

<https://doi.org/10.3176/oil.1992.1.09>

A. OTS

FORMATION OF AIR-POLLUTING COMPOUNDS WHILE BURNING OIL SHALE

Introduction

In the Estonian Republic there are some large thermal power plants burning oil shale. The output of electrical power generated in oil shale power plants is about 16.5–17 TWh per year and they consume for this about 22.2 Mt oil shale. The oil shale used in power engineering belongs to the low-grade fuel group and is characterized by high mineral matter content. One of the peculiarities of oil shale is the high calcium oxide and alkali metal content in ash and moderate quantity of nitrogen in the organic part. The total sulphur content in dry mass is 1.5–1.6 %. The nitrogen oxides, sulphur oxides, cancerogeneous polycyclic aromatic hydrocarbons (PAH) formation processes and fly ash composition while burning Estonian oil shale are discussed in this paper.

Utilization of Estonian Oil Shale at the Power Plants

Deposits of oil shale in Estonia are known since the 18th century. The oil shale of Estonian deposits has been in focus since 1916, when their commercial extraction commenced. A wide use of Estonian oil shale in power engineering dates back to 1924 when Tallinn Thermal Power Plant was rearranged to oil shale and the capacity of which reached 22 MW_e by 1933. The most typical for that time were steam boilers with grate furnaces.

The first pulverized oil shale boilers with hammermill furnaces were the modernized coal boilers with the steam output of 14–18 kg/s and steam parameters of 3.5–4 MPa and 420–450 °C.

A new period in the development of oil shale power plants has begun in 1959–1960 when the first power units were applied at Baltic Thermal Power Plant. The project capacity of the plant was 1624 MW_e. In 1973, the Estonian Thermal Power Plant with the capacity of 1610 MW_e was put into operation.

At the Baltic Thermal Power Plant there are eight turbines, each with the capacity of 100 MW_e, and two extractional turbines of 12 MW_e, which receive steam from 18 boilers with steam output of 61 kg/s and steam parameters 9.8 MPa and 515 °C. Four power units, 200 MW_e each, have two boilers with the steam output of 89 kg/s, and parameters of superheated (reheated) steam 13.8/2.2 MPa and 520/530 °C.

Turbines with the capacity of 200 MW_e have been installed at the Estonian Thermal Power Plant, as well as boilers with the steam output of 89 kg/s, the pressure 13.8/2.2 MPa and temperature 535/535 °C.

Figure 1 illustrates a technological scheme of oil shale power plant and Fig. 2 shows the amount of the oil shale consumed to generate electric power, the output of electric power and variation of technical character-

istics of oil shale according to the years. Maximum output of electric power generated by power plants burning oil shale was achieved in 1979 and was equal to 19.1 TWh per year. In the following years the output of electric power somewhat decreased.

Figure 3 shows the material balance of the pulverized oil shale fired power plants which used 22 Mt oil shale per year (on 1990 level).

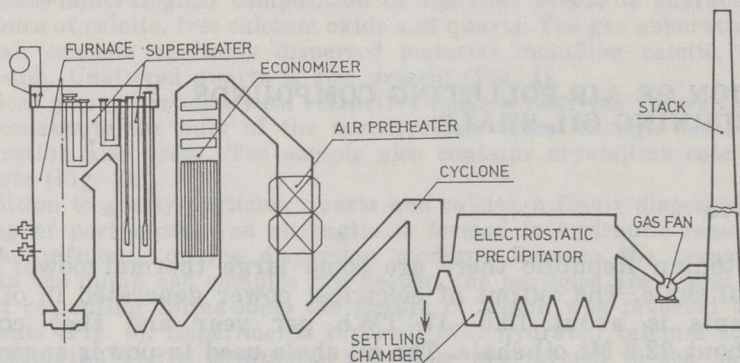


Fig. 1. Technological scheme of oil shale power plant

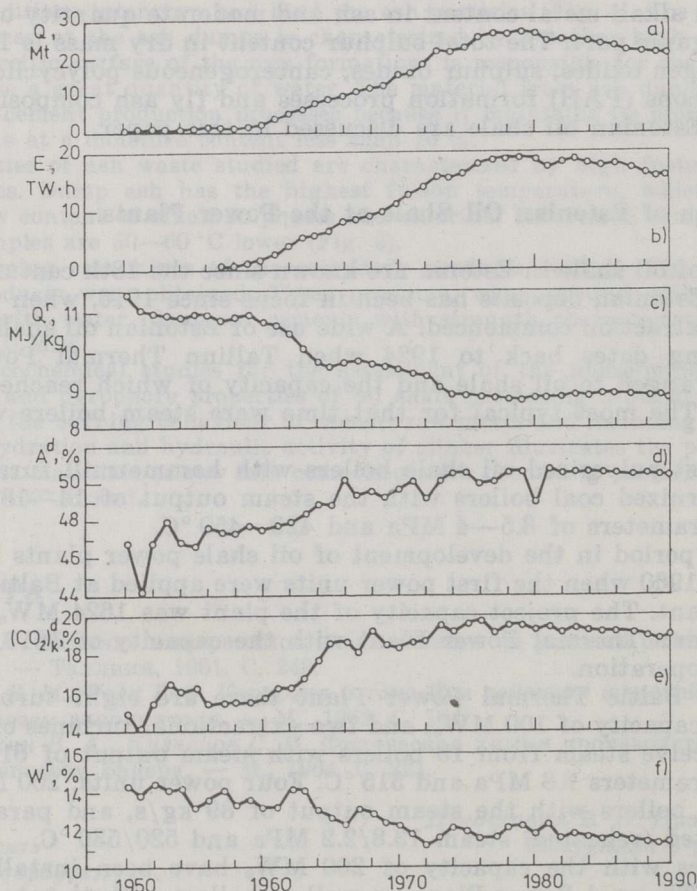


Fig. 2. Utilization of Estonian oil shale in power plants. A — amount of oil shale consumed to generate electric power; B — electric power output; C — net heating value; D — ash content; E — carbonate dioxide content; F — moisture content

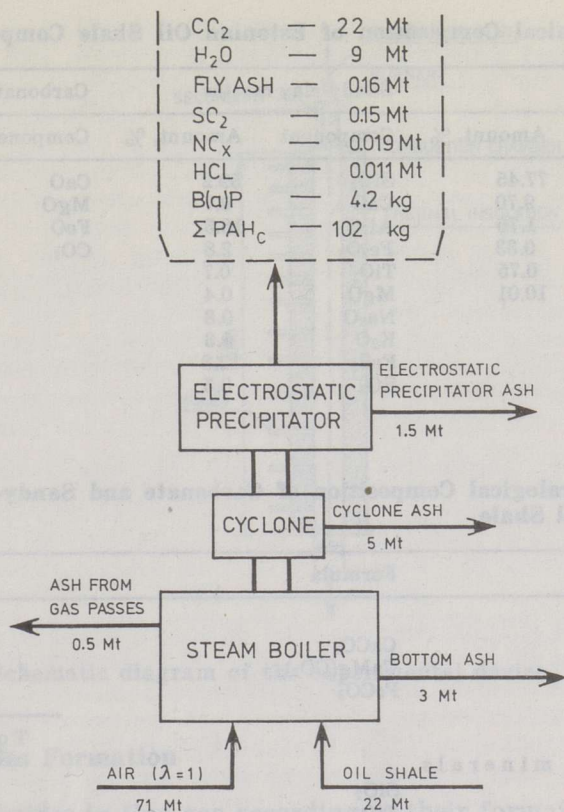


Fig. 3. Material balance of the oil shale power plants consuming 22 Mt oil shale per year

Characteristics of Estonian Oil Shale

The carbonate oil shale deposits are located in North-East part of Estonia. The Estonian oil shale is characterized as a solid fuel with high content of mineral matter (60–75%), moderate moisture content (11–13%) and low heating value (net heating value of moist fuel 8.5–9 MJ/kg).

The oil shale deposits lie in layers alternately with mineral seams. The main constituent in a mineral matter seam is limestone. In shale layers organic matter is mainly joined with sandy-clay minerals. About 50% of oil shale is mined underground and the remainder is quarried in open cuts.

Oil shale dry mass includes the following three constituents: organic, sandy-clay and carbonate. The chemical composition of separate parts of oil shale is given in Table 1 and the mineralogical composition of carbonate and sandy-clay parts is shown in Table 2.

A high content of hydrogen and oxygen and a low quantity of nitrogen are typical for the organic matter of oil shale. The C/H ratio is about 8 and is close to that for liquid fuels. The volatile matter content in organic part of oil shale is 85–90%. The chlorine combined with the organic matter of Estonian oil shale is one of its peculiar features.

The basic mineral components of the carbonate part are calcite and dolomite. The main minerals of the sandy-clay part are: quartz, orthoclase, hydromica and marcasite.

Table 1. Chemical Composition of Estonian Oil Shale Components

Organic matter		Sandy-clay matter		Carbonate matter	
Component	Amount, %	Component	Amount, %	Component	Amount, %
C	77.45	SiO ₂	59.2	CaO	53.5
H	9.70	CaO	0.7	MgO	2.0
S	1.76	Al ₂ O ₃	16.3	FeO	0.2
N	0.33	Fe ₂ O ₃	2.8	CO ₂	44.3
Cl	0.75	TiO ₂	0.7		
O	10.01	MgO	0.4		
		Na ₂ O	0.8		
		K ₂ O	6.3		
		FeS ₂	12.3		
		SO ₃	0.5		

Table 2. Mineralogical Composition of Carbonate and Sandy-Clay Parts of Estonian Oil Shale

Mineral	Formula	Amount, %
Carbonates		
Calcite	CaCO ₃	90.5
Dolomite	CaMg(CO ₃) ₂	9.2
Siderite	FeCO ₃	0.3
		Total 100.0
Sandy-clay minerals		
Quartz	SiO ₂	23.2
Rutile	TiO ₂	0.7
Orthoclase	K ₂ O · Al ₂ O ₃ · 6SiO ₂	28.1
Albite	Na ₂ O · Al ₂ O ₃ · 6SiO ₂	5.8
Anorthite	CaO · Al ₂ O ₃ · 2SiO ₂	1.4
Hydromuscovite	[K _{1-x} (H ₂ O) · Al ₂ Si ₃ O ₁₀ (OH) ₂] ₂	23.0
Amphibol	[NaCa ₂ Mg ₄ (Fe,Al)Si ₈ O ₂₂ (OH) ₂] ₂	2.0
Marcasite	FeS ₂	12.0
Limonite	Fe ₂ O ₃ · H ₂ O	2.8
Gypsum	CaSO ₄ · 2H ₂ O	1.0
		Total 100.0

Experimental

The experiments on the forming of nitrogen oxides (NO_x) while burning pulverized oil shale were carried out in a device whose diagram is shown in Fig. 4. The main part of the device is the vertical combustion chamber with diameter 56 mm and length 1 m, which have external heating. The combustion chamber has holes for taking gas samples and temperature measurement. At the top of the combustion chamber there is a burner for introducing pulverized fuel with air. The parameters of the test device are: maximum flue gas temperature 1350 °C, fuel capacity 100—500 g/h, velocity of air's leaving the burner 5—15 m/s, secondary-air temperature 500 °C.

Investigations in oil shale thermal power plants were carried out in the steam boilers with capacities of 61 and 89 kg/s. In these tests NO_x, SO₂, HCl, fly ash and PAH concentrations were determined in flue gas as well as chemical composition of fly ash leaving electrostatic precipitator.

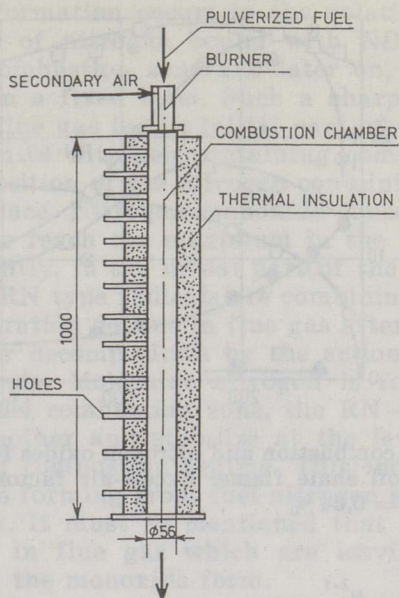


Fig. 4. Schematic diagram of the experimental device

Nitrogen Oxides Formation

The nitrogen oxides in flue gas according to their formation are divided into three groups: thermal, fast-forming and fuel ones.

Thermal NO_x is formed from atmospheric nitrogen as a result of reaction with oxygen. Thermal- NO_x -formation theory has been worked out by Zeldovich. The thermal NO_x concentration in flue gas is considerable if the gas temperature is higher than 1500–1550 °C.

The Fenimor's fast-forming-nitrogen-oxides forming mechanism is well known. This mechanism is based on the hydrocarbons radicals reactions with molecular nitrogen. The concentration of fast-forming NO_x in flue gas can be considerable by burning solid fuels with high content of volatile matter, particularly in oxygen-shortage zones.

The fuel NO_x is formed from nitrogen-containing organic compounds in reactions with oxygen.

The fuel NO_x concentration in flue gas depends on the type of nitrogen-containing molecules. For instance, if nitrogen-containing molecules also have oxygen then the NO_x concentration in gas is higher as compared with the nitrogen oxide concentration formed from molecules without oxygen. Generally the fuel NO_x concentration increases with increasing of the total nitrogen content in fuel and especially with the growing of oxygen concentration in flame. The fuel NO_x concentration does not depend much on gas temperature.

The main parameters characterizing the combustion of pulverized oil shale along the length of the combustion chamber in laboratory devices (Fig. 4) are given in Fig. 5. According to the combustion regime (temperature and oxygen concentration) the volatile matter combustion takes place along the length of 250–300 mm.

Figure 5 also illustrates the nitrogen oxides formation dynamics along the flame length. In the vertical axis N the amount of nitrogen bound with oxygen in a normal cubic metre of flue gas is shown. The most

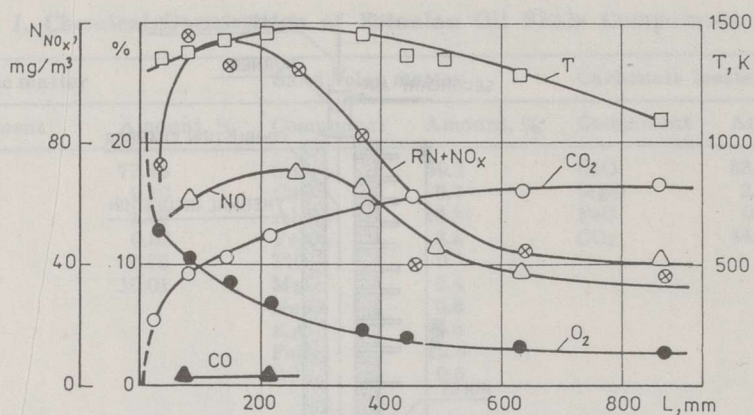


Fig. 5. The combustion and nitrogen oxides formation characteristics along the oil shale flame. Excess-air factor 1.21, nitrogen content in fuel $N^F = 0.34\%$

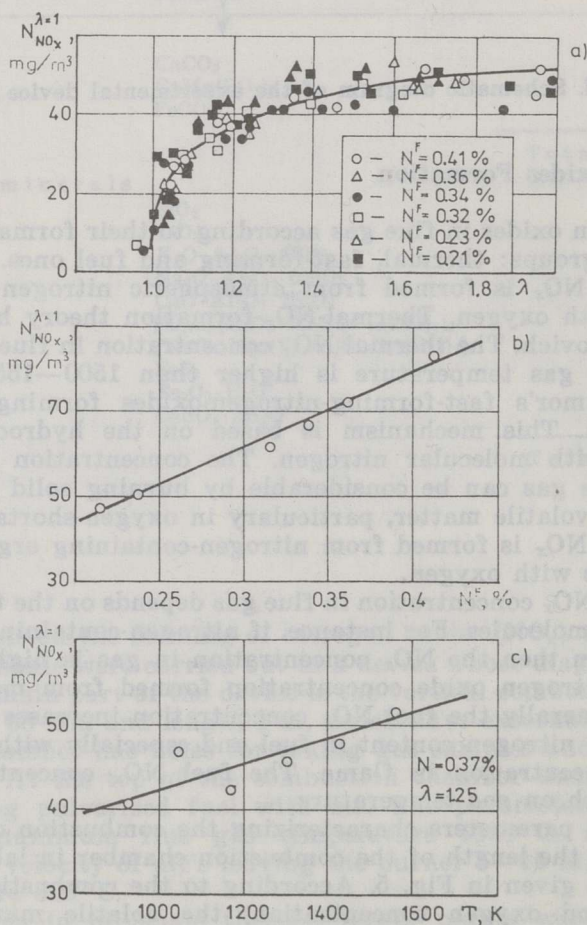


Fig. 6. The influence of the excess-air factor (A), nitrogen content in organic matter (B) and temperature (C) on nitrogen oxides concentration while burning oil shale

intensive nitrogen oxides formation occurs in the volatile matter combustion zone. The amount of nitrogen bound with NO_x and radicals rapidly increases in this combustion zone and later on, after reaching the maximum, stabilizes on a fixed level. Such a sharp rise of bound nitrogen concentration in flue gas in the initial part of flame refers to the intensive decomposition of nitrogen containing compounds. Simultaneously with the decomposition of the nitrogen containing compounds, the NO formation takes place. Nitrogen monoxide concentration lines, like $\text{RN} + \text{NO}_x$ curves, also reach the maximum in the volatile matter combustion zone. Consequently, in the initial part of the flame, the NO emission takes place when RN type radicals are combining with oxygen. Nitrogen monoxide concentration decline in flue gas after the maximum can be explained with their decomposition by the action of radicals of unstable nitrogen compounds. Molecular nitrogen is formed in these reactions. At the end of fuel combustion zone, the $\text{RN} + \text{NO}_x$ and NO curves approach to one another and stabilize at the level, defined by the parameters of the fuel combustion regime. This indicates the termination of nitrogen oxides forming from fuel nitrogen and the absence of radicals RN in flue gas. It must be mentioned that by burning oil shale the nitrogen oxides in flue gas which are leaving combustion chamber exist generally in the monoxide form.

The main parameters affecting NO_x concentration in flue gas are the nitrogen content in the fuel and the excess-air factor. To a certain extent, nitrogen oxides formation depends on burning temperature as well. The influence of the excess-air factor on NO_x concentration in flue gas is shown in Fig. 6A. In the vertical axis of this Figure there is the concentration of nitrogen bound with oxygen in flue gas on the normal conditions by the excess-air factor 1. These results have been obtained in a laboratory device using probes of oil shale with different nitrogen content (0.21—0.41 % in organic matter). Taking into account the linear dependence of nitrogen oxides concentration in flue gas on nitrogen content in fuel, the NO_x has been reduced to one and the same nitrogen amount in the organic matter of fuel — 0.3 %. Up to excess-air factor 1.15—1.20 the nitrogen concentration combined with oxygen in flue gas sharply increases and afterwards the oxygen concentration influence on NO_x emission decreases.

Depending on the excess-air factor (in the range of 1.1—1.4), 12—24 % of fuel nitrogen is converted into oxides. The NO_x concentration in flue gas also depends on the quantity of nitrogen in the organic part of fuel. It can be seen in Fig. 6B, where the dependence between the amount of nitrogen bound with oxygen in flue gas and nitrogen content in oil shale organic matter is given. The effect of the flue gas temperature on the concentration of fuel NO_x is relatively negligible. Figure 6C shows the dependence of nitrogen bound with oxygen on maximum gas temperature in laboratory combustion chamber.

One essential factor that affects NO_x concentration in flue gas is sulphur. The effect of sulphur content in the fuel on NO_x formation was investigated by burning liquid fuel. Sulphur in the fuel reduces NO_x concentration in flue gas. This can be explained by the fact that sulphur is more active to nitrogen oxides as compared with atomic oxygen which is the base of SO_3 formation. It is shown by SO_3 concentration measurements in flue gas.

Figure 7 presents a diagram, which shows the effect of sulphur content in the fuel on NO_x concentration in flue gas when burning liquid fuel. Factor k in the Figure expresses the ratio of NO_x concentration in flue gas to nitrogen oxides concentration when burning sulphur-free

oil. It becomes evident that due to the effect of sulphur, NO_x concentration in the flue gas can be noticeably reduced. Since this kind of investigations on burning solid fuel are missing, we can only assume that the effect of sulphur on the NO_x concentration in flue gas when burning liquid fuel is in principle analogous. The use of artificial mixtures, in order to get different N/S ratios, is considered to be one of such possibilities.

Investigations like these were carried out using the laboratory combustion device. The mixture of pyrite FeS_2 and carbamide NH_2CONH_2 was used in order to achieve different N/S ratios. The carbamide easily decomposes giving off nitrogen-containing hydrogen radicals. The results show that when the S/N ratio increases from 0 to 35, the nitrogen oxides concentration in flue gas decreases about 70–80 %.

When burning Estonian oil shale in Thermal Power Plants boilers, due to relatively low temperature in the furnace (maximum flame temperature is in range of 1400–1500 °C), the thermal NO_x concentration in flue gas leaving the boiler as NO_2 is not more than 50–70 mg per normal cubic metre by oxygen concentration 7 %. The total NO_x concentration depends on the NO_2 formation which is determined by the combustion conditions and the nitrogen content in fuel is in the range of 150–200 mg per normal cubic metre by oxygen concentration 7 %. The relatively low NO_x concentration in oil shale flue gas is caused by the low nitrogen content in the organic part of oil shale as well as by the influence of sulphur on NO_x formation.

Formation of Sulphur Oxides

The sulphur oxides concentration (SO_x) in flue gas while burning solid fuels does not depend only on the sulphur content of fuel but it depends on the composition of ash as well because some component of ash can bind sulphur. Due to these sulphation reactions, SO_x concentration in flue gas is lower as compared with the conditions when all sulphur goes into combustion products.

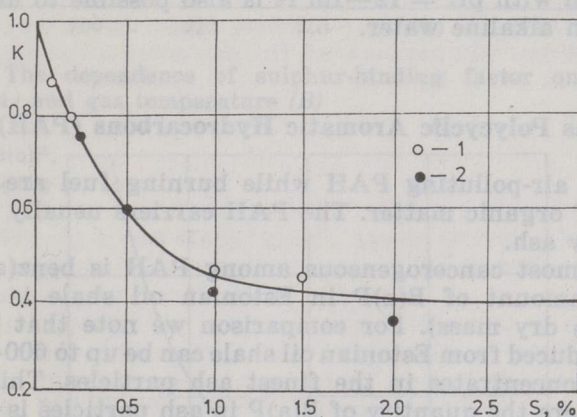
The sulphur-binding factor of ash (the relative amount of total sulphur in fuel combined with ash) depends on some parameters, the most important of them being ash chemical and mineralogical composition. If the fuel ash has acidic composition and contains mainly such components as SiO_2 , Al_2O_3 , Fe_2O_3 , etc. with a moderate amount of basic components such as CaO , MgO , Na_2O , K_2O , etc. then it is not capable to bind sulphur oxides to a considerable amount and the most part of sulphur goes into flue gas as SO_2 . While burning solid fuel with acidic ash the sulphur binding factor usually does not exceed 0.05.

While burning solid fuels with basic ash, a great amount of ash component is capable of binding sulphur. For instance, the sulphur-binding factor of Estonian oil shale ash can be up to 0.8–0.85. In this case the main sulphur-binding component is calcium oxide, and to some extent also magnesium oxide and alkali metals.

The starting materials of calcium oxide in oil shale ash are calcite and dolomite (Table 2). At high-temperature medium in the furnace, calcite and dolomite decompose rapidly giving off calcium oxide and carbon dioxide. One part of the formed calcium oxide combines with sandy-clay minerals and the other remains in a free form. The free calcium oxide is the most active sulphur-binding component in oil shale ash. Secondary ash minerals containing calcium oxides (such as mullite, belite and others) may combine with sulphur oxide too, but the

Table 3. Estonian Oil Shale Fly Ash Composition after Electrostatical Precipitator (after Pets et al.)

Macrocomponents, %		Microcomponents, g/t					
		Easily volatilizing		Moderately volatilizing		Hardly volatilizing	
CaO	30.45	Cl	7600	Sr	259	Zn	120
Al ₂ O ₃	8.82	Br	685	Ba	256	Cr	85.83
K ₂ O	6.84	Zn	183.6	Ni	53	V	39
Fe ₂ O ₃	4.20	Rb	167.75	Cu	33	Mo	12.3
MgO	1.96	Pb	163.5	Ga	21	Nb	11
TiO ₂	0.48	As	45.13	Y	17	Th	10.6
Na ₂ O	0.17	Cs	10.8	Sc	8.3	U	5.8
MnO	0.04	Sb	1.63	Co	6.4	Hf	3.6
		Se	0.6	Ag	0.5	Ta	1.9
		Hg	0.1	Au	0.019	Ir	0.002

Fig. 7. The effect of sulphur on nitrogen oxides concentration in flue gas while burning liquid fuel. 1 — fuel NO_x; 2 — thermal NO_x

intensity of these reactions is very low as compared with the sulphating of free calcium oxide.

The sulphating reaction with ash (mainly with calcium oxide) depends on the oxygen concentration (excess-air factor) and the flue gas temperature in furnace and gas passes of the boiler. Figure 8 shows the effect of excess-air factor and of flue gas temperature in oil shale boiler gas passes on sulphur-binding factor with ash. The sulphur-binding factor increases with increasing oxygen concentration (or with excess-air factor) in flue gas. Temperature also plays an essential role in binding reactions of sulphur oxides with calcium oxide. The sulphur-binding factor is maximal within the range of 750–800 °C in convective gas passes.

The sulphur-binding-with-ash factor in real condition is not higher than 0.88. This maximum value is determined by chemical active surface of ash particles that makes reactions with sulphur possible. It means that the fractional composition of ash particles also affects the activity

of sulphur oxides binding with ash. The smallest particles of oil shale ash always contain more sulphur in a sulphate form than the biggest ones.

In spite of the high sulphur-binding effect of ash, it does not guarantee a low enough sulphur dioxide concentration in oil shale flue gas yet. The sulphur dioxide concentration in oil shale flue gas leaving boiler depends on the regime (excess-air factor in burners, boiler load, etc.) and is in the range of 1100—1800 mg per normal cubic metre of flue gas by oxygen concentration 7 %.

While burning acidic ash fuels in order to desulphurize the flue gas, there are possibilities to use different units. Despite the difference in these units to flue gas desulphurization, supplied lime is used almost without exception. When burning fuels with a high calcium and alkali metal content, for instance Estonian oil shale, it is possible to use the fuel ash itself for desulphurization of flue gas. There we have got several possibilities. One alternative is cleaning the flue gas from sulphur oxides in a scrubber using clarified alkaline water from a hydraulic ash removal system with $\text{pH} = 12\text{--}13$. It is also possible to use ash-soaking basin to obtain alkaline water.

Cancerogeneous Polycyclic Aromatic Hydrocarbons (PAH)

The source of air-polluting PAH while burning fuel are the processes of pyrolysis of organic matter. The PAH carriers usually are the finest particles of fly ash.

One of the most cancerogeneous among PAH is benz(a)pyrin $\text{C}_{20}\text{H}_{12}$ (B(a)P). The amount of B(a)P in Estonian oil shale is not great — 4.31 $\mu\text{g}/\text{kg}$ (in dry mass). For comparison we note that B(a)P content in shale oil produced from Estonian oil shale can be up to 600—1.500 $\mu\text{g}/\text{kg}$.

The B(a)P concentrates in the finest ash particles. This can be seen in Fig. 9A, where the quantity of B(a)P in ash particles is given depending on their diameter. These results were established according to the analysis of ash samples from the different fields of electrostatic precipitator. The finest fly ash particles are good condensing centres for B(a)P vapour. The B(a)P desublimation temperature is about 180 °C.

B(a)P quantity is the greatest in the ash leaving the electrostatic precipitator with the flue gas (15—22 $\mu\text{g}/\text{kg}$). Thus it is approximately 30—40 times greater than B(a)P amount of finest particles separated in the fourth field of electrostatic precipitator. The total amount of B(a)P in the fly ash leaving the electrostatic precipitator together with flue gas is not more than 50—10 % of total B(a)P quantity in oil shale itself.

The main parameter that enables B(a)P to concentrate in flue gas is the oxygen concentration. This can be seen in Fig. 9B, where the dependence of B(a)P concentration in flue gas after electrostatic precipitator on excess-air factor in burners is given. The B(a)P concentration has been reduced to flue gas volume by the excess air factor 1. It becomes evident that when the oxygen concentration in burners increases, the B(a)P concentration is diminishing. It is connected with oxygen concentration influence on B(a)P which is responsible for organic compound oxidation reactions intensity.

Besides B(a)P, oil shale flue gas contains other cancerogenic PAH. The total PAH concentration in flue gas is in region $\Sigma\text{PAH} = 250\text{--}500 \mu\text{g}/100 \text{ m}^3$ and the total cancerogeneous PAH concentration is $\Sigma\text{PAH}_c = 65\text{--}170 \mu\text{g}/100 \text{ m}^3$ (in 100 normal cubic metre of flue gas

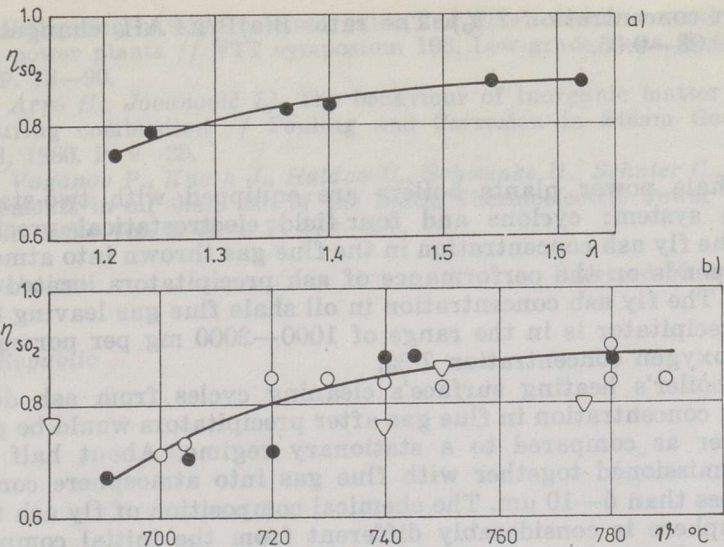


Fig. 8. The dependence of sulphur-binding factor on excess-air factor (A) and gas temperature (B)

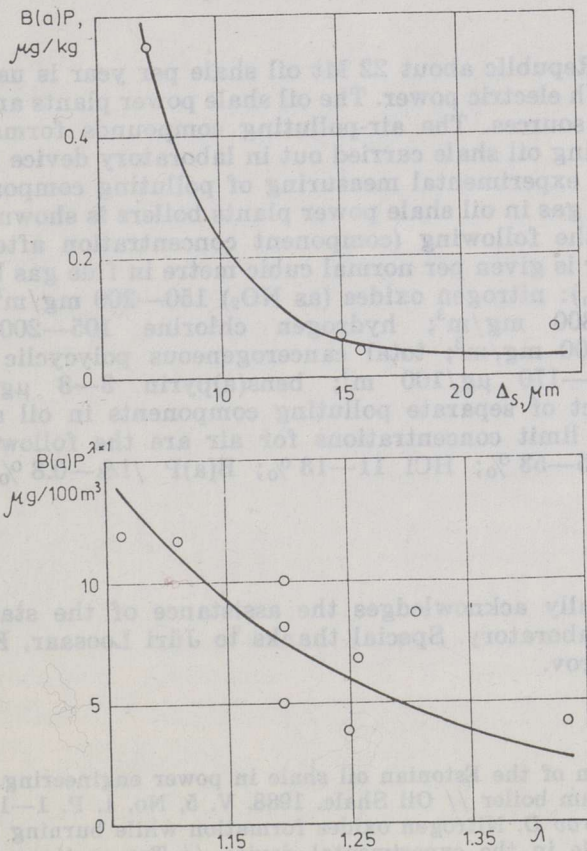


Fig. 9. The quantity of benz(a)pyrin depending on fly ash particles diameter (A) and the benz(a)pyrin concentration in flue gas after electrostatic precipitator depending on excess air factor (B)

by oxygen concentration 7 %). The ratio $B(a)P/\Sigma PAH_c$ changes in the range of 0.03—0.05.

Fly Ash

The oil shale power plants boilers are equipped with two-stage ash separation system: cyclone and four-field electrostatic precipitator (Fig. 1). The fly ash concentration in the flue gas thrown into atmosphere mainly depends on the performance of ash precipitators located behind the boiler. The fly ash concentration in oil shale flue gas leaving electrostatic precipitator is in the range of 1000—2000 mg per normal cubic metre by oxygen concentration 7 %.

In the boiler's heating surface's cleaning cycles from ash deposits, the fly ash concentration in flue gas after precipitators would be periodically higher as compared to a stationary regime. About half of the particles emitted together with flue gas into atmosphere consist of particles less than 5—10 μm . The chemical composition of fly ash thrown into atmosphere is considerably different from the initial composition of ash. The chemical composition of fly ash after electrostatic precipitator is given in Table 3.

Conclusions

In the Estonian Republic about 22 Mt oil shale per year is used to produce 16.5—17 TWh electric power. The oil shale power plants are environmental-polluting sources. The air-polluting compounds formation processes while burning oil shale carried out in laboratory device are shown in Fig. 4 and the experimental measuring of polluting components concentration in flue gas in oil shale power plants boilers is shown in Fig. 1. The results are the following (component concentration after electrostatic precipitator is given per normal cubic metre in flue gas by oxygen concentration 7 %): nitrogen oxides (as NO_2) 150—200 mg/m^3 ; sulphur dioxide 1100—1800 mg/m^3 ; hydrogen chloride 105—200 mg/m^3 ; fly ash 1000—2000 mg/m^3 ; total cancerogeneous polycyclic aromatic hydrocarbons 65—170 $\mu\text{g}/100 \text{ m}^3$; ben(a)pyrin 3—8 $\mu\text{g}/100 \text{ m}^3$. The relative effect of separate polluting components in oil shale flue gas to permitted limit concentrations for air are the following: NO_x 32—42 %; SO_2 45—53 %; HCl 11—13 %; $B(a)P$ 1—0.8 %.

Acknowledgments

The author gratefully acknowledges the assistance of the staff of the Thermal Power Laboratory. Special thanks to Jüri Loosaar, Karl Saar and Dimitri Yegorov.

REFERENCE

1. Ots A. Utilization of the Estonian oil shale in power engineering. Problems concerning a steam boiler // *Oil Shale*. 1988. V. 5, No. 1. P. 1—14.
2. Loosaar J., Yegorov D. Nitrogen oxides formation while burning pulverized Estonian oil shale in the experimental device // *Transactions of Tallinn Technical University*, 1985. No. 600. P. 33—39.
3. Yegorov D., Loosaar J. Emission of toxic compounds while burning pulverized Estonian oil shale and argillite in the experimental device // *Ibid*. 1984. No. 579. P. 3—15.

4. Ots A. Utilization of high calcium oxide and alkali metal content fuels at thermal power plants // VTT symposium 108. Low-grade fuels. Espoo, 1990. Vol. 2. P. 73—90.
5. Ots A., Arro H., Jovanovič Lj. The behaviour of inorganic matter of solid fuels during combustion // Fouling and Corrosion in Steam Generators. Beograd, 1980. P. 9—28.
6. Pets L., Vaganov P., Knoth J., Haldna Ü., Schwenke H., Schnier C., Juga R. Microelements in oil shale ash of the Baltic Thermoelectric Power Plant // Oil Shale. 1985. Vol. 2, № 4. P. 379—390.

Tallinn Technical
University
Tallinn,
Estonian Republic

Received 19 April 1991