНЦИЯХ

Р е з ю м е
Сланцы являются осадочным образованием из органического вещества. Они относятся к группе сапропельного топлива. Эстония располагает большими ресурсами сланцев. Она является единственной страной в мире, использующей сланцы в качестве топлива для электростанций, которые надежно обеспечивают электроэнергией собственных энергопотребителей и покрывает нужды экспорта в соседние страны.

Эстонские сланцы являются топливом карбонатного класса (типа), состоящего из сложных органических и минеральных веществ. Сложная структура и состав данного топлива вызывают много проблем, влияющих на функционирование и работу оборудования электростанций и их надежность. В статье рассматриваются свойства сланцев как энергетического топлива и проблемы его использования.

Ключевые слова: органическое и минеральное вещество, характеристики горения, пылевое сжигание, горение в кипящем слое, защита окружающей среды