

FORMATION AND EMISSION OF COMPOUNDS AFFECTING ENVIRONMENT

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This paper gives an overview of the formation of nitrogen oxides, sulfur oxides, carbon monoxide, carbon dioxide and other harmful components emitted by oil shale-fired plants. Formation of these compounds and their concentration in flue gas are determined mainly by the properties of fuel and combustion technology. Some information is given on oil shale pulverized firing and combustion in circulating fluidized bed.

Introduction

At burning of fuel formation and concentration of compounds in flue gas affecting the environment is mainly determined by properties of fuel and combustion technology, however, in the case of particulate emissions, also by the efficiency of fly ash precipitators. Design characteristics of a combustion device and its operating conditions are also important.

In this paper the formation of harmful compounds released to the environment during combustion of oil shale – nitrogen oxides, sulfur oxides, carbon monoxide, hydrogen chloride, carbon dioxide, polycyclic aromatic hydrocarbons and light-volatile heavy metals – is examined. In addition, factors influencing the formation of those compounds during oil shale burning are studied. Some information is given about the emissions of harmful compounds formed by burning of oil shale applying pulverized firing (PF) and fluidized bed combustion (FBC) technologies.

The following characteristics of the composition of oil shale have the strongest influence on formation and emission of compounds affecting the environment.

Organic Matter Poor in Nitrogen (average nitrogen content is 0.33%). Nitrogen oxides form during combustion of a fuel from both nitrogen in the air and nitrogen present in organic matter. At both PF and FBC of oil shale, the main part of nitrogen oxides forms from nitrogen present in the fuel. As the concentration of nitrogen oxides in flue gas is proportional to nitrogen

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content of fuel, the amount of nitrogen oxides in oil shale flue gas cannot be high. Their formation is not much affected by temperature; oxygen partial pressure in the initial combustion zone is of a much greater importance. Concentration of nitrogen oxides in flue gas is affected also by sulfur compounds.

High Molar Ratio of Ca/S (usually 8–10). Concentration of sulfur dioxide in flue gas is directly related to the content of combustible sulfur (organic + pyretic) and behavior of calcium oxide at combustion of oil shale. High value of molar ratio Ca/S is a good prerequisite for extensive binding of sulfur by calcium oxide (mainly to CaSO_4), which simultaneously reduces concentration of SO_2 in flue gas. The ability of ash to capture sulfur dioxide depends also on combustion technology. At high-temperature PF, a large portion of calcium oxide is converted into new minerals, which are less reactive towards sulfur oxides. This reduces the content of free CaO in ash and decreases the ability of ash to capture SO_2 . Therefore, the concentration of sulfur oxides in flue gas at oil shale PF is relatively high. It is possible, within certain limits, to influence the extent of sulfur capture by ash through the parameters of combustion process.

At low-temperature FBC, lime formed at thermal decomposition of carbonate compounds remains in an active free form. Therefore, the extent of sulfur capture is high, and the concentration of SO_2 in flue gas is small. At FBC of oil shale, there is no need to feed additional sorbent for sulfur capture into the combustion chamber as molar ratio of Ca/S in fuel is high.

Chlorine-Rich Organic Matter (average chlorine content of organic matter is 0.75%). The main source of hydrogen chloride (HCl) in flue gas of oil shale combustion is chlorine from organic matter. Concentration of HCl in flue gas is many times lower than total chlorine content of fuel would allow it to be. This is caused by binding of HCl by ash in the furnace and convective gas passes of the boiler. Chlorine itself is mainly concentrated into finest particles of ash.

High Content of Carbonate Minerals (content of mineral CO_2 in dry oil shale is 18–20%). Carbon dioxide formed during combustion of oil shale can be divided into two parts: i) carbon dioxide which forms during combustion of organic carbon, ii) carbon dioxide formed as a result of decomposition of carbonate minerals. The first part is determined by organic carbon content of fuel and combustion efficiency (which in the case of modern burning technologies is very high). Concentration of CO_2 from decomposition of carbonate minerals depends upon the content of mineral CO_2 in oil shale mineral matter and its extent of decomposition in combustion process (which is highly dependent on firing technology). The lower the extent of carbonate decomposition, the less the total concentration of CO_2 in flue gas.

Formation of Nitrogen Oxides

Mechanism of Formation of Nitrogen Oxides

At first a general overview on formation of nitrogen compounds is given, followed by description of the reactions occurring at oil shale combustion.

There are three well-known mechanisms of nitrogen oxide formation:

1. Thermal nitrogen oxides – form as a result of reactions between atmospheric nitrogen and oxygen.
2. Prompt nitrogen oxides – form in reactions between molecular nitrogen and hydrocarbon radicals.
3. Fuel nitrogen oxides – form as oxidation products of nitrogen present in organic matter of fuel.

Thermal Nitrogen Oxides. In the combustion process, nitrogen and oxygen from air react forming the following compounds: NO, NO₂, N₂O, N₂O₃, N₂O₄, and N₂O₅. The most important compounds are nitric oxide (NO) and nitrogen dioxide (NO₂). The sum NO + NO₂ is usually expressed as NO_x. The content of nitric oxide is more important, because its contribution to total nitrogen oxides is 90–95%. The share of N₂O₃, N₂O₄, and N₂O₅ is negligible, and contribution of these compounds can be neglected. Nitric oxide emitted into the air is oxidized to nitrogen dioxide, and a subsequent reaction with water vapor results in the formation of nitric acid. Nitric acid can damage the environment as acid rain. The influence of NO_x on the environment is local.

Emission of nitrous oxide N₂O (laughing gas) as a greenhouse gas may contribute to the global warming. The more N₂O in the atmosphere, the higher the absorption of infrared radiation and the stronger its influence on the temperature of the environment. As a greenhouse gas N₂O is more powerful than carbon dioxide. Nitrous oxide emission also contributes to the depletion of the protective ozone layer in the upper part of the earth atmosphere.

At high-temperature combustion of fuel, the following attachment reaction of molecular nitrogen to oxygen is possible:



However, actually this reaction is very slow, and its contribution to the formation of thermal nitrogen oxides is insignificant.

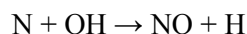
The formation of nitric oxide from air nitrogen as a chain reaction through the mechanism proposed by Zeldovič [1, 2] is more acknowledged:



Reaction (2) whose rate depends on the concentration of atomic oxygen determines the overall rate of the process. This reaction is characterized by a high activation barrier, primarily due to high binding energy of N₂.

Concentration of atomic oxygen is determined by dissociation of molecular oxygen, which depends on the concentration of oxygen and largely on temperature. Increase in temperature enhances the concentration of oxygen atoms.

It is generally believed that the reaction between atomic nitrogen and hydroxide radical is important when oxygen concentration is low:



The equilibrium concentration of nitric oxide can be calculated by the following well-known formula:

$$c_{\text{NO}} = k \sqrt{c_{\text{O}_2} c_{\text{N}_2}} \exp\left(-\frac{90100}{RT}\right) \quad (4)$$

where k – coefficient;

c_{O_2} – concentration of oxygen;

c_{N_2} – concentration of nitrogen;

R – universal gas constant;

T – absolute temperature.

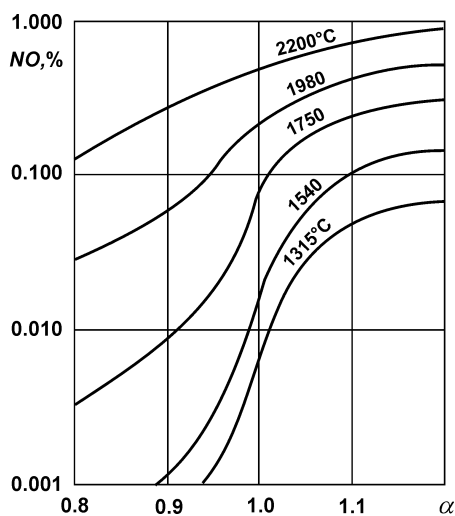


Fig. 1. Equilibrium concentration of nitric oxide as a function of excess air factor and temperature

Figure 1 demonstrates the equilibrium concentration of thermal nitric oxide in flue gas as a function of excess air factor α and temperature. Concentration of NO increases with an increase in temperature and α . The share of NO becomes significant starting from temperatures 1300–1400 °C. Therefore, the amount of thermal NO_x can be remarkable in high-temperature PF processes. However, the importance of thermal NO_x at FBC of fuel is modest.

Prompt Nitrogen Oxides. Another possibility for formation of NO_x is through attachment reactions between molecular nitrogen and radicals of hydrocarbons formed during combustion of fuel:



and



A subsequent reaction between nitrogen compounds and oxygen-containing compounds results in formation of NO (prompt nitric oxide).

The formation of prompt NO_x according to this scheme was first proposed by Fenimore [3], who studied ethylene flame.

The concentration of prompt nitric oxides in flue gas increases with an increase in temperature. The share of prompt nitric oxides becomes significant starting from temperatures 1300–1400 °C. However, the influence of temperature on the formation of prompt NO_x is many times weaker than on the formation of thermal NO_x . The importance of prompt NO_x in flue gas at combustion of solid and liquid fuels remains below 5% [4, a.o.]. Therefore, prompt NO_x can obtain some importance only in the case of high-temperature combustion processes. The role of prompt NO_x in fluidized bed combustion of fuel is insignificant.

Fuel Nitrogen Oxides. At combustion of solid fuels, the main part of nitrogen oxides in flue gas comes from nitrogen present in fuel organic matter, which contributes considerably also to NO_x formation at burning liquid fuels. The content of nitrogen in fuel organic matter can vary between 0.5 and 2.5%.

At thermal decomposition of solid fuel organic matter, a part of nitrogen is released along with volatile matter, and a part remains in char. Both volatilized nitrogen compounds and nitrogen in char converted into oxides and molecular nitrogen through homogeneous, heterogeneous and catalytic reactions. The formation mechanism of nitrogen oxides at thermal decomposition and combustion of solid fuels proposed by Kilpinen and coworkers [5, 6] is shown in Fig. 2.

Nitrogen released along with volatile matter is present either as ammonia (NH_3) or hydrogen cyanide (HCN). Ammonia is oxidized by homogeneous and heterogeneous reactions catalyzed by char to NO and to molecular nitrogen. Hydrogen cyanide is usually converted to nitric oxide, nitrous oxide and molecular nitrogen. In the high-temperature environment (for instance, at PF of fuel), N_2O is converted to NO and N_2 . However, at lower temperatures (for instance, at FBC) N_2O is stable.

Nitrogen present in char is also converted into NO, N_2O and N_2 . It is also possible that during thermal decomposition of fuel, a part of nitrogen is released as molecular nitrogen.

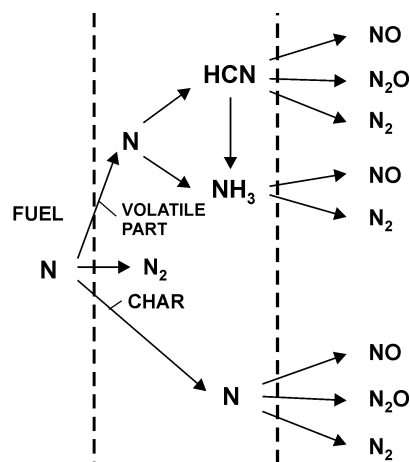


Fig. 2. Schematic representation of formation of nitrogen oxides from fuel nitrogen

Generally, the formation of NO_x during fuel combustion is a complex of various reactions between radicals and molecules, reaction rate and equilibrium of reactions depending on many parameters. The sequence of reactions is also important.

The dynamics of NO_x formation has not been studied extensively – some information can be found from researches performed by Kilpinen, Kallio, Hupa [6], Jegorov, Saar [7–9], Loosaar [9, 10], Ots [11].

The formation of nitrogen oxides during combustion of volatile matter of a solid fuel is rather similar to the formation of NO_x during combustion of a liquid fuel.

Experimental results of transformation processes of nitrogen compounds during combustion of nitrogen-free liquid fuel (diesel fuel) with additives pyridine ($\text{C}_5\text{H}_5\text{N}$) or nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) are shown in Fig. 3 [7]. In both cases, 0.5% of nitrogen was added to the fuel. On the vertical axis – the total amount of bound nitrogen, and nitrogen in NO in normal cubic meter of flue gas at excess air factor $\alpha = 1$ ($N_{\alpha=1}$), and also volumetric oxygen concentration (O_2 , %) in flue gas. On the horizontal axis – the distance from the burner exit (L). The highest temperature in the furnace was $1450\text{ }^\circ\text{C}$. The combustion of fuel ended at about 0.8–1.2 m from the burner – judging by changes in oxygen concentration along the furnace.

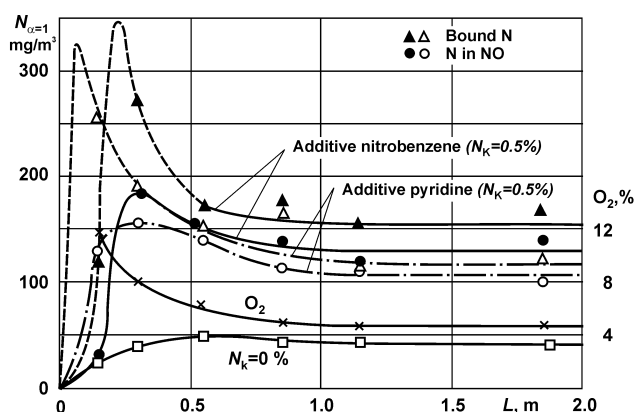


Fig. 3. Formation dynamics of nitrogen compounds along the combustion chamber

The concentration of NO_x formed from air nitrogen reaches its maximum at the distance 0.5 m from the burner.

The results presenting bound nitrogen compounds in flue gas include also nitrogen oxides formed from air nitrogen. One can see that the amounts of bound nitric oxide formed on the account of nitrogen compounds increase steeply at the beginning of the combustion process, and thereafter begin to decrease and stabilize at a certain value. Therefore, in the initial stage of combustion nitrogen present in additive (fuel) is released as radicals to flue gas indicating at very fast thermal decomposition of nitrogen compounds. Decomposition of nitrogen compounds is, in principle fast, depending to some extent on the additive.

In the initial part of the flame decomposition of nitrogen compounds and formation of NO take place simultaneously. There is a delay in NO formation after the beginning of decomposition of nitrogen-containing compounds. The concentration of NO reaches maximum after a certain time and thereafter diminishes to a constant level. The decrease in the concentration of nitric oxide in flue gas after the maximum can be explained by decomposition of nitrogen-containing radicals and NO and by release of molecular nitrogen. If nitrogen in the fuel is bound to oxygen (for instance, in experiments with oxygen-containing nitrobenzene as an additive), the concentration of NO in flue gas is higher than in oxygen-free nitrogen compounds.

Similar results have been obtained from combustion of heavy oil and shale oil with nitrogen content of 0.55 and 0.50%, respectively [8]. Such a phenomenon, combustion of organic nitrogen, takes place also at PF of oil shale.

Basing on many studies (for instance, [6]) one can make the following conclusions about the behavior of fuel nitrogen during combustion.

The concentration of NO_x in flue gas grows with an increase in temperature. However, the increase of NO_x concentration is much slower than NO_x formation from air nitrogen. The amount of N_2O in flue gas decreases with an increase in temperature. The influence of temperature on formation of NO_x depends on the binding characteristic of nitrogen in the fuel. In high-temperature combustion conditions (for instance, PF), only a negligible amount of N_2O forms, however, in low-temperature processes (for instance, FBC) N_2O concentration can be significantly higher. At higher oxygen concentration the larger amount of fuel nitrogen are converted to nitrogen oxides (both to NO_x and N_2O).

Most fuels contain also different quantity of sulfur. There is a definite relationship between sulfur content and nitrogen oxide concentration in flue gas.

The influence of sulfur on NO_x concentration in flue gas formed during combustion of liquid fuel has been studied [8] adding different amounts of ethyl mercaptane to fuel that contained 1% nitrogen (as pyridine). As a result, sulfur content of fuel changed from 0.1 to 1.5%. The results are presented in Fig. 4. On the vertical axis – the ratio of NO_x concentration (for given sulfur content in fuel) to concentration of NO_x which forms during combustion of fuel without sulfur. On the horizontal axis – sulfur content of fuel. The results about the influence of sulfur on formation of nitrogen oxides from nitrogen present in the air, also shown in Fig. 4 [12], demonstrate that the effect of sulfur on NO_x concentration in flue gas formed from both fuel nitrogen and nitrogen in the air is the same. They prove that amount of NO_x in flue gas decreases with an increase in sulfur content of fuel – 1–2% sulfur in fuel can reduce the concentration of NO_x approximately by 50–60%. Similar processes take place at PF of solid fuels,

as proved by the results on sulfur influence on concentration of NO_x in flue gas formed at oil shale combustion.

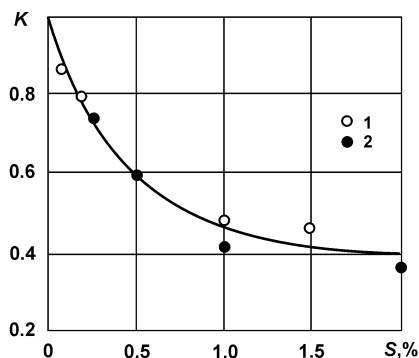
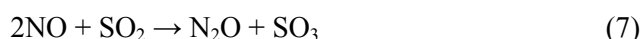


Fig. 4. Relative content of nitrogen oxides in flue gas as a function of sulfur content when burning liquid fuel. 1 – fuel nitrogen; 2 – air nitrogen

Basing on research on the influence of sulfur on NO_x concentration in flue gas formed from both fuel nitrogen and nitrogen in the air, the following reaction is likely to occur:



Nitrous oxide formed decomposes in the high-temperature medium to molecular nitrogen, however, at low-temperature combustion (in fluidized bed) N_2O is stable.

The probability of the Reaction (7) is supported by experiments [8], which showed an increase in SO_3 concentration in flue gas with an increase in nitrogen content of fuel.

When using FBC technology, limestone is often fed into the furnace to capture sulfur dioxide from flue gas. The extent of sulfur capture by burning of solid fuels is highly dependent on molar ratio of calcium to sulfur. An increase in Ca/S molar ratio and a decrease in SO_2 concentration in flue gas (extent of sulfur capture with ash is higher) is accompanied by a simultaneous increase in NO_x concentration and decrease in N_2O emission.

An increase in concentration of NO_x in flue gas with an increase in Ca/S molar ratio has been proved by many studies [13–16, a.o.]. This phenomenon has two possible explanations. Firstly, limestone catalytically enhances conversion of fuel nitrogen into NO_x and inhibits decomposition of formed N_2O . Secondly, feeding of limestone into fluidized bed reduces the amount of SO_2 in flue gas and, therefore, increases the concentration of NO_x and decreases that of NO_2 . Basing on observations presented above, the second explanation seems to be more realistic. The last conception is supported also by investigations of Schäfer and Bonn [17]. As mentioned earlier, hydrogen cyanide formed during pyrolysis, which is an important precursor of nitric oxide formation. They suggested that conversion of HCN to NO is inhibited by SO_2 . In contrast to nitric oxide, the formation of N_2O increases with increasing concentration of SO_2 in gaseous medium.

Formation of Nitrogen Oxides at Oil Shale Combustion

Formation of nitrogen oxides at combustion of oil shale has been examined in [9–11]. The results allow drawing important conclusions about emission of nitrogen oxides and factors influencing their formation.

The effect of oxygen partial pressure (excess-air factor), temperature, nitrogen and sulfur present in fuel on the concentration of nitrogen oxides in flue gas of oil shale combustion has been studied by Loosaar and Jegorov [10, a.o.] in a laboratory device. The main part of the device (combustion chamber) is an externally heated downflow tube with height 1 m and internal diameter 56 mm. There are ports for taking gas samples and measuring the temperature along the chamber. Pulverized oil shale is fed into the upper part of the chamber. Fuel feeding rate can be regulated between 100–150 g/h. Temperature of air introduced into the combustion chamber along with fuel is 500 °C. The highest combustion temperature is 1350 °C, and residence time of gas in the device is approximately 1 s. Combustion efficiency of pulverized oil shale at the exit of combustion chamber $\eta > 0.99$.

Nitrogen present in fuel is the major source of nitrogen oxides emitted at burning of solid fuel. The amount of nitrogen and its position in the structure of oil shale organic matter plays also an important role in formation of nitrogen oxides. Nitrogen content of oil shale organic matter is moderate. Its average value is 0.33%. The amount of nitrogen in organic matter of oil shale taken from different mines varies slightly (usually between $\pm 0.1\%$). Nitrogen content of oil shale used in experiments varied between 0.21–0.41%, which gave a good possibility to study the effect of nitrogen content on formation of NO_x . Content of pyritic and organic sulfur in dry matter of oil shale $S_p^d = 0.84\text{--}1.03\%$, and $S_o^d = 0.46\text{--}0.68\%$, respectively.

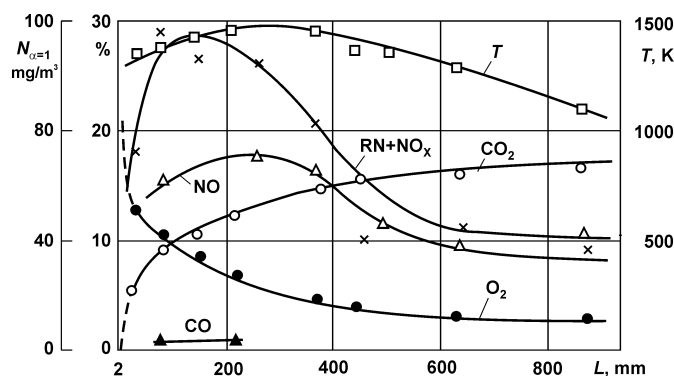


Fig. 5. Dynamics of changes in nitrogen compounds along the combustion chamber by burning of pulverized oil shale

General combustion characteristics of pulverized oil shale and conversion dynamics of fuel nitrogen along the combustion chamber are shown in Fig. 5. The dynamics of conversion processes of nitrogen present in oil shale

and formation of nitrogen oxides are similar to the processes taking place at combustion of a liquid fuel (see Fig. 3).

Combustion of volatile matter ends at about 250–300 mm from the burner depending on the combustion regime (temperature, excess-air factor). In addition to changes in O_2 concentration and gas temperature along the combustion chamber, the concentration of bound nitrogen released to flue gas ($RN + NO_x$) and the amount of nitrogen in NO per normal cubic meter of gas are also shown.

Intensive formation of nitrogen oxides takes place in the zone of volatile matter combustion, where the concentration of nitrogen-containing compounds (NO_x and radicals) increases quickly, reaches the maximum, and thereafter starts to decrease until reaching a constant level. This rapid increase in the concentration of bound nitrogen at the beginning of combustion process shows intensive release of nitrogen compounds from oil shale organic matter along with other volatiles. Also nitric oxide forms simultaneously with decomposition of nitrogen-containing compounds.

The curve representing the concentration of NO in flue gas has a maximum like the curve corresponding to the concentration of $RN + NO_x$. Formation of NO occurs with a slight delay with respect to decomposition of nitrogen compounds. The decrease in the concentration of NO after reaching the maximum can be explained by combination reactions between NO and nitrogen radicals, and N_2 formation. At the end of the combustion chamber, the amount of $RN + NO_x$ is determined by fuel nitrogen content and parameters influencing nitrogen conversion processes. Difference in the values of $RN + NO_x$ and NO in this zone is very likely equal to the amount of NO_2 .

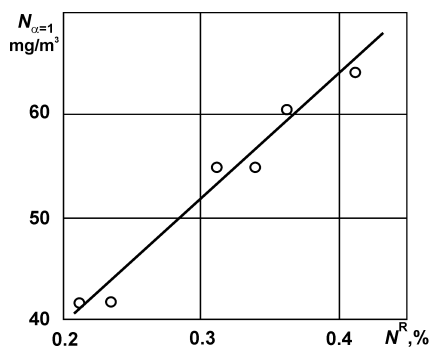


Fig. 6. Content of bound nitrogen in flue gas as a function of nitrogen content of organic matter of oil shale. Excess air factor $\alpha = 1.25$, combustion temperature $t = 1300$ °C

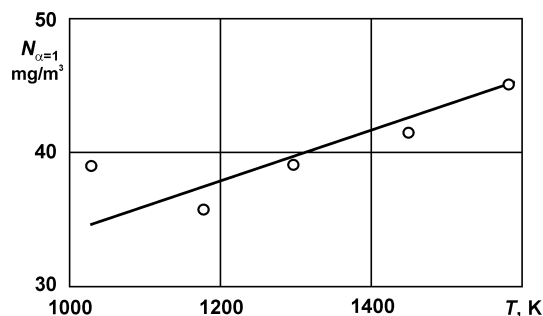
one can estimate the concentration of nitrogen oxides formed from nitrogen in the air – it is around 12 mg/m^3 .

The main parameters that determine the concentration NO_x in flue gas are nitrogen content of fuel, excess air factor and temperature. Sulfur content of fuel and related processes has also a significant effect.

The influence of nitrogen content of oil shale on the total concentration of nitrogen oxides (as bound in NO_x nitrogen) in flue gas at the end of the combustion process is explained in Fig. 6. The concentration of NO_x in flue gas as a function of nitrogen content of oil shale organic matter can in the first approximation be treated as linear. By extrapolating the experimental line to the value $N = 0$,

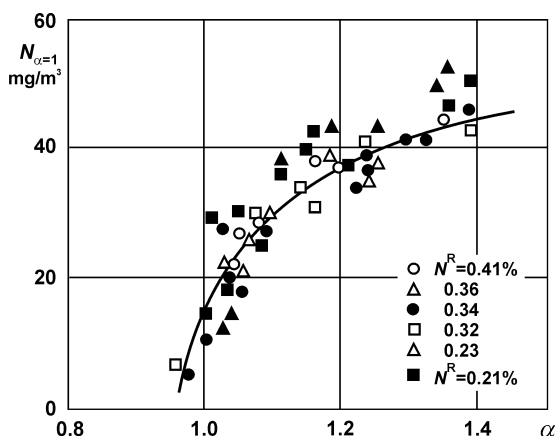
Basing on average nitrogen content of oil shale organic matter ($N = 0.33\%$), one can find that the amount of NO_x formed from fuel nitrogen is about 40 mg/m^3 , which accounts for 18% of total amount of nitrogen in oil shale. Therefore, the extent of nitrogen conversion into NO_x $\eta_N^f = 0.18$. The share of thermal NO_x is approximately 30% of the total amount of nitrogen oxides in flue gas depending upon combustion temperature and excess air factor.

Fig. 7. Concentration of bound nitrogen in flue gas as a function of temperature. Results are reduced to excess air factor $\alpha = 1.25$ and nitrogen content of oil shale $N = 0.33\%$



The effect of combustion temperature on formation of NO_x from fuel nitrogen is weak. Figure 7 shows the concentration of NO_x formed from oil shale nitrogen as a function of temperature. In the first approximation this dependence is linear. Increase in combustion temperature by 100 K increases the amount of bound nitrogen in flue gas by approximately 4 mg/m^3 .

Fig. 8. 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 $t = 1300 \text{ }^\circ\text{C}$



The most important parameter that influences nitrogen oxide content of flue gas is concentration of oxygen (excess air factor α). In order to determine the influence of α on concentration of NO_x formed from fuel nitrogen in flue gas, experimental results are reduced to an average nitrogen content of fuel 0.33% and temperature $1300 \text{ }^\circ\text{C}$. Results obtained in this way are presented in Fig. 8.

One can see a rapid growth in concentration of NO_x with an increase in excess air factor up to $\alpha = 1.25$. In the region $\alpha > 1.25$, the influence of

oxygen concentration on NO_x persists, being, however, much weaker. The dependence presented in Fig. 8 can be approximated by the following formula derived by Loosaar and Jegorov [10]:

$$N_{\text{NO}_x}^{\alpha=1} = [24.4 + 200.5 \left(\frac{\alpha-1}{\alpha}\right)^{0.4}] N^R, \text{ mg/m}^3 \quad (8)$$

Concentration of nitrogen oxides can be considerably influenced by the concentration of SO_2 in flue gas or by addition of limestone into fluidized bed as a sorbent of sulfur compounds. As explained below, sulfur present in oil shale influences also the concentration of NO_x in flue gas.

To elucidate the influence of sulfur on emission of nitrogen oxides, crushed pyrite was mixed with pulverized oil shale before feeding it into the experimental device. The impact of sulfur on NO_x emissions is shown in Fig. 9 which presents the ratio of NO_x concentration after addition of pyrite to fuel to the initial NO_x concentration (without additional sulfur) as a function of the added amount of pyritic sulfur.

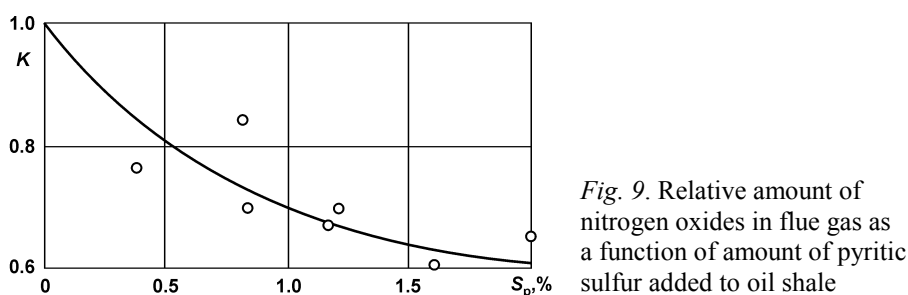


Fig. 9. Relative amount of nitrogen oxides in flue gas as a function of amount of pyritic sulfur added to oil shale

The content of combustible sulfur in oil shale was 1.55%. Figure 9 shows that the emission of NO_x decreases considerably with an increase in the amount of additional sulfur. An increase in sulfur content of 1% decreases the emission of NO_x by approximately 30%. This is caused by the increase in partial pressure of SO_2 in flue gas caused by oxidation of pyrite sulfur and its influence *via* the Reaction (7). At given burning conditions in this experimental device, approximately half of combustible sulfur is released to flue gas as oxides formed during the combustion process. The rest is captured by basic components of ash. Low extent of sulfur capture by ash, as compared with the process in an industrial boiler, is probably caused by too short residence time of flue gas in the combustion chamber.

Basing on the results obtained studying the influence of individual parameters of the process on formation and emission of nitrogen oxides, and also on data of industrial combustion of pulverized oil shale (nitrogen content of organic matter $N = 0.33\%$, content of combustible sulfur $S_p^d = 1.6\%$, temperature $T = 1720 \text{ K}$, excess air factor $\alpha = 1.25$), the concentration of nitrogen bound to nitrogen oxides $N_{\alpha=1} = 100\text{--}105 \text{ mg/m}^3$, which corresponds to the concentration of NO_2 (if O_2 content of dry flue gas

is 6%) $(\text{NO}_x)_{\text{NO}_2}^{\text{O}_2=6\%} = 240\text{--}260 \text{ mg/m}^3$. This is in good agreement with the results of measurements performed in industrial boilers.

Emission of Nitrogen Oxides from Oil Shale in Industrial Boilers

The concentration of nitrogen oxides in flue gas leaving oil shale PF boilers has been measured by VTT (Technical Research Centre of Finland) [18] and Department of Thermal Engineering of TUT.

Basing on the results presented above, one can assert that emission of NO_x from industrial boilers depends upon the following factors: boiler load (combustion temperature), oxygen concentration (excess air factor, distribution of air at the entrance to the furnace, etc.), residence time of flue gas in the furnace (depends upon boiler load and air feeding regime), composition of the fuel (nitrogen content of organic matter, sulfur content, heating value, etc.). In addition, design of the furnace and boiler has a significant influence on emissions of NO_x .

It is very difficult or even impossible to estimate the amount of NO_x emissions from a boiler with given design and operating parameters precisely. However, it is possible to assess the influence of individual factors on NO_x emissions. Experimental results obtained from industrial boilers are quantitatively valid only for a given design and test regime parameters.

According to measurements performed by Department of Thermal Engineering of TUT in industrial PF oil shale boilers, average concentrations of NO_x in flue gas leaving the boiler (flue gas contained 6% O_2) (the results obtained by VTT [18] are given in brackets) are as follows: 220 mg/m^3 in boiler BKZ-75-39F, 220 (270) mg/m^3 in boiler TP-17, 260 (285) mg/m^3 in boiler TP-67, and 270 (250) mg/m^3 in boiler TP-101.

The concentration of NO_x in flue gas formed during combustion of oil shale in a pilot 1-MW combustor with circulating fluidized bed were measured in laboratories of Foster Wheeler (FW) and Lurgi Lentjes Babcock (LBB). Content of NO_x in the FW pilot device was 180–265 mg/m^3 and in LLB combustor 265–370 mg/m^3 . Measurements in industrial oil shale CFBC boiler performed by Department of Thermal Engineering of TUT showed that NO_x concentration is in the range 140–160 mg/m^3 (flue gas contained 6% O_2).

At oil shale PF in industrial boilers, the share of thermal nitrogen oxides in total NO_x is 35–40% (maximum combustion temperature 1400–1500 °C). As the concentration of thermal NO_x is strongly dependent upon combustion temperature, the share of NO_x formed from air nitrogen in FBC, where combustion temperature remains about 800–900 °C, is very small. Therefore, at FBC nitrogen oxides form primarily from fuel nitrogen. Their formation quickens with an increase in temperature, too, however, this dependence is weaker.

At FBC of oil shale the distribution of bound nitrogen between different individual oxides is different compared with PF. If the emission of N_2O at

PF is almost negligible due to high combustion temperature, the emission of nitrous oxide from the combustion device of LLB was measured to be 10–45 mg/m³. The emission of N₂O in an industrial oil shale CFBC boiler is 10–45 mg/m³.

The emission of NO_x in a classical PFBC pilot device (pressure 1.2 MPa, bed temperature 860 °C) with capacity 1 MW (ABB) was measured to be 120–190 mg/m³ (flue gas contained 6% O₂), which is a little less than emissions of NO_x from CFBC. In general, the opinion dominates that an increase in pressure reduces the emission of nitrogen oxides into flue gas [19].

Formation of Sulfur Oxides

Mechanism of Formation of Sulfur Oxides

Sulfur oxides form at combustion of solid fuels from sulfur present in organic and mineral matter of fuel.

Usually more than half of organic sulfur in fuel is present in aromatic compounds (thiophenes), and the rest in aliphatic compounds (mercaptanes, sulfides, disulfides, etc.). During heating of fuel aliphatic sulfur relatively easily volatilizes already at low temperatures, however, aromatic compounds are more stable, and sulfur present in those compounds is released at higher temperatures.

The main sulfur-containing mineral in solid fuel is pyrite (marcasite) FeS₂. Mineral matter can also contain smaller amounts of gypsum (CaSO₄·2H₂O), melanterite (FeSO₄·7H₂O), and other sulfur-containing minerals.

Pyritic sulfur is converted into oxides by oxidation, however, in the case of other minerals oxides form during thermal decomposition. During heating of marcasite (pyrite), one sulfur atom is released and iron monosulfide (pyrrhotite) FeS forms. Release of sulfur from pyrite starts already at low temperature (about 500 °C, depending on conditions) proceeding at a high rate. However, reaction rate between formed FeS and oxygen is relatively low. A part of formed SO₂ is oxidized further to sulfur trioxide (SO₃), which accounts for only some per cent from the total amount of sulfur oxides in flue gas.

Sulfur trioxide forms in the high-temperature medium (>1100 °C) through the reaction with atomic oxygen according to the equation



and at lower temperature with molecular oxygen through catalytic reaction



The equilibrium constant of the system SO₂–O₂–SO₃ can be calculated by the following expression [20]:

$$\ln k_p = \ln \frac{p_{SO_3}}{p_{SO_2} \sqrt{p_{O_2}}} = \frac{93,600}{RT} - 10.68 \quad (11)$$

where p_{SO_3} – partial pressure of sulfur trioxide;

p_{SO_2} – partial pressure of sulfur dioxide;

p_{O_2} – partial pressure of oxygen;

R – universal gas constant;

T – absolute temperature.

An attachment reaction between sulfur dioxide and atomic oxygen occurs provided that the latter is present in the high-temperature medium. Temperature dependence of sulfur dioxide conversion to sulfur trioxide $SO_3/(SO_2 + SO_3)$ (along the boiler gas pass) presented by Hedley [21] is shown in Fig. 10. Solid lines correspond to thermodynamic equilibrium at two different values of excess air factor, while dashed line expresses actual (measured) results. In the high-temperature region, the actual concentration of SO_3 has a maximum, which exceeds several times the equilibrium value of SO_3 according to the reaction between SO_2 and molecular oxygen. This is possible in the case of Reaction (9).

After reaching the maximum, concentration of SO_3 starts to decrease, as partial pressure of atomic oxygen decreases, and SO_3 concentration reaches the equilibrium value according to Equation (10). A subsequent increase in the concentration of SO_3 is associated with catalytic reactions in the presence of molecular oxygen, while components of ash deposit (including iron and chrome oxides) on the convective heat-transfer surface act as catalysts. The majority of SO_3 forms in the high-temperature medium of the furnace. The amount of SO_3 formed through catalytic processes depends upon catalytic properties of ash deposit, oxide film on tube surfaces, etc., and mass exchange conditions. These conditions can change with time.

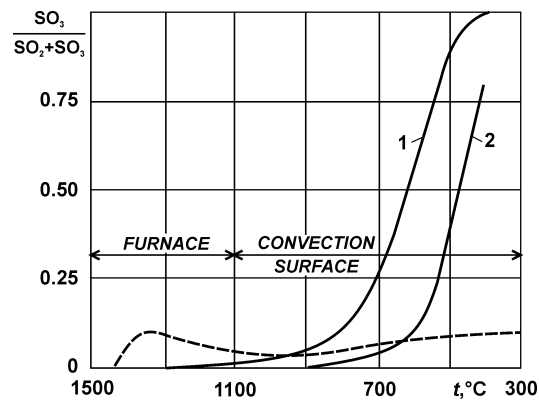


Fig. 10. Conversion of sulfur dioxide to sulfur trioxide as a function of temperature. $1 - \alpha = 1.10$; $2 - \alpha = 1.01$

Binding of Sulfur Oxides with Ash in Industrial Oil Shale Boilers

The processes occurring at oil shale combustion in PF boiler furnace and gas pass yield sulfur compounds (mainly as sulfur dioxide) in amounts much less than expected basing on sulfur content of oil shale. This is due to the ability of oil shale ash to bind sulfur. That is why sulfur is removed from the boiler along with ash. Binding of sulfur compounds by ash during PF of oil shale has been examined in the studies [11, 18, 22–27, a.o.].

The extent of sulfur capture by ash in the boiler furnace and gas passes is characterized by two dimensionless quantities.

The release of sulfur to flue gas is expressed by the extent of sulfur volatilization (relative amount of sulfur released into flue gas):

$$k_v = \frac{S^v}{S_v} \quad (12)$$

where S^v – amount of sulfur transferred into flue gas;
 S_v – content of combustible sulfur in fuel.

In addition to factor k_v , one can use the extent of sulfur capture, which shows how much sulfur present in fuel is captured by ash:

$$k_s = 1 - k_v = 1 - \frac{S^v}{S_v}. \quad (13)$$

The extent of sulfur capture by ash depends on the following parameters: composition of fuel, temperature regime (combustion technology, temperature profile in the gas pass of the boiler), particle size distribution, oxygen partial pressure in flue gas, and duration of sulfation process.

The main sulfur-binding component in fuel is usually calcium. Therefore, for characterization of the potential of sulfur capture, Ca/S_v molar ratio is used (Ca and S_v are the content of calcium and combustible sulfur in fuel, respectively). Often additional calcium in the form of limestone or dolomite is fed into the furnace and gas passes of the boiler (especially at FBC). Then Ca/S_p ratio expresses the molar ratio of total calcium fed into boiler to the content of combustible sulfur in the fuel.

If the fuel contains alkali metals, then a part of sulfur is bound with those compounds, usually in the form of sulfates. However, not all alkali metals present in fuel are converted into sulfates, but only some part of them (this depends primarily on the extent of alkali metals volatilized from mineral matter during combustion).

The extent of sulfur volatilization changes along the boiler gas pass determined by the nature of chemical reactions taking place between sulfur and ash components. Sulfation of ash occurs in the furnace and continues in the gas pass after it if the flue gas temperature is favorable.

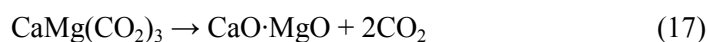
The main components of mineral matter, which influence capture of sulfur by ash, are minerals in the carbonate part of oil shale containing

calcium, and partially also potassium compounds in sandy-clay minerals. The importance of minerals containing sodium is low, because the amount of sodium in oil shale is negligible.

At atmospheric combustion of fuel, at first thermal decomposition of calcium carbonate and formation of lime take place, followed by sulfation of calcium (calcium sulfate forms). The process is described by the following reactions:



In the case of dolomite, the reactions are



Sulfation starts from the outside surface of a particle and progresses towards the center. As the molar volume of CaSO_4 is larger compared to that of CaCO_3 , at the outside surface of the particle pores become blocked, which restricts diffusion of SO_2 and oxygen. This effect is considerable in the case of particles with lower specific surface area and larger diameter. Many studies have shown higher extent of sulfation in the case of smaller particles (keeping other conditions constant) [24, 25, 27, a.o.].

According to the data [25], about 70–80% of CaO formed during decomposition of carbonate minerals at high-temperature PF of oil shale combines with components of the sandy-clay part (so-called new minerals are formed). Sulfation of new minerals is also possible, but its importance in sulfation processes in the gas pass is small. There is not enough time for sulfation processes to occur, because the residence time of ash particles is too short. The Ca/S_V molar ratio in oil shale is 8–10. However, the same ratio with respect to free lime (Ca_f) leaving the furnace together with flue gas $\text{Ca}_f/\text{S}_V = 1.5\text{--}2.5$. Low ratio of calcium to sulfur Ca_f/S along with the so-called blocking effect does not allow binding sulfur completely by CaO despite the high initial value of molar ratio Ca/S . Therefore, a part of combustible sulfur is transferred into flue gas as oxides and is emitted to the atmosphere through the stack.

The extent of sulfur volatilization after the furnace at PF of oil shale is, depending on the combustion regime, between $k_V = 0.3\text{--}0.4$ (data were measured in 2-MW combustion chamber). If the extent of sulfur volatilization is determined basing on concentration of SO_2 in flue gas leaving an industrial boiler, this value remains, as a rule, below the values of k_V presented. This indicates that binding of sulfur oxides in an oil shale boiler continues also in the gas passes after the combustor.

The total extent of sulfur volatilization can be determined either from the ash balance or by measuring the concentration of sulfur oxides in flue gas directly. In the first case, the amount of ash deposited along the gas passes and its sulfur content are used. Both methods have been widely accepted for determination of sulfur balance in industrial boilers [18, 24, 25, a.o.].

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

Sulfur Content of Fuel. The dry mass of oil shale consists of three individual sulfur constituents whose average composition is quite constant. Only sulfur content in organic matter varies to a certain extent depending on oil shale deposit and seam (organic sulfur in organic matter $\pm 0.2\%$ and pyritic sulfur in the sandy-clay part $\pm 2.1\%$). The proportions of those three constituents mentioned above in oil shale as received depend on mining and enrichment technologies. It means that the content of combustible sulfur is also determined by the ratio of oil shale components.

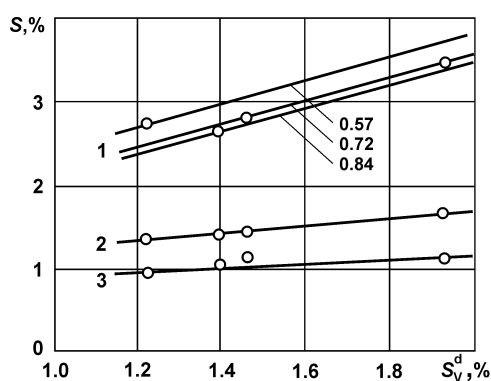


Fig. 11. Total sulfur content of ash as a function of the content of combustible sulfur in dry oil shale. 1 – fly ash; 2 – ash from reversing chamber; 3 – slag. Numbers by the curves 1 denote relative load of boiler

increase in partial pressure of sulfur dioxide in flue gas due to an increase in total sulfur content of fuel (molar ratio Ca/S in fuel being approximately the same).

Particle size of fly ash is much finer compared to slag particles and ash from the reversing chamber. This favors the reaction between sulfur dioxide and fly ash particles which have larger active surface area. Higher sulfur content of smaller ash particles can also be influenced by separation of larger particles with lower sulfur content from the ash flow in the boiler gas passes [26].

The effect 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 PF oil shale boiler TP-17 is shown in Fig. 11 [24, 25].

This result clearly indicates that the amount of sulfur in fly ash, in ash from reversing chamber and slag increases with an increase in sulfur content of oil shale. Sulfur content of fly ash exceeds that of slag and ash from reversing chamber 2.0–3.5 times. This dependence can be explained primarily by the

Grinding Rate of Fuel. The effect of grinding rate of pulverized oil shale on the extent of sulfur capture by ash has not been directly studied. The effect of fuel particle size can be indirectly deduced from the relationship between the total sulfur content of ash particles and particle size distribution. The main component that reacts with sulfur dioxide is calcium oxide. Calcium oxide and free lime are much more concentrated in coarser ash particles, the finest fractions are characterized by the highest sulfur content, whereas coarser particles contain less sulfur.

This conclusion can be drawn from Fig. 12, where sulfate sulfur (as SO_3) content of ash particles is given as a function of median particle size. The diagram is based on the analysis of ash precipitated on the gas passes of oil shale PF boiler TP-101. Finer ash particles have a higher potential for binding sulfur oxides owing to their greater specific surface area, which favors the contact between sulfur oxides in flue gas and active components of ash, mainly free lime. One can assert that finer crushing of oil shale will increase specific surface area of ash particles containing calcium oxide and therefore their ability to capture sulfur oxides from flue gas.

Load of Boiler. An increase in boiler load (steam production) reduces the amount of sulfur captured by ash, and, therefore, emissions of sulfur oxides increase [24, 25, 27, a.o.]. Figure 12 also demonstrates that a decrease in boiler load increases the content of sulfate sulfur in precipitated ash particles. It means that the total content of sulfur bound with ash increases, or emissions of sulfur oxides decrease.

Boiler load affects the processes between sulfur and ash through the following phenomena.

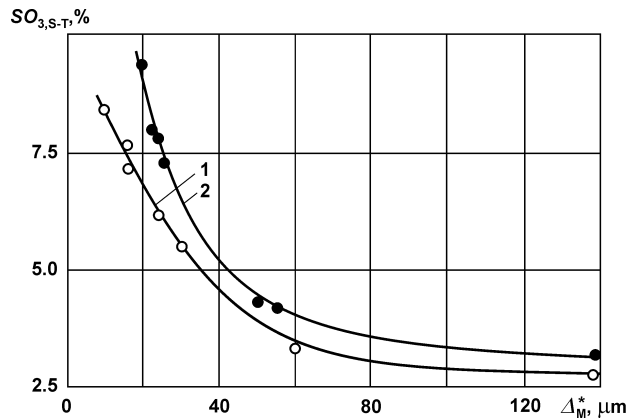


Fig. 12. Content of sulfate sulfur in ash precipitated in gas passes of oil shale boiler TP-101 as a function of median particle size. Relative boiler load: 1 – 0.94; 2 – 0.69

As in oil shale PF boilers the direct-firing system is used without storage of pulverized fuel, particle-size distribution of fuel depends on boiler load.

An increase in boiler load increases air rate through the mill, and pulverized fuel remains coarser. Specific surface area of ash particles decreases, and the extent of sulfur capture by ash diminishes.

Boiler load affects also combustion temperature, and through this the ratio of free lime to bound calcium oxide. An increase in boiler load increases temperature in the furnace and decreases the content of active free calcium oxide in ash. This is the primary cause why the extent of sulfation of ash particles diminishes, and emission of sulfur oxides increases.

Boiler load influences on sulfation of ash through the time of contact between sulfur oxides and ash particles. An increase in boiler load intensifies gas flow rate through the gas pass, residence time decreases, and the extent of sulfation of ash particles diminishes.

Partial Pressure of Oxygen in Flue Gas. As already mentioned, calcium oxide is the main component of oil shale ash that reacts with sulfur dioxide. The rate of sulfation of CaO is proportional to $\sqrt{p_{O_2}}$ (where p_{O_2} – oxygen partial pressure in flue gas). Oxygen concentration in flue gas is expressed by excess air factor α . Figure 13 shows the dependence of the extent of sulfur capture by ash on α . These results were obtained from experiments performed in PF oil shale boiler TP-101. The data show that an increase in α or partial pressure of oxygen in flue gas enhances sulfation of ash particles and the extent of sulfur capture. However, one has to point out that the value of α influences not only oxygen concentration in flue gas, but also, to a certain extent, the temperature in the combustion chamber. An increase in α (in the region >1) reduces combustion temperature, and, as mentioned earlier, reduces the amount of new minerals, hard to sulfatize in the gas flow.

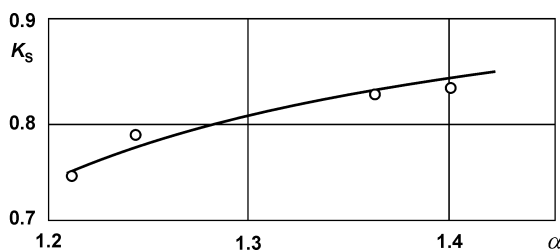


Fig. 13. Extent of sulfur capture by ash particles as a function of excess air factor at pulverized firing of oil shale in boiler TP-101. Relative boiler load 0.88

In conclusion, emission of sulfur oxides in an industrial boiler depends on particle size distribution of fuel, air regime (excess air factor, primary/secondary air ratio, etc.), residence time of particles in the gas passes (depending on boiler load, excess air factor) and fuel properties. In addition, the design of the furnace and the boiler has a significant effect on emissions of sulfur oxides. Their design, for example, affects the distribution of temperature and concentration of flue gas components in the furnace chamber and temperature profile along the gas pass of the boiler. Basing on the previously presented experimental results one can estimate the effect of parameters of individual processes on emission of sulfur oxides.

The measurements of sulfur dioxide emission in oil shale PF boilers have been performed by VTT [18] and Thermal Engineering Department of TUT.

According to measurements of TUT in industrial PF oil shale boilers, average concentration of sulfur dioxide in flue gas leaving the boiler (flue gas contained 6% O₂) is as follows (the results obtained by VTT [18] are given in brackets): 2,100 mg/m³ in boiler BKZ-75-39F, 2,700 (3,500) mg/m³ in boiler TP-17, 2,350 (2,300) mg/m³ in boiler TP-67, and 1,750 (2,100) mg/m³ in boiler TP-101.

The extent of sulfur capture by ash according to data obtained by TUT were as follows:

$$k_s = 0.72 \text{ in boiler TP-17,}$$

$$k_s = 0.78 \text{ in boiler TP-67, and}$$

$$k_s = 0.81 \text{ in boiler TP-101.}$$

Binding of Sulfur Oxides by Ash at Fluidized Bed Combustion of Oil Shale

Circulating Fluidized Bed Combustion

The behavior of sulfur at FBC was studied in a pilot device with thermal capacity 1 MW [28]. The study showed that the concentration of sulfur dioxide in flue gas was <15 mg/m³ (concentration of O₂ in flue gas was 6%), which is more than 100 times less than in flue gas from PF oil shale boiler. The measurement of SO₂ emissions in an industrial CFBC oil shale boiler confirmed these results. Therefore, there is no need to feed additional binding material for sulfur capture. The main component in ash reacting with sulfur oxides is free CaO forming at thermal decomposition of carbonate minerals. The high value of molar ratio Ca/S plays here an important role.

A high degree of sulfur capture at burning oil shale in CFBC is associated with low combustion temperature (750–850 °C), which is sufficient for dissociation of carbonate minerals and formation of active free calcium oxide, but not enough for intensive formation of CaO-containing new minerals. This temperature range is usually favorable for ensuring rapid sulfation of free lime [5, 28, 29, a.o.].

One of the characteristics of FBC of oil shale is the formation of soft lime during decomposition of limestone, which, owing to collisions and friction with other particles in fluidized bed, is crushed to fine particles. Therefore the ash particles carried out from the bed are many times finer than the original ones, and their specific surface area is higher than that of the original material [28]. Binding of sulfur by ash is also favored by high concentration of ash particles in circulating flow and long contact time between the particles and sulfur oxides.

Arro and coworkers have discussed the great influence of contact time between the particles and surrounding atmosphere on the extent of sulfation [26]. The extents of sulfation of ash samples taken from a circulating fluidized bed combustor k_{SO_2} are as follows: for fly ash 0.08–0.09, for

intermediate ash 0.12–0.13, for circulating ash 0.16–0.22 and for bottom ash 0.13–0.15.

The extent of sulfation of fine fly ash particles turns out to be lower than that of coarser circulating ash. Finer ash particles have shorter contact time with components of the gaseous phase before entering the separator and smaller possibilities to sulfate after it due to low concentration of sulfur oxides in flue gas and low temperature in gas pass. Sulfur capture by calcium oxide is highly dependent on temperature, molar ratio Ca/S, particle size distribution, oxygen partial pressure in flue gas, and in some cases also on sorbent properties [5, 29, 30, a.o.]. The main differences between FBC and PF are combustion temperature and particle-size distribution characteristics.

There exists an optimal combustion temperature (800–850 °C), which corresponds to the highest rate of sulfur capture by lime. An increase in molar ratio Ca/S increases the extent of sulfur capture, however, the optimal combustion temperature itself does not depend on molar ratio Ca/S much. The decrease in the extent of ash sulfation at combustion temperatures below this optimum is associated with the influence of temperature on the rate of sulfation reaction. At temperatures higher than the optimum the processes of ash sintering start to influence sulfation reactions reducing active surface area of particles and thus the extent of sulfur binding.

Sulfation of oil shale ash is a decelerating phenomenon. At the initial stage processes progress quickly, but thereafter sulfation reactions start slowing down and reaction rate decreases drastically. This is caused by the formation of sulfate layer on the outside surface of particles, increasing their diffusion resistance towards both sulfur dioxide and oxygen flow. In the center of a particle there remains an unreacted core of lime. The sulfate layer effect is more significant in large particles. This is the main reason why only partial sulfation of calcium oxide is possible even when molar ratio Ca/S is high and contact time is long.

The concentration of sulfur dioxide in flue gas leaving an industrial oil shale CFBC boiler does not exceed 15 mg/m³ (O₂ concentration in dry flue gas 6%).

Pressurized Fluidized Bed Combustion

The behavior of sulfur during oil shale combustion has been studied in a classical PFBC pilot device with thermal capacity of 1 MW in the laboratory of ABB Carbon [31]. Pressure and temperature in the combustion chamber were 1.5 MPa and 840 °C, respectively. The results showed that sulfur is completely captured by ash (the actual oxygen concentration in dry flue gas was 3%). Emission of sulfur dioxide is practically zero. Ash flow in the device under study can be divided into three parts: bottom ash (22%), ash precipitating in cyclones (78%) and ash passing through cyclones (<0.2%). Approximately 40% of combustible sulfur present in fuel is bound by bottom ash, and the rest of sulfur (60%) is captured by cyclone ash. At that the

extent of sulfation of bottom ash ($k_{\text{SO}_3} = 0.15$) is significantly higher than the extent of sulfation of cyclone ash ($k_{\text{SO}_3} = 0.08$). This is due to higher content of CaO in the bottom ash, but also to a higher rate of mass transfer between particles and gas in the fluidized bed.

It is characteristic of PFBC that partial pressure of CO₂ in flue gas exceeds the equilibrium pressure of decomposition of calcium carbonate, and this avoids the formation of free lime. Sulfation of CaO occurring in calcium carbonate and dolomite takes place according to the following reactions:



and



Therefore, the mechanism of sulfation of carbonate minerals at atmospheric and pressurized combustion is different.

Direct sulfation of carbonate minerals in pressurized combustion conditions of fuel has been shown in many studies [19, 32–36, a.o.].

The study [32] demonstrated that a film of calcium sulfate with low diffusion resistance forms on the surface of calcium carbonate particle as a result of CO₂ release during a reaction between CaCO₃, SO₂ and O₂. The same study showed that the extent of sulfation increases with a decrease in particle size and an increase in temperature, until it reaches an equilibrium value corresponding to the partial pressure of carbon dioxide. The initial porosity plays also an important role in the sulfation process. Content of magnesium carbonate (for instance, in dolomite) has a significant effect on porosity of particles. This is mainly caused by the fact that partial pressure of CO₂ in flue gas remains below the dissociation pressure of MgCO₃, and, therefore, magnesium oxide forms, which increases particle porosity and enhances diffusion of SO₂ and O₂ to the active surface.

A study by Lisa and others [34] showed that direct sulfation of calcium carbonate depends on partial pressure of SO₂, but is not much affected by the concentration of oxygen and carbon dioxide in the medium surrounding the particle.

Concentration of Carbon Monoxide and Hydrogen Chloride in Oil Shale Flue Gas

Carbon Monoxide (CO) is a product of incomplete combustion of fuel. Carbon monoxide can form both at thermal decomposition of organic matter of fuel and at combustion of char. Heat effect of combustion of CO is formed a part of heat losses boiler due to incomplete combustion (Q_3). Carbon monoxide is a toxic compound.

The concentration of CO in flue gas leaving the boiler is determined by completeness of fuel combustion, which depends on temperature and oxygen concentration (excess air factor). Combustion rate of CO is influenced by the presence of water vapor.

Formation conditions of combustible mixture in the furnace chamber are of great, often even of crucial, importance. Non-uniform distribution of air can cause appearance of local reducing zones containing CO. Decrease in the average value of excess air factor often increases the probability of carbon monoxide formation.

At PF firing of oil shale only small amounts of CO can occur in the zone of intensive combustion of volatile matter. Emission of CO in normal operating conditions in oil shale PF boilers is negligible. However, flue gas contains some traces of CO due to non-uniform distribution of air (for instance, some burners are not in operation), or at low load of the boiler, when combustion process is not uniform and temperature is low.

The emission of CO formed at oil shale fluidized bed combustion has been determined in a CFBC boiler with thermal capacity of 1 MW [28]. Average concentration of CO in dry flue gas (contained 6% O_2) at combustion temperature 850 °C was approximately 150 mg/m³. As it turned out, emission of CO at lower combustion temperatures was higher. Similarly, emission of CO increased at utilization of coarser particles of fuel (particles larger than 25–35 mm).

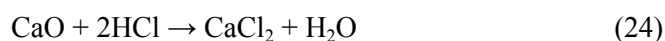
Carbon monoxide emission measurements in an industrial CFBC oil shale boiler showed that CO emission was very low being in the range of 40–60 mg/m³ (concentration of O_2 in dry flue gas 6%). Emission of carbon monoxide at CFBC of different fuels is between 30–240 mg/m³ (dry flue gas contains 6% O_2). Measurements showed that emission of CO at oil shale combustion in a classical PFBC pilot device with thermal capacity of 1 MW (pressure and temperature in the combustion chamber were 1.5 MPa and 840 °C, respectively) was CO <4 mg/m³.

Hydrogen Chloride (HCl) is an acidic compound. Presence of HCl in the atmosphere increases air acidity and decreases pH of precipitation. Chlorine in organic matter is the source of hydrogen chloride in oil shale flue gas. Assuming that all Cl present in oil shale is released into flue gas as HCl during combustion, the concentration of hydrogen chloride would be about 600 mg/m³ (dry flue gas contains 6% O_2). The actual concentration of HCl in flue gas is remarkably lower.

Content of HCl in flue gas leaving a PF oil shale boiler is about 100–200 mg/m³. Therefore, about 20–35% of chlorine present in oil shale is emitted as HCl. The rest of Cl is bound by ash during processes taking place in the boiler furnace and gas passes. Chlorine is mainly concentrated in finer ash particles. Reactions between chlorine and alkali metals in the high-temperature region of the furnace play an important role during PF of oil shale. Chlorides of alkali metals (mainly potassium) formed in the high-temperature medium in the furnace desublimates in the low-temperature region of the gas passes as aerosols or precipitate on the surface of finer ash particles as condensation centers. A part of Cl is also bound with calcium.

Emission of hydrogen chloride at oil shale combustion has been determined in a CFBC with the capacity of 1 MW_{th}. Concentration of HCl (before dust collector filters) was 60–245 mg/m³ (dry flue gas contained 6% O₂). Great differences in the concentration of HCl are caused by special features of combustion devices and various combustion regimes. These results show that also in FBC conditions a considerable part of chlorine is bound with ash. In this case, most of chlorine is concentrated in finer ash particles.

While at PF of oil shale, volatilization of alkaline metals plays an important role in redistribution of chlorine, at low-temperature FBC, where volatilization of alkaline metals from mineral matter is low, heterogeneous reactions between ash particles and HCl dominate in the process. This was shown in a study performed by Arro and coworkers [28] who noticed that concentration of HCl in flue gas dropped notably after passing through the bag filter (in some cases the concentration changed more than 10 times). Taking into account high content of free calcium oxide in oil shale ash of the FBC process, one can assume that the following reaction takes place:



Several studies have shown that Reaction (24) occurs at a high rate at temperatures below <650 °C.

Emission of Carbon Dioxide

Carbon dioxide (CO₂) belongs to the group of greenhouse gases. Its content in the air atmosphere may influence the temperature regime of the environment. Carbon dioxide is formed in combustion reactions of organic carbon and from carbon-containing minerals, which are present in fuels mainly as carbonates. Full conversion of organic carbon to CO₂ is possible only at complete combustion. The release of carbon from minerals (mainly as CO₂) is determined by fuel behavior in combustion processes.

Carbon in oil shale is present both in organic and mineral part. Organic carbon is expressed as carbon content of organic part, and it may be converted into CO₂ during oxidation reactions. In any case, a part of organic

carbon does not react with oxygen (in modern combustion devices its share is negligible), or it is oxidized to carbon monoxide. Therefore, the actual amount of CO₂ formed from organic carbon differs from the theoretically possible amount according to the reaction: $C + O_2 \rightarrow CO_2$. Carbon dioxide formed from organic carbon is called organic carbon dioxide.

Mineral carbon is bound with mineral matter of fuel, mainly carbonate minerals in oil shale. The amount of mineral carbon in fuel is usually expressed as mineral or carbonate carbon dioxide (CO₂)_c. Mineral carbon dioxide is completely or partially released from minerals during their thermal decomposition or during chemical attachment reactions. Carbon dioxide formed from carbonate minerals is called mineral or carbonate carbon dioxide.

The amount of CO₂ formed from organic carbon does not depend much upon the combustion technology of fuel. However, combustion technology may strongly influence the emission of mineral CO₂. Concentration of mineral CO₂ formed from carbonate compounds is determined by conditions of thermal decomposition of minerals and also by direct combination of gaseous components present in flue gas and CO₂-containing minerals. Possibility of those reactions depends on CO₂ partial pressure in the gaseous medium. The equilibrium pressure of carbon dioxide that determines thermal decomposition of carbonate minerals is the most important factor influencing the process.

Concentration of CO₂ in flue gas at combustion of a fuel containing carbonate minerals (like oil shale) can be determined by the following expression:

$$V_{CO_2} = 0.01866 \varphi C^r + 0.0051 k_{CO_2} (CO_2)_c^r, \text{ m}^3/\text{kg} \quad (25)$$

or, taking into account the elemental composition of oil shale,

$$V_{CO_2} = 0.0145 \varphi R^r + 0.0051 k_{CO_2} (CO_2)_c^r, \text{ m}^3/\text{kg} \quad (26)$$

where φ – extent of conversion of organic carbon into carbon dioxide;

C^r – carbon content of fuel, %;

k_{CO_2} – extent of decomposition of carbonate minerals;

$(CO_2)_c^r$ – content of mineral carbon dioxide in fuel, %;

R^r – organic matter content of oil shale, %.

The total volume of CO₂ released per mass unit of oil shale depends on the amount of organic matter, content of mineral carbon dioxide and decomposition extent of carbonates. The amount of organic carbon in oil shale is comparable to the organic carbon quantity in liquid fuels, because these fuels have approximately the same mass ratio of C/H. The concentration of mineral CO₂ in flue gas can be expressed by a product $k_{CO_2} \cdot (CO_2)_c^r$, which is strongly influenced by the extent of carbonate decomposition depending on the combustion technology.

The influence of extent of carbonates decomposition on concentration of carbon dioxide in flue gas can be expressed by the following formula:

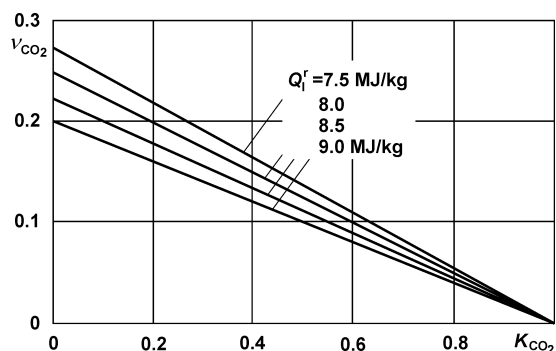
$$v_{\text{CO}_2} = 1 - \frac{(V_{\text{CO}_2})_{k_{\text{CO}_2}}}{(V_{\text{CO}_2})_{k_{\text{CO}_2}=1}} \quad (27)$$

where $(V_{\text{CO}_2})_{k_{\text{CO}_2}=1}$ – the highest possible concentration of CO_2 in flue gas, which corresponds to complete decomposition of carbonate minerals ($k_{\text{CO}_2} = 1$), m^3/kg ;

$(V_{\text{CO}_2})_{k_{\text{CO}_2}}$ – concentration of CO_2 in flue gas, which corresponds to the arbitrary decomposition extent of carbonates, m^3/kg .

Basing on the relationship between the composition of oil shale and its heating value, Fig. 14 shows the dependence between factor v_{CO_2} and the extent of carbonate decomposition at three different lower heating values. If carbonate minerals do not decompose ($k_{\text{CO}_2} = 0$), the emission of CO_2 from oil shale, whose heating value is 8.5 MJ/kg, is by about 22% lower compared to conditions when $k_{\text{CO}_2} = 1$. Decomposition extent of carbonate minerals at different combustion technologies of oil shale is following: for PF 0.97; for CFBC 0.65–0.85; for PFBC 0.30–0.40.

Fig. 14. Changes in carbon dioxide concentration depending on extent of carbonates decomposition at different heating values of oil shale



Emission of Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are toxic high-molecular compounds consisting of carbon and hydrogen. Many of these are carcinogenic. One of the best-known carcinogenic compounds is benzo[a]pyrene (B[a]P) $\text{C}_{20}\text{H}_{12}$, whose molecular mass is 252, melting and boiling temperature 179 and 480–500 °C (according to different sources), respectively.

Table 1. Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in Oil Shale Flue Gas after Electrostatic Precipitator of the Boiler (Oxygen Concentration in Dry Flue Gas 6%), ng/m³

Compound	Molecular mass	Activity*	Boiler load 0.9			Boiler load 1.0	
			Excess air factor in burner				
			1.13	1.25	1.38	1.24	1.26
9,10-Dimethyl anthracene	206	+	434	366	205	–	–
Fluoranthene	202	–	1072	882	663	1046	1347
Pyrene	228	–	434	454	364	372	805
Benzo[a]anthracene	228	+	434	187	218	51	148
Chrysene	228	–	523	247	223	509	948
Triphenylene	228	+	600	295	221	434	923
Naphthalene	228	–	179	175	129	238	396
Benzo[b]fluoranthene	252	++	256	182	148	72	109
Benzo[k]fluoranthene	252	–	293	166	220	428	66
Benzo[a]pyrene	252	+++	89	32	36	34	72
Perylene	252	–	–	–	–	80	280
20-methylkolanthrene	268	+++	–	–	–	57	106
Benzo[g,h,i]perylene	276	–	370	132	199	33	89
Dibenzo[a,e]anthracene	278	+	–	–	–	37	30
ΣPAH			4686	3118	2628	3393	5319
ΣPAH _{cars} **			1814	1063	829	686	1388

* “–” passive; “+” – active.

** Carcinogenic compounds.

PAHs can be also present in fuel organic matter. Concentration of B[a]P in dry oil shale has been measured to be 4.3 µg/kg. PAHs are mostly formed during thermal decomposition of organic matter of fuel and during secondary pyrolysis. Therefore, PAHs content of heavy fuel oil produced by thermal treatment of oil shale can reach 15 mg/kg.

There are three different ways in which PAHs can get into flue gas: i) along with compounds formed during thermal decomposition of fuel organic matter (primary pyrolysis), ii) during pyrolysis of the products of primary pyrolysis (secondary pyrolysis), iii) from hydrocarbon products of the combustion process.

The main hydrocarbon, a product of combustion, from which the PAHs can form is acetylene C₂H₂.

The highest concentration of PAHs in flue gas occurs in the initial stage of combustion in the burning region of volatile matter, or in the case of multy-stage combustion, in the oxygen-lean region. In the subsequent run of combustion at a sufficient concentration of oxygen oxidation of PAHs occurs, and their amount in flue gas starts to decrease. It is obvious that conversion of PAHs to carbon dioxide and water vapor in the oxygen-containing medium depends on temperature and partial pressure of oxygen in flue gas.

Emission of PAHs, measured in flue gas after electrostatic precipitator in the PF oil shale boiler TP-101 at its different loads and different values of excess air factor, are presented in Table 1.

The content of B[a]P in slag, and ashes taken from different fields in the electrostatic precipitator, and in ash particles after the electrostatic precipitator of the PF oil shale boiler TP-101 has been studied more thoroughly in [9, 11]. The results show that the content of B[a]P in ash very strongly depends on fuel particle size. Figure 15 gives the amount of B[a]P in the ash from the electrostatic precipitator as a function of particle median size. It is evident that B[a]P mostly concentrates in the finest particles as autonomous condensation centers. The concentration of B[a]P in slag (median particle size 230–270 μm) is 23 ng/kg, in ash from different fields of the electrostatic precipitator (median particle size 15–24 μm) 50–55 ng/kg, and in fly ash particles after the electrostatic precipitator (median particle size 4–5 μm) 380 ng/kg. The last number is 7–10 times higher than the content of B[a]P in the finest fraction of ash particles precipitated in the last field of the electrostatic precipitator.

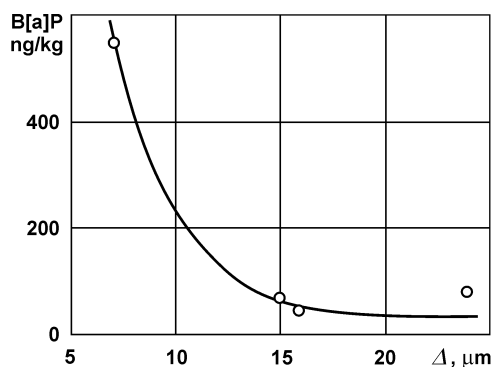
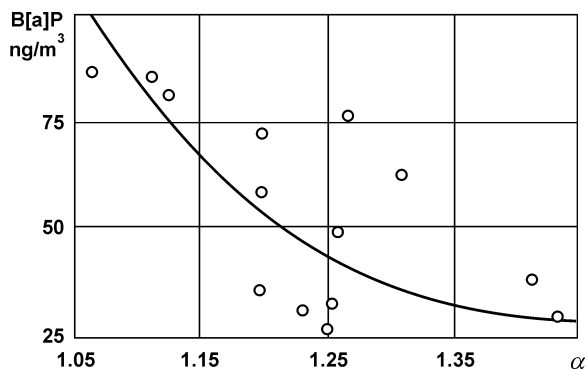


Fig. 15. B[a]P content of the ash from electrostatic precipitator as a function of particle size

Fig. 16. Concentration of B[a]P in flue gas leaving electrostatic precipitator as a function of excess air factor in burners. Volume of flue gas has been reduced to 6% oxygen concentration in dry flue gas



An important parameter that influences the emission of PAHs is partial pressure of oxygen in flue gas in the zone of intensive fuel combustion. An increase in oxygen concentration intensifies oxidation of PAHs, and their quantity in flue gas decreases. This follows from Fig. 16 which shows the concentration of B[a]P in flue gas (O_2 concentration in dry flue gas 6%) at the exit of the electrostatic precipitator as a function of excess air factor in burners. Data in Table 1 point at a similar tendency.

Concentration of PAHs in flue gas depends on the efficiency of electrostatic precipitators after the boiler. The higher the capturing efficiency of ash, the more PAH compounds are separated from flue gas, and the less PAHs are emitted.

Oil shale combustion experiments performed in the VVT laboratory on a circulating fluidized combustor with thermal capacity of 50 kW showed that the total content of PAHs in bottom ash and fly ash was 49 and 104 $\mu\text{g}/\text{kg}$, respectively. The content of B[a]P in bottom ash was <0.5 , and in fly ash 3 $\mu\text{g}/\text{kg}$.

The experiments performed by Mastral and coworkers [37, 38, a.o.] showed results similar to those presented in Fig. 16. A decrease in oxygen concentration in flue gas increases the content of PAHs in ash particles at burning coal in a FBC unit. The change in oxygen concentration from 5 to 10% reduces the content of B[a]P from 3.4 to 0.5 $\mu\text{g}/\text{kg}$. However, the temperature dependence of the amount of B[a]P in ash on the temperature of fluidized bed has a complicated shape. At temperatures >750 °C, both the total content of PAHs and content of B[a]P in the ash decreases with an increase in temperature.

Trace Elements in Oil Shale Ash

Solid fuels contain, in addition to macrocomponents, also large amounts of trace elements including heavy metals. Trace elements are the elements whose content in the fuel is below 1,000 mg/kg (usually below 100 mg/kg). Some trace elements and compounds containing them are toxic. Trace elements are mainly constituents of fuel mineral matter. However, some of them can belong also into composition of organic matter (for instance, Be, Cr, Ni, Sb).

Release of trace elements and their combination with each other and with other components of fuel takes place both during combustion in the furnace and also in the gas passes after the furnace. Depending on conditions they would volatilized in the high-temperature medium, desublimates as independent aerosols in gas passes, condense on fine ash particles or remain in the gaseous phase.

The behavior of trace elements depends, besides fuel composition, also on temperature, oxygen concentration in flue gas (excess air factor), and resident time. A part of trace elements precipitates out in gas passes along with ash particles, but some part is emitted with flue gas from the stack. Combustion technology of fuel (various combustion temperatures and burning conditions) has a significant effect on the behavior of trace elements. The efficiency of the system catching particulates after the boiler plays also an important role.

Table 2. Content of Heavy Metals Precipitated in Ash Flows along Gas Pass of Oil Shale PF Boiler TP-67, µg/kg

Substance	Share in precipitation, %	Pb	Cd	Zn	Cu	Ni	Cr	Co	As	Hg	Mn	V	Tl	Sb
Dry oil shale		30	<0.4	84	7.5	15	17	3.0	21	0.22	340	24	0.5	<0.4
Slag	39.3	24	<0.3	96	9.9	27	19	4.5	16	–	700	33	<0.1	0.4
Ash from hopper under superheater	3.1	44	<0.4	101	11	29	23	4.9	18	–	700	40	<0.2	0.8
Ash from hopper under economizer	4.7	34	<0.3	92	9.5	26	19	4.5	14	–	690	35	<0.002	<0.6
Ash from cyclone	32.2	45	<0.3	93	9.3	26	21	4.5	16	–	650	38	0.3	0.6
Ash from electrostatic precipitator:														
1st and 2nd fields	14.1	130	<0.8	160	9.6	31	33	5.3	42	–	470	52	1.6	0.9
3rd and 4th fields	0.7	210	1.8	310	12	38	49	6.6	59	–	440	73	2.3	1.1
Ash after electrostatic precipitator:														
>4–5 µm	1.5	200	1.7	300	13	38	58	6.6	68	0.1	350	81	2.7	2.0
<4–6 µm	0.5	380	3.5	380	18	45	48	7.4	92	0.3	340	210	7.5	2.4

The amounts of trace elements in oil shale, their behavior and distribution has been studied by Pets, Vaganov, Haldna, Aunela-Tapola, Fransen and others [39–44]. Depending on the behavior of trace elements at high-temperature conditions of PF combustion, they were divided by Pets and others [39] into three groups:

- i) easily volatile (As, Hg, Sb, Se, Br, Rb, Db, Zn, Pb, Cd, Cs),
- ii) moderately volatile (Sr, Ba, Sc, Y, Co, Ni, Cu), and
- iii) hardly volatile (Th, U, Zr, V, Mo, Cr) elements.

The largest redistribution of trace elements concerns easily volatile compounds whose concentration in fly ash particles increases along the gas passes. Some of easily volatile trace elements can pass through ash filters as aerosols and can be carried to the air atmosphere along with flue gas.

Table 2 presents the content of easily volatile heavy metals in ash flows along the gas passes of an oil shale PF boiler TP-67 [44].

An overview about the changes taking place with easily volatile heavy metals along the gas passes of a boiler is given in Table 3. The table gives data about relative enrichment factor EF expressing enrichment of ash with heavy metals (this is the ratio of heavy metal content of a given ash fraction to the amount of the same metal in the laboratory ash).

Factor EF compares heavy metal content of the ash fraction precipitated in the gas passes of the boiler and the content of the same heavy metal in fuel. Therefore, the average content of a given component in oil shale is the basis for comparison. Actually, the redistribution of trace elements, present in oil shale, between ash fractions starts already in the grinding processes before combustion. Because the components of oil shale behave differently during grinding, the distribution of trace elements, bound with different constituents of fuel, between ash fractions is not similar. As most of trace elements are concentrated into the sandy-clay part of oil shale, their behavior during grinding is similar to the behavior of minerals of the sandy-clay part. There are no exact data about distribution of trace elements between different fractions of pulverized oil shale.

Table 3. Enrichment Factor EF of Ash Fractions with Heavy Metals

Substance	Pb	Cd	Zn	Cu	Ni	Cr	Co	As	Hg	Mn	V	Tl
Slag	0.3	0.3	0.5	0.6	0.8	0.5	0.7	0.3	–	0.9	0.6	–
Ash from hopper:												
under superheater	0.6	0.5	0.5	0.6	0.9	0.6	0.7	0.4	–	0.9	0.6	–
under economizer	0.5	0.3	0.5	0.6	0.8	0.5	0.7	0.3	–	0.9	0.6	–
Ash from cyclone	0.6	0.4	0.5	0.5	0.8	0.5	0.7	0.3	–	0.8	0.7	0.3
Ash from electrostatic precipitator:												
1st and 2nd field	1.9	1.0	0.8	0.6	0.9	0.8	0.8	0.9	–	0.6	0.9	1.2
3rd and 4th field	3.0	2.1	1.6	0.7	1.1	1.2	1.0	1.2	–	0.6	1.3	2.1
Ash after electrostatic precipitator:												
>4–5 μm	2.9	2.0	1.6	0.7	1.1	1.5	1.0	1.4	0.3	0.5	1.5	2.7
<4–6 μm	5.5	4.2	2.0	1.0	1.3	1.2	1.1	1.9	0.6	0.4	3.8	6.7

The largest ash flow is slag precipitated onto the furnace hopper-shaped bottom; however, the content of trace elements in slag is much less than their amount in fuel. Cyclone ash contains already somewhat more heavy metals. The largest portion of heavy metals is concentrated in ash particles cached in electrostatic precipitator.

Data in Table 3 show that heavy metals like Pb, Cd, Zn, Cr, AS, V and Tl concentrate into finer fractions of ash. According to the data by Pets and others, Sb compounds behave similarly. However, the content of these compounds in slag is significantly less. The presence of Hg in finer ash particles is low due to its high volatility. Despite the fact, according to classification by Pets and others, that vanadium belongs to the class of hardly volatile trace elements, its content in finer ash fractions is relatively high. This is caused mainly by the formation of vanadium oxide, which condenses at low temperatures. This has been also proved by combustion experiments performed with vanadium-rich heavy fuel oil. The content of manganese is higher in coarser slag compared to smaller ash particles.

The results presented considered distribution of trace elements by individual elements occurring in fuel. However, such an approach leaves open the question: in which compound these elements are present in the gas pass under various conditions. The formation of compounds from trace elements in the state of thermodynamic equilibrium of the system has been examined in several studies [44–47, a.o.].

This theoretical study is based on determination of the composition of compounds containing trace elements corresponding to the minimum value of Gibbs free energy for the system. This methodology has been applied in the study [44] for oil shale. The results of the study are presented below.

- Below 1400 K, the only one stable arsenic compound is $\text{Ca}_3(\text{AsO}_4)(\text{s})$, and above that temperature $\text{AsO}(\text{g})$.
- Below 600 K, a stable cadmium compound is $\text{CdCl}_2(\text{s})$, and above that temperature (up to 1150 K) also the same compound but in the gaseous phase. Above this temperature, Cd is stable as metal in the gaseous phase. At temperatures $T > 1000$ K a small amount of cadmium can be present as $\text{CdO}(\text{g})$.
- Below 1100 K, cobalt exists as $\text{Co}_3\text{O}_4(\text{s})$, and at higher temperatures as $\text{CoO}(\text{s})$. At temperatures above 1200 K, a small portion of Co is present as $\text{CoCl}_2(\text{g})$ and $\text{Co}(\text{g})$.
- Chromium occurs (up to 700 K) mainly as $\text{Cr}_2\text{O}_3(\text{s})$. At higher temperatures also $\text{CrO}_2(\text{OH})_2(\text{g})$ begins to form, and at temperatures above 1400 K the following compounds are present in the gaseous phase: $\text{CrO}(\text{OH})$, $\text{CrO}_2(\text{OH})$, $\text{CrO}(\text{OH})_2$ and CrO_3 .
- Mercury is present in HgCl_2 at temperatures below 800 K, however, at temperatures above 850 K it exists mainly as mercury vapor.
- Nickel is present as $\text{NiO}(\text{s})$ up to temperatures 1500 K, but at higher temperatures $\text{NiO}(\text{g})$, $\text{Ni}(\text{g})$, and $\text{NiCl}(\text{g})$ can be found.

- The main lead compound at temperatures below 1100 K is $\text{PbCl}_4(\text{g})$. If temperature increases over 1300 K, $\text{PbO}(\text{g})$ becomes predominant. At around 1200 K $\text{PbCl}_2(\text{g})$ dominates among lead compounds.
- Selenium is present as $\text{SeO}_2(\text{g})$ up to 1300 K. Above that temperature the oxide loses one oxygen atom, and $\text{SeO}(\text{g})$ is formed.
- Up to 1400 K, $\text{ZnO}(\text{s})$ is a stable zinc compound existing in flue gas, at higher temperatures zinc is present as zinc vapor. Between 600–1600 K zinc can also exist as $\text{ZnCl}_2(\text{g})$.
- It has been shown theoretically that chlorine influences significantly the behavior of trace elements like Co, Ni, Pb, and Zn during oil shale combustion. Formation of the following stable chlorine compounds is possible: CoCl_2 , NiCl , NiCl_2 , PbCl , PbCl_2 and ZnCl_2 . The influence of chlorine on behavior of trace elements was also shown by Yan and coworkers [47]. They demonstrated also an important influence of excess air factor on the behavior of trace elements in boiler gas passes.

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