

## OIL SHALE COMBUSTION TECHNOLOGY

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*The research activities at Thermal Engineering Department of Tallinn Technical University conducted in the field of ash deposit formation, heat transfer, high-temperature corrosion and wear of heat-transfer surface metal were aimed at developing constructions, installation schemes and calculation methods of boiler burning low-grade fuel. On the basis of this research activity, oil shale boilers for both the Baltic and Estonian power plants were designed and erected.*

### Behavior of Fuel Mineral Matter in Combustion

Combustion of fuels concerns not only oxidation of the fuel organic components, but also simultaneous phenomena in the mineral matter. These processes determine quite a lot of the properties of ash formed at the burning of fuel.

The oil shale ash melting characteristics ( $t_A$  – the initial deformation temperature;  $t_B$  – the softening temperature and  $t_C$  – the fluid temperature) depending on the calcium oxide content of ash have been investigated. Also the relative amounts of separate melting state phases in ash depending on temperature were determined. These results have been the basis for explaining the fouling mechanism of the steam boiler heat-transfer surfaces in the flue-gas high-temperature region.

In Figure 1 the dependence of relative amounts (mass%) of integrated fusion states of oil shale ash upon temperature is given [1]. The areas I, II, III and IV represent solid, deformed, soft and molten state of ash, respectively. For instance, at  $t = 1200$  °C about 8% of ash is in molten, 8% in soft, 52% in deformed and 32% in solid state. Deposition of the melted ash particles onto the heat-transfer surface tubes is possible at the flue-gas temperature  $t > 1030$ – $1050$  °C.

Calcium oxide present as calcium carbonate and dolostone is the most important component in oil shale mineral matter. The behavior of carbonates

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in combustion processes is of great importance regarding  $\text{SO}_2$  and  $\text{CO}_2$  emissions, heat release in burning, and ash deposit formation on heat-transfer surfaces. The behavior of carbonate minerals depends upon the temperature,  $\text{CO}_2$  partial pressure in the flue gas, and also on the ratio between calcium oxide and sandy-clay minerals in ash [2, 3].

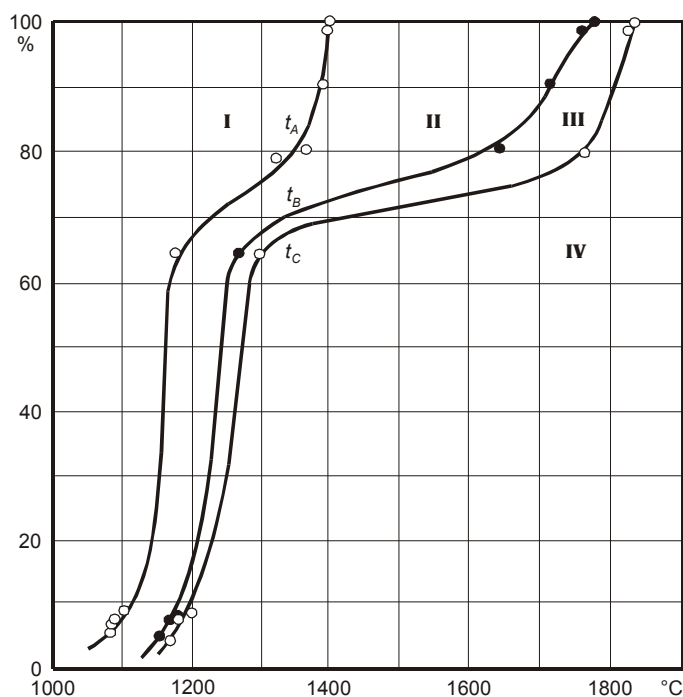


Fig. 1. The dependence of relative amounts (mass%) of integrated fusion states of oil shale ash upon temperature

Decomposition of carbonates in the combustion process of the fuel is characterized by the extent of carbonate decomposition (ECD). At burning oil shale the ECD is in the following range: PF (pulverized firing) – 0.97 to 0.99; AFBC (atmospheric fluidized-bed combustor) – 0.80 to 0.90 and PFBC (pressurized fluidized-bed combustor) – 0.30 to 0.40.

The behavior of  $\text{CaO}$  is determined mainly by the flue-gas temperature in combustor. A part of calcium oxide originating from the carbonate stays in free form, a part combines with sandy-clay minerals and forms new minerals, such as  $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$ ,  $\text{CaO} \cdot \text{Al}_2\text{O}_3$ ,  $3\text{CaO} \cdot 2\text{SiO}_2$  etc., or reacts with sulphur oxides [4]. In PF conditions 25 to 30% of total calcium oxide stays in free form.

Intensive formation of new minerals during PF makes the ash less sensitive to the capture of sulphur dioxide from flue gas. Free calcium oxide is the most active  $\text{SO}_2$ -binding component of ash. For instance, the  $\text{Ca/S}$  molar ratio of oil shale in its initial state is approximately 8 to 10. The same

ratio determined on the basis of free CaO in ash under PF combustion conditions is only 2 to 2.5, which is not enough to full capture of SO<sub>2</sub> from the flue gas. The real sulphur dioxide binding factor for oil shale ash is in the range between 0.75 to 0.85, and SO<sub>2</sub> emission is in the range 400–600 ppm (calculated to 6% oxygen in dry flue gas).

At AFBC, due to the low combustion temperature, the formation of new minerals is not intensive, and CaO stays largely in the free form. This makes the ash very reactive towards SO<sub>2</sub> at its capture from the combustion products. The tests made with oil shale at ACFBC (atmospheric circulating fluidized-bed combustor) show that the sulphur dioxide emission is below 5 ppm (calculated to 6% oxygen in dry flue gas).

The behavior of sulphur in fuel combustion depends on oxygen partial pressure in the flue gas as well as on temperature [3].

Organic sulphur is released during combustion in pure form or as hydrogen sulphide, reacts with oxygen and goes mainly into the flue gas as SO<sub>2</sub>. There is also the possibility that a part of the organic sulphur rests in ash in the sulphate form.

Depending on the oxygen concentration and temperature, compounds like SO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> can be finally formed from pyrite. During these conversions the ferric monosulphide (pyrrhotite) FeS is formed as an intermediate product, which has a very important role in boiler water-wall tube fouling processes [4].

Figure 2 gives the balance of sulphur depending upon the excess air factor at burning pulverized oil shale [4]. The curves correspond to the moment 0.8 s after the dust inlet to the combustor. In the figure:  $m_{s-a}$  – sulphate sulphur,  $m_{s-i}$  – sulphide sulphur (mainly as FeS) and  $m_v$  – volatilized sulphur (mainly as SO<sub>2</sub> in flue gas). Obviously  $m_{s-a} + m_{s-i} + m_v = 1$ .

It is characteristic that the content of sulphide sulphur in ash particles continuously decreases with increasing of the excess air factor, but at the same time the quantities of sulphate and volatilized sulphur increase.

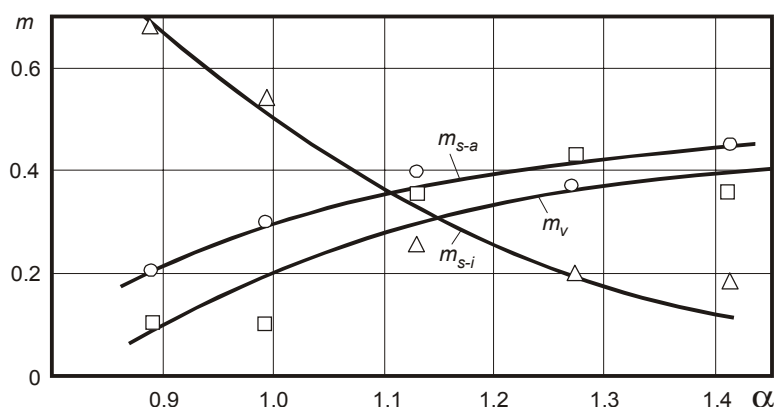


Fig. 2. The dependence of sulphur mass balance upon the excess air factor at burning pulverized oil shale

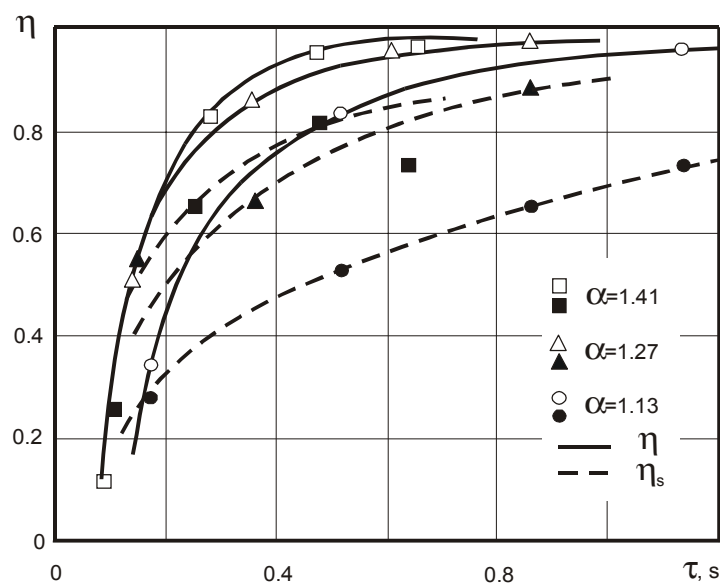


Fig. 3. The dependence of organic carbon ( $\eta$ ) and sulphide sulphur ( $\eta_s$ ) combustion rates upon time and excess air factor at burning pulverized oil shale

Oxidation of sulphide sulphur occurs much less intensely than combustion of the organic carbon as seen from Fig. 3.

Alkali metals and chlorine present in fuels favor the formation of ash deposits and intensify the high-temperature corrosion and wear of boiler heat-transfer surfaces. The most important alkali metal in oil shale is potassium present as aluminosilicates. Chlorine is bound in fuel organic matter. In the high-temperature combustion process (for instance, PF), volatilization of potassium from minerals and release of chlorine from organic matter take place. The intensity and extent of volatilization of alkali metals strongly depend upon the temperature and surrounding atmosphere. The degree of potassium volatilization within a reducing environment is greater than within an oxidizing atmosphere.

For instance, it was established that the intensity of alkali metals volatilization in the carbon monoxide environment is about fifty times higher than in the air. The significant influence of the surrounding medium on the volatilization of potassium compounds is explained by destroying effect of reducing components (mainly CO) on the crystal lattice of the minerals containing potassium and oxygen. The removal of oxygen from the crystal promotes the reduction of the bound atoms of alkali metals.

The behavior of alkali metals during the combustion process can be characterized by their solubility in the boiling water. The alkali metal compounds which were subjected to deeper changes during combustion of the fuel, were also more water-soluble.

Proceeding from that, alkali metal compounds can be divided into the following three groups:  $p_{s,l}$  – easily water-soluble,  $p_{s,h}$  – heavily water-soluble and  $p_{s,n}$  – water insoluble compounds. Obviously  $p_{s,l} + p_{s,h} + p_{s,n} = 1$ .

In the balance of water-soluble potassium presented in Fig. 4 the curves correspond to the moment 0.8 s after the dust inlet to the combustor. With the increase in oxygen concentration in the flue gas, the amount of the easily and heavily water-soluble potassium compounds decrease, but those of insoluble ones go up simultaneously. Such behavior of alkali metals at excess air shows the great influence of the air regime on the alkali metal form in ash. It is in accordance with the influence of the surrounding environment on volatilization of alkali metals from aluminosilicate minerals.

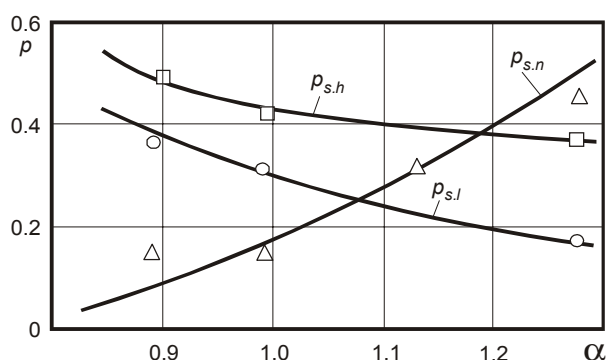


Fig. 4. The dependence of potassium balance upon excess air factor at burning pulverized oil shale

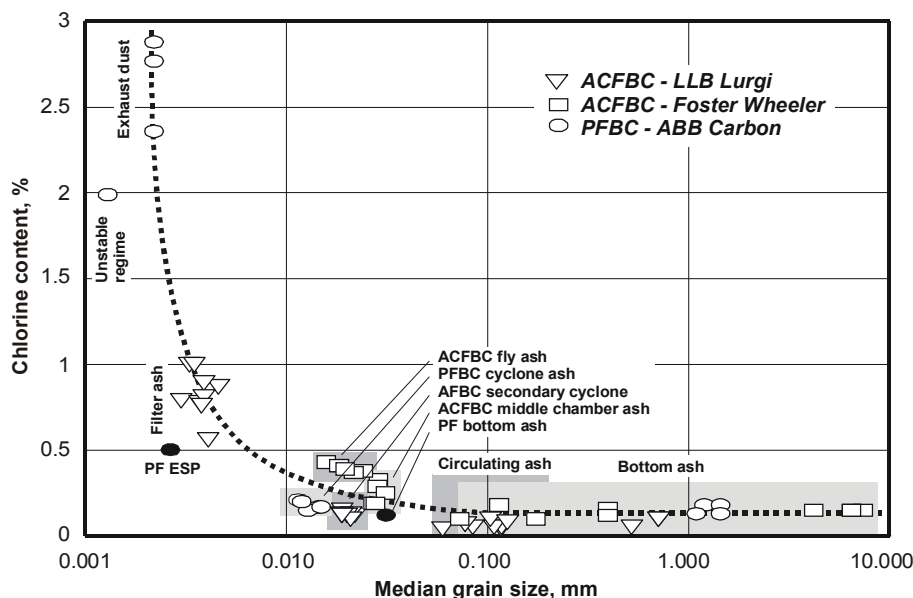


Fig. 5. Chlorine content of oil shale ash particles depending upon median grain size

Chlorine from the organic part of oil shale is released as HCl which further reacts with alkali metals and sulphur oxides. Finally, alkali metal chlorides and sulphates are formed. Independently on oil shale combustion technology, the chlorine concentration is highest of the finest ash fractions [5, 6] (Fig. 5). A very sharp increase in chlorine quantity starts with particle median grain size 10 to 20  $\mu\text{m}$ . At burning oil shale in AFBC, the maximum content of Cl (reaching 2.5 to 3%) is found in the filter fly-ash particles (2 to 3  $\mu\text{m}$ ).

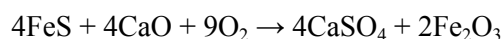
### **Fouling of Water-Wall Tubes and Heat Transfer**

The mechanism of ash deposit formation on water-wall tubes of oil shale boilers depends upon the flue-gas temperature in the combustor (flame radiation intensity on the wall is the indicator of temperature level in combustor). Iron, calcium oxide and alkali metal compounds are the main components determining the fouling.

Ash deposits on water-wall tubes at oil shale PF are distinguished by their high content of iron oxides, especially on the flame high-radiative zones. The iron quantity in deposits is very sensitive to burning conditions of the fuel, which is related to existing reducing and semi-reducing environment near the water-wall tubes. Formation of such eutectic systems as FeS–FeO, FeS–S and FeS–Fe has a great effect on fouling process. From these systems the first complex is the most important one. All these complexes are intermediate states of oxidation of sulphide sulphur and have fusion points below 1000 °C. These complexes are transported onto the wall tubes where ferric sulphide oxidizes to Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>. The reaction extent and intensity depend on the deposit layer temperature and oxygen partial pressure in flue gas. As the deposit layer temperature near the tube wall is much lower than in the outside area, the deposits of the lower layer often consist of residual sulphide sulfur and FeO.

Sulphation of calcium oxide and condensation or desublimation of potassium sulphate also play an important role in fouling processes of water-wall tubes. Potassium sulphate is formed from volatilized potassium components.

In conditions when calcium oxide and ferric monosulphide are simultaneously transported onto the surface, the following sulphation reaction is possible:



The combustor aerodynamic characteristics (design, size, location of burners), fuel burning conditions (mainly the fuel/air ratio), and especially the technology of cleaning heat-transfer surfaces from ash deposits are also factors determining the fouling intensity of the radiative heat-transfer

surfaces. The ash deposits formed on the water-wall tubes have typically a layer structure.

Heat transfer in the combustor is a non-stationary process due to changes in time of thermal resistance and surface emissivity of the ash-deposit layers formed on tubes [4]. The non-stationarity of heat transfer can be regarded as a result of temporal changes in the flue-gas temperature after the combustor.

It was established that the radiant heat flux density in the combustor increases with the increase in the distance from the wall tubes. The ratio of radiant heat flux intensity on the combustor wall to the heat flux intensity on the distance of the thermal boundary layer is used to characterize the non-isothermality rate.

The thermal boundary layer located at the combustor wall adds the conventional resistance to the heat flux from flame onto heat-transfer surface. Proceeding from the conventional thermal resistance conception of the thermal boundary layer it is possible to estimate the radiative heat-transfer intensity in combustor. The conventional thermal resistance of the non-isothermal boundary layer is determined by the convective mass transfer in combustion chamber and it is influenced by such factors as burner location and design, combustor heat load, etc.

### **Fouling of Convective Tubes and Heat Transfer**

The fouling of the convective heat-transfer surfaces of the boiler has been theoretically and experimentally studied and a mathematical model has been proposed.

The factors that influence the ash-deposit layer formation on boiler heat-transfer surface tubes and its thermal resistance are the following: ash particle size, flue-gas velocity (kinetic energy of particles), aerodynamic conditions, chemical and mineralogical composition of ash particles and also the composition of the flue gas. Ash deposits on the convective heat-transfer surfaces can be divided into the three following groups: unbound, loose and hardbound deposits. The loose and hardbound deposits form as a result of reactions between chemically active ash particles already deposited on the surface and flue-gas components.

The transfer of ash particles from flue gas onto the tube surface takes place by inertia and diffusion. Also the influence of electrostatic forces cannot be excluded. In the first case, due to the great kinetic energy of the particles, they leave the flow because the trajectory of the stream is curving near the tube, and ash particles can make a contact with the tube surface. In the second case, the ash particles move toward the surface tube by Brownian motion, by turbulent diffusion, or as a result of thermodiffusion through the boundary layer. The maximum size of the particles following the gas flow is determined by the Stokes number.

Under the conditions usually observed in the convective gas passes of a boiler, sub-micron particles up to 6–15  $\mu\text{m}$  are transported to the surface mainly by diffusion, but the large ones - by inertial forces.

Small particles have negligible kinetic energy at the moment of impact and are deposited on the surface, and all their energy will be expended on adhesion to the surface. The behavior of large particles is entirely different. With the increase in the particle size their kinetic energy also increases. When the kinetic energy of particles exceeds a certain value, the energy is expended on the wear of the deposit or on the wear of the tube metal.

The situation is different when the ash does not contain large particles, in which case wear of the deposit layer is not favored. For instance, by burning oil shale in ACFBC, a very intensive formation of sub-micron particle deposit takes place [5]. The median grain size of particles after the ACFBC cyclone is in the range 15 to 25  $\mu\text{m}$ . The reason is pulverizing of CaO as a consequence of dissociation of carbonate containing minerals. The experiment shows an intensive fouling of convective heat-transfer surfaces by diffusion of the finest ash fraction and uniform coverage of the perimeter of tubes with ash deposit.

The formation of bound ash deposit on convective heat-transfer surface is possible only if, after the initial retention of the particles on the surface, their further consolidation and attachment of other particles occur. The prerequisite for this is the presence of particles containing chemically active and reactive compounds (usually free CaO and CaO containing minerals) that can influence one another through reactions with flue-gas components (for instance,  $\text{SO}_2$  and  $\text{O}_2$ ). Under such conditions only those particles that have subsided on the surface will be retained on it. This can form a bound ash deposit during a relatively short period. Other particles, due to the impact by the large ones, would be knocked off the surface. Hence, the influence of large ash particles leads to the consolidation of the deposit and to their enrichment with chemically active components, which promote the formation of a monolithic substance in the deposit (mainly calcium sulphate).

The model of formation of bound ash deposits may be considered a result of subsiding of neutral particles and subsiding and binding active particles of ash under the influence of flue-gas components. This combines the influence of physical and chemical factors on the fouling process [1, 4, 7, 8].

At low flue-gas velocities the destruction effect of large particles is negligible. Due to the inconsiderable wear and prevalence of usually neutral particles, the formed under such condition deposits also consist mainly of neutral substances. Since the latter prevent the close contact and binding of relatively small quantities of active ash particles in the deposit, these are weakly bound deposits. With a rise in the flue-gas velocity the destruction effect of the large particles rises at even greater rate. Therefore, the fouling intensity begins to fall steeply after achieving a maximum value because the concentration of neutral particles in the deposit decreases. At the same time



the ratio of active particles in the deposit increases assisting their consolidations. With a further increase in flue-gas velocity (up to the first critical velocity) the destruction effect rises so that only the active particles remain in the surface and very hard deposits are formed. At a very high flue-gas velocity (up to the second critical velocity), the impact of particles is intensified up to a limit from which any further formation of deposit is impossible.

Figure 6 illustrates the ash deposit growth intensity depending upon flue-gas velocity at burning oil shale. The fly ash chemical composition was the following (mass%):  $\text{SiO}_2$  29.7,  $\text{Fe}_2\text{O}_3$  6.0,  $\text{Al}_2\text{O}_3$  8.5,  $\text{CaO}$  41.4,  $\text{MgO}$  2.5,  $(\text{K}_2\text{O} + \text{Na}_2\text{O})$  3.4,  $\text{SO}_3$  6.4, free  $\text{CaO}$  9.6.  $\text{SO}_2$  concentration in flue gas was 450 to 500 ppm.

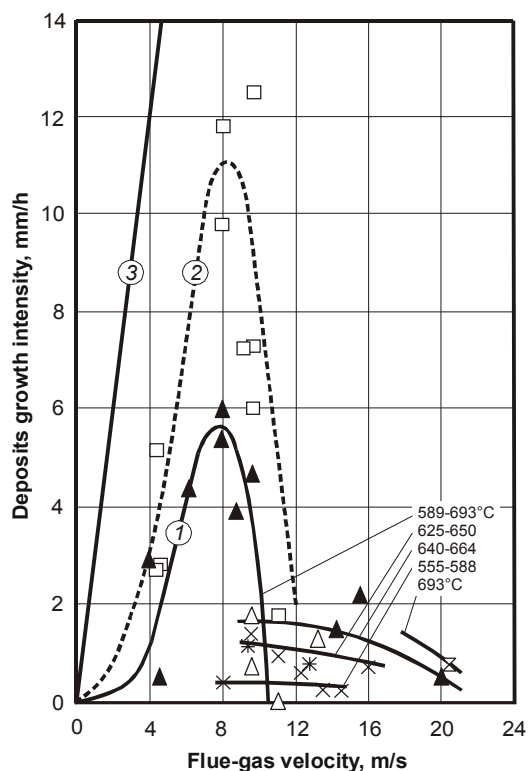


Fig. 6. Bounded ash deposit growth intensity depending upon flue-gas velocity

Curve 1 shows the average and curve 2 – the local maximum deposit growth intensity at flue-gas temperature in the range 500 to 700°C. This result was obtained when the median grain size diameter of particles was 35  $\mu\text{m}$ , the maximum diameter of particles – 250  $\mu\text{m}$ , and the ash concentration in flue gas – 10  $\text{mg}/\text{m}^3$ . Curve 3 shows the result of an analogous experiment with particles of the median grain size diameter of 5  $\mu\text{m}$  (maximum diameter 35  $\mu\text{m}$ ). Ash concentration of flue gas was 12  $\text{mg}/\text{m}^3$ . The flue-gas

temperature was 550 to 1100 °C. The deposit had a loosely bound character. Under these conditions the ash deposit grew very intensively because of the lack of large particles in the flow.

The formation of bound ash deposit is mainly based on the sulphation reactions between CaO, SO<sub>2</sub> and O<sub>2</sub> in the flue gas. The most active component in oil shale ash is free CaO. Also sulphation of other CaO-containing minerals takes place in deposit layer.

Alkali metal sulphates and chlorides also play an important role in the deposit formation processes. The deposition (condensation) intensity of alkali metal compounds depends mainly upon the partial pressure of their vapors in the flue gas. The dew point (the initial point of condensation) of the particular alkali metal compounds is the determining factor. If the temperature of a heat-transfer or ash-deposit surface is lower than the dew point of an alkali metal compound, the condensation process occurs simultaneously with the deposit formation. Experiment shows that at burning oil shale the direct condensation of K<sub>2</sub>SO<sub>4</sub> on the surface takes place in the temperature range 900 to 950 °C, and that of KCl vapor at 550 to 650 °C. Under the influence of sulphur oxides, alkali metal chlorides deposited on the surface are transformed into alkali metals sulphates over time.

The bound ash deposit on convective heat-transfer surfaces has a layer structure and exhibits an unlimited growth. Cleaning of heat-transfer surfaces is used to decrease the growth intensity of the ash-deposit layer. The influence of permanent growth of deposits and their cyclic removing on cleaning cycles made the heat transfer through the heat-transfer surface tubes a non-stationary process.

### **High-Temperature Corrosion and Wear of Heating Surface Metal**

The problem of high-temperature corrosion and wear of metal is associated with the lifetime of the boiler heat-transfer surfaces tubes.

High-temperature corrosion of heat-transfer surface metals depends largely upon the ash deposit composition, the type of metal and metal temperature. Alkali metals, chlorides and also sulphur are the most important components affecting metal corrosion intensity. It is interesting to mention that relative acceleration of corrosion impact by oil shale ash on Cr-Ni austenitic alloy is more notable than on chromium perlitic steel, in spite of the fact that the absolute value of corrosion depth in the first case is lower. Such behavior of Cr-Ni austenitic steel, compared to perlitic one is induced by the extremely strong action of potassium chloride containing compounds on chromium.

Usually at burning alkali metal- and chlorine-rich fuels, the ash deposit contains large quantities of chlorine in the initial stages, but under the influence of sulphur oxides from flue-gas chlorides transform into alkali metal sulphates over time, and corrosion activity of ash deposit decreases

[9]. The presence of sulphur dioxide in flue gas in the convective gas passes is typical for the PF technology. The situation would be different when burning high-sulphur and high-CaO fuels in FBC. Due to the low temperature, the sulphur-binding factor by calcium oxide is very high, and sulphur dioxide partial pressure in the flue gas is very low.

The nature of the corrosive-erosive wear of the boiler heat-transfer surface tubes lays in the periodic (partial or total) destruction of the protective oxide film on the metal during the cleaning cycles of the heat-transfer surface. This cleaning action is a factor accelerating the corrosion process. The metal corrosion does not become more intensive not only as a result of destruction of the oxide film within the cleaning cycles, but also due to the higher chlorine content of the deposits formed onto the clean surface (initial deposit). It means that the corrosive activity of the initial ash deposits is higher compared to the “older” ones due to their less chlorine content.

The problem of the metal corrosive-erosive wear is foremost associated with the lifetime of superheater and reheater tubes. Proceeding from this scheme a mathematical model of corrosive-erosive wear of the heat-transfer surfaces metal has been compiled [9]. This model enables to calculate analytically the metal lifetime depending on the type of metal, corrosive activity of ash deposits, tube wall temperature, frequency of cleaning cycles, etc.

The correct placement of the heating surface in boiler gas passes depending on corrosion activity of ash and metal temperature is essential. In the case of oil shale FBC technology, the behavior of the chlorine-containing compounds is very important. With the increase in chlorine content the corrosion activity of oil shale ash goes up. According to Fig. 5, the majority of chlorine concentrates in smaller particles. As the ACFBC is a good separator of ash particles, it creates favorable conditions for placing high-temperature heat-transfer surfaces in the area where the ash corrosion activity is lower [10].

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