

FOULING AND CORROSION OF HEAT TRANSFER SURFACES OF FB BOILERS BURNING ESTONIAN OIL SHALE

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The question of replacing oil shale pulverized firing (PF) boilers with fluidized-bed (FB) boilers arose due to the need to renew Estonian power plants. The data needed for designing FB boilers for oil shale were obtained at test facilities of different companies and by additional laboratory investigations. The results of the investigations demonstrated that combustion of oil shale in circulating fluidized bed is the best way to burn oil shale under atmospheric pressure. This paper deals with the problems of fouling and corrosion of heating surfaces under conditions of FB technology.

Background

Oil shale pulverized firing (PF) boilers have been in use in Estonian power plants for decades already. However, exploitation of these boilers has shown that PF of Estonian oil shale brings about a number of serious troubles at boiler operation like intensive fouling of boiler heating surfaces by hard sulfate-bound fly-ash deposits, and intensive corrosion and wear of superheaters under the action of aggressive components of fly ash, mainly KCl [1]. Therefore boiler load and operation temperatures of heating surfaces were reduced (515/520 °C instead of designed 540 °C), and continuous cleaning and repairing of boiler heating surfaces is expensive. Besides, exhaust gas of oil shale PF boiler contains more than 1500 mg/Nm³ of SO₂ though ~80 % of fuel sulfur is bound by ash in boiler. Due to the ageing of power plants replacing of oil shale PF boilers by fluidized-bed (FB) boilers in the nearest future is required.

As FB boilers for firing Estonian oil shale or any fuel with similar properties do not exist yet, test combustions were made to get the data needed for designing them. The tests were carried out at 1 MW_{th} test facilities in Ahlström (later Foster Wheeler (FW)), Finland, in 1994 [2], in LLB Lurgi Lentjes Babcock (LLB), Germany, in 1996, and at a laboratory FB test facility of ABB Combustion Engineering (ABB), Canada, in co-operation with the University of British Columbia in the same year.

The tests with Estonian oil shale were carried out in circulating FB conditions (CFB) under atmospheric pressure because the first tests made at the FW test facility showed unsuitability of the classic FB because of the high volatile matter content of oil shale. At both (FW and LLB) test facilities 160 tons of oil shale were fired. On the order of *Estonian Energy AS* the experts of Thermal Engineering Department (TED) of Tallinn Technical University (TTU) took part at these tests.

In addition, test combustion of oil shale at a pressurized test facility of ABB Carbon, Sweden, was carried out. These tests showed that in spite of some theoretical advantages of pressurised FB, in the case of using it in oil shale boilers some practical questions need solution. Therefore it was decided to renovate Estonian oil shale power plants on the basis of CFB technology.

Test combustions and following laboratory investigations showed that oil shale behaved at various atmospheric test facilities of all companies more or less in the same way. That allows generalizing the results. On their basis TED of TTU in co-operation with *Estonian Energy AS* has given recommendations for designing oil shale CFB boilers, and they are published in the scientific-technical journal of Estonian Academy Publishers *OIL SHALE* [3].

In the case of oil shale boilers fouling and corrosion of heating surfaces have been the basic problems. Therefore the operating conditions of FB boiler heating surfaces are of great interest, and their detailed analysis is given in the present paper. It bases on the main regularities and conditions determining fouling and corrosion of heating surfaces of oil shale PF boilers investigated during some decades. These regularities may be used to prognosticate the possible operating conditions of FB boiler heating surfaces basing on the composition and properties of products formed at oil shale FB combustion tests.

General Regularities Determining Fouling and Corrosive Wear of Oil Shale PF Boilers

Fouling of Heating Surfaces

Due to relatively low temperature conditions ($\sim 850^\circ\text{C}$), fouling of heating surfaces of FB boilers proceeds in conditions where the temperature of ash particles deposited on heating surfaces is lower than their initial deformation temperature. Therefore in the present chapter only the case without “sticking” of softened ash particles onto heating surfaces is observed. In this case the formation of hard ash deposits occurs only as a result of chemical reactions between ash particles deposited on the heating surface, or between ash particles and flue gas components.

Formation of hard deposits in such conditions is possible when three main preconditions are fulfilled [9]:

- (1) the ash should contain chemically active components able to react quickly with other ash particles or flue gas components (in the case of free CaO in oil shale)
- (2) the flue gas should contain components reacting with ash (SO_2 , SO_3)
- (3) the dusty gas stream washing heating surface should have thickening and wearing influence on the deposit.

Formation of deposits may assist also the vaporised mineral components of the flue gas to condense onto heating surfaces (KCl in the case of oil shale). In addition to the influence of dusty gas stream, also cleaning of heating surfaces may act thickening and wearing of formed deposit.

CaSO_4 is the main compound binding an oil shale ash deposit. As shown by investigations, hard deposit forms after deposition of particles containing CaO on the heating surface where sulfation of CaO takes place. During sulfation the CaSO_4 layer forms around particles and binds them. Particles sulfated earlier in the gas stream and then deposited onto the heating surface do not take part in this binding process. To allow a bound layer to be formed, the KCl condensation should take place on the heating surface, not on ash particles in the gas stream.

Ash particle size, velocity of gas stream (ash particles) and shape of the heating surface play an essential role at deposit formation. As for deposit formation, there are two kinds of ash particles in the gas stream:

- (1) small particles, whose kinetic energy is not sufficiently high to wear the deposit laying on the heating surface. They only touch it softly and may attach themselves to heating surface mainly by molecular forces
- (2) coarse particles, whose kinetic energy in collision with the heating surface is great enough to reverberate back into the gas stream use a part of their kinetic energy for thickening and wearing the deposit on the heating surface.

The higher the gas stream velocity, the smaller particles will wear the heating surface. Under the wearing influence of the gas stream, only the particles having reacted quickly and being fixed quite strongly before the attack of the coarser particles may stay in the deposit. Weakly bound or chemically unbound neutral particles will be kicked off from the deposit by coarser particles. As a result, the deposit is enriched by active components, and a better contact between ash particles can take place. That, in turn, favours the formation of a monolithic layer of CaSO_4 formed at sulfation of ash particles and binds the deposit.

Therefore, at slow velocities, when the mass of particles softly ground and fixed onto heating surface sufficiently exceed the mass of particles kicked off by the coarser ones, only soft, easily removable scattered deposits will form, even in the case of sulfation of particles. In that case the deposit growth velocity is relatively high. The higher the speed of the gas stream, the more intensive the wearing influence will be. Deposit growth intensity decreases when the deposit hardens being enriched by active components. At

velocities higher than a certain critical velocity (w_{cr1}) the growth of the deposit theoretically may occur only on the account of active particles. At further increase in velocity up to a so-called second critical velocity (w_{cr2}), the formation of a deposit is not possible because of too high wearing action of the dusty stream. The influence of the velocity on the formation of a deposit is given in Fig. 1. The influence of the contact time between ash particles themselves at their sulfation on the deposit hardness is illustrated in Fig. 2 [1].

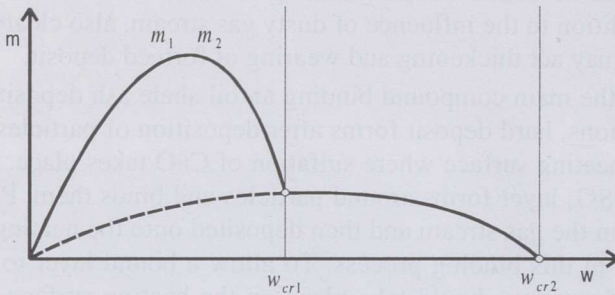


Fig. 1. Influence of the flue gas velocity on the intensity of ash deposit formation: m_1 – growth velocity of deposits due to subsiding of the neutral particles of ash, m_2 – growth velocity of deposits due to subsiding of the binding particles of ash, w_{cr1} and w_{cr2} – first and second critical velocities of gas

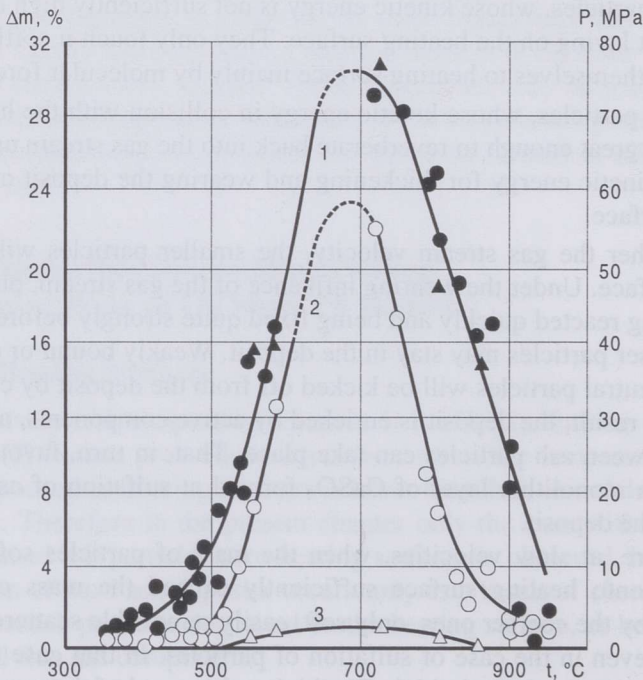


Fig. 2. Influence of mass and compressive strength of tablets and bulk of oil shale samples ash versus temperature in SO_2 atmosphere: 1 – increase in mass; 2 – strength of tablets; 3 – strength of bulk samples

Erosive Wear of Heating Surfaces

In oil shale boilers high-temperature corrosion of heating surfaces is caused mainly by KCl present in deposits [4–6]. Due to high content of free CaO binding sulfur compounds, the low-temperature corrosion in oil shale boilers does not take place.

Initial oil shale contains no KCl. It forms at the reaction between HCl formed at burning of chlorine present in the organic part and potassium volatilised at thermal decomposition of fuel minerals. At higher temperatures KCl in flue gas evaporates and may condensate on heating surfaces. In the initial phase of deposit formation the condensed KCl may form on the heating surface even a dense, very chlorine-rich (Cl >10 %) bottom layer. The corrosive action of KCl on heating surfaces depends on chlorine content of the deposit and temperature as well as on the deposit density. At the same chlorine content, corrosion of heating surfaces under hard and dense deposits is less than under softer ones. Figure 3 shows the influence of chlorine content and temperature on corrosion of heating surfaces [6].

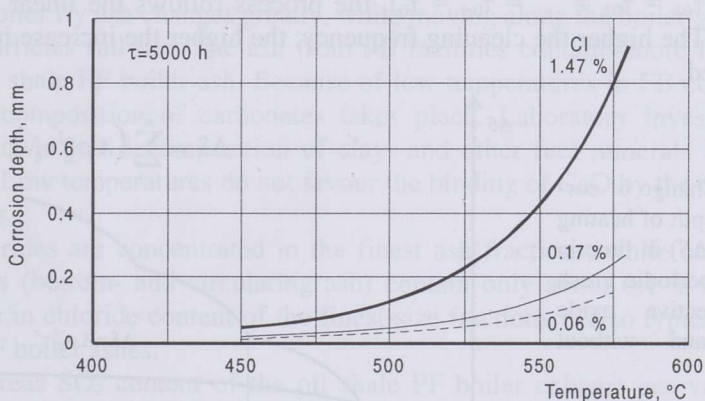


Fig. 3. Corrosion depth versus temperature at different chlorine content

Cleaning of heating surfaces from fly ash deposits affects very strongly their corrosive wear. Generally, in the case of stabilized deposits on the heating surface the corrosion process theoretically meets the following parabolic law:

$$\Delta S = A \rho_M^{-1} \tau^n,$$

where ΔS – corrosion depth;
 A – constant ($A = f(T)$);
 ρ_M^{-1} – material density;
 τ – time;
 n – power rate (<1).

According to that formula the corrosion velocity continuously decreases in time due to the increase in diffusion resistance of a protective oxide layer formed at its thickening. The circumstances change when fouling of heating surfaces demands their periodical cleaning. If cleaning is carried out in conditions of periodical crushing of the protective oxide layer it leads to intensification of corrosion. The more intensive the crushing of the oxide layer, the more intensive the corrosion. If during cleaning protective layers are removed completely, the corrosion process starts from the beginning (the intensive initial period is repeated), being as follows:

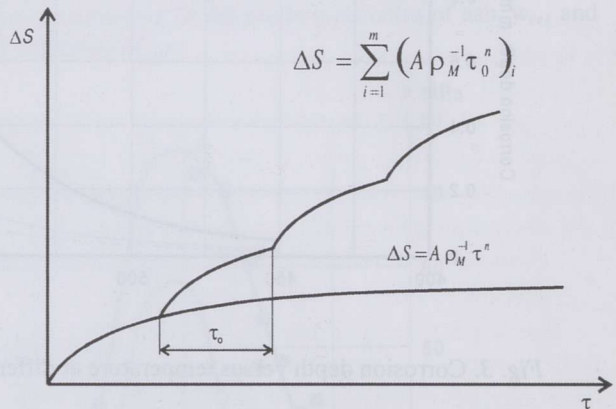
$$\Delta S = \sum_{i=1}^m (A \rho_M^{-1} \tau_{0i}^n)_i$$

where m – number of cleaning cycles;

τ_0 – time between consecutive cleaning cycles.

In the given case the total velocity of corrosion is higher than that in the case of stabilised oxide layers. In the case of cleaning cycles of regular frequency ($\tau_{01} = \tau_{02} = \dots = \tau_{0m} = \tau_0$), the process follows the linear law [7] (Fig. 4). The higher the cleaning frequency, the higher the increase in corrosion speed.

Fig. 4. Change of corrosion depth of heating surface (ΔS) in time in case of periodic crush of protective oxide layers and without latter



Fouling and Corrosion of Heating Surfaces of Oil Shale FB Boilers (Prognosis)

Composition and Qualities of Combustion Products

As mentioned above, the aim of the present investigation was to elucidate the possible working conditions of heating surfaces of oil shale FB boilers. The main attention was focused to those characteristics which are important for heating surface fouling and corrosion:

1. Grain composition of oil shale ash
2. Chemically active components (free CaO, KCl) content of ash
3. SO₂ content of flue gas

Deposits on the heating surfaces originate from fly ash. Because of that fly ash composition and qualities were studied.

Oil shale ashes from FB test facility ash cyclones and fly ash from a PF combustor differ in their grain composition [8]. In the first case the mean size of ash particles is between 0.013–0.026 mm (LLB tests show even 0.013–0.016 mm). In the case of the PF boiler TP-101, the mean size of ash particles leaving the combustor is between 0.15–0.015 mm. The finest ash fraction is captured in the electrostatic precipitator. The ash from FB combustion devices is comparable with the ash from electrostatic precipitators of PF boilers. The amount of fly ash in the case of FB test facilities is between 39–82 % of the total ash. PF boiler electric precipitators catch the ash in an amount 20 % of the total ash. Large amounts of fine fly ash in the case of FB boilers can be explained by decomposition of carbonates, while the particles of the sandy-clay part are initially very fine. Because of low temperature in FB boilers sintering of particles does not take place.

The chemical composition of fly ash from FB test facilities is more homogeneous than that of PF boiler ash. The chemical and grain composition of PF boiler fly ash changes greatly, while moving along the boiler stack flue large particles fall out. The ash from FB facilities contains more free CaO than oil shale PF boiler ash. Because of low temperatures in FB combustor only decomposition of carbonates takes place. Laboratory investigations have shown that decomposition of clay- and other fuel minerals has only started. Low temperatures do not favour the binding of CaO by the other ash minerals.

Chlorides are concentrated in the finest ash fractions, while coarse ash fractions (bottom- and circulating ash) contain only about 0.1 % chlorine. Increase in chloride content of the finest-size fractions is also typical for oil shale PF boiler ashes.

Whereas SO₂ content of the oil shale PF boiler exhaust gas varies between 1500–2000 mg/Nm³, the SO₂ content is below 5 ppm in the case of FB, as practically all sulfur dioxide emitted at burning process is bound by ash in combustor. Sulfur dioxide is an important component of the flue gas playing an essential role in fouling processes of heating surfaces.

Fouling of FB Boiler Heating Surfaces

As exploitation parameters of high-temperature superheaters and low-temperature heating surfaces differ much, they are discussed separately in the following chapters.

High-Temperature Superheaters

In the LLB and FW FB boilers, high-temperature superheaters are placed in the so-called fluidized-bed heat exchangers (FBHE), where simultaneous recycling ash cooling and air preheating take place. In this case the high-temperature heating surfaces work in conditions where they are surrounded by relatively coarse ash separated by cyclones and gas medium is the air that

contains no SO_2 . Flow rate of the medium in FBHE is only 0.5–1 m/s, and chlorine content of ash is approximately 0.1%. Because of low velocities the deposits will not thicken even in the case of somewhat coarser particles, SO_2 -free medium prevents sticking of ash to the heating surfaces and so no hard deposits will be formed even in the case when ash contains free lime. This supposition was confirmed by observation of heating surfaces during the LLB test [9].

Low-Temperature Heating Surfaces Placed in Stack Flue

These heating surfaces are washed by the gas stream containing superfine ash. Superfine ash particles are able to stick to the heating surfaces by molecular forces. The dusty gas stream containing superfine ash particles is not able to erode the heating surface and has also no ability to thicken the deposit [9]. Therefore only the formation of a crumbly fly ash deposit at heating surfaces is possible. It was confirmed by probe tests carried out at the LLB test facility.

Binding of ash particles to a hard deposit was obstructed because of two reasons: firstly – extremely low SO_2 content of FB boiler flue gases (SO_2 is bound prevalently in combustor) does not allow sulfation like it happens on oil shale PF boiler heating surfaces. Secondly – there are no erosive and deposit-thickening particles in the gas stream [9]. Large amounts of superfine fly ash in the flue gas is the reason for fast growing of crumbly deposits, one has to consider.

The influence of chlorides on the deposit formation process is known from the investigations made at PF oil shale boilers [5]. Because of low temperatures in combustor, the volatilisation of potassium from fuel minerals like it happens in oil shale PF boilers will not occur. Therefore the content of KCl vapour in the FB boiler flue gas is very low or lacking, and KCl will probably not condense on the heating surfaces. Most likely the chlorides present in ash are formed by reacting ash particles with HCl in flue gas. As HCl content of flue gas is relatively low, the ash particles deposited on the heating surface and reacting with HCl cannot give bound deposits.

Crumbly deposits have a great influence on the heat absorption of heating surfaces [9], and because of intensive fouling continuous cleaning of low-temperature heating surfaces is important. There are no needs to use extensive cleaning methods like steam blowing and other similar equipment for crumbly deposits. Cleaning equipment must be usable frequently or continuously. Sonic cleaning might be useful, but there is no experience to use this method in the case of oil shale FB boilers. For solving this problem further investigations are needed.

Erosive Wear of FB Boiler Heating Surfaces

As mentioned above, the high-temperature superheaters in the case of FB boilers have to be placed into the FBHE, outside the corrosion-danger zone. Low chlorine content of ash, air environment and low flow rate avoid inten-

sive corrosion and erosion. Intensive corrosion and erosive wear of high-temperature superheaters are serious problems for the oil shale PF boilers. Low corrosion activity of circulating ash in FBHE is confirmed by laboratory corrosion tests. The results of these tests have shown that ash has practically no corrosive activity compared to air [8].

The fine fly ash washing the low-temperature heating surfaces contains relatively large amounts of chlorine compounds. The results of laboratory corrosion tests have shown high corrosion activity of fly ash and filter ash [8]. As for corrosion, crumbly deposits on heating surfaces are preferred to dense deposits. So, low-temperature heating surfaces of FB boiler are objected to corrosion.

Situation will improve to some extent, because the corrosive activity of chlorides diminishes with reducing the temperature, especially at temperatures below 450 °C [6] (see Fig. 3). It may be assumed that in FB boilers, where only low-temperature heating surfaces are influenced by chlorine present in ash, corrosion problems will be significantly less compared to the oil shale PF boilers.

Cleaning of low-temperature heating surfaces needs special attention. Intensive fouling of these heating surfaces demands for frequent cleaning. Usage of extensive cleaning methods like steam blowing may destroy the oxide layer protecting the heating surface resulting in intensive erosion (see Fig. 4). It may happen even at a moderate corrosive activity of deposits. It means that relatively weak and continuous cleaning is to be used to clean low-temperature heating surfaces of FB boilers.

Conclusions

While comparing the working conditions of heating surfaces of PF and FB combustion technology one may draw the following conclusions:

1. Fouling and corrosion of high-temperature superheaters, serious problems for oil shale PF boilers, practically do not exist in the case of FB boilers whose heating surfaces are placed into the FBHE.
2. Fouling process on low-temperature heating surfaces in the FB boiler stack flue completely differs from that occurring in oil shale PF boilers. Instead of hard, sulfate-bound deposits there are crumbly unbound fly ash deposits on FB boiler heating surfaces. The growth rate of these deposits is high, and for keeping heat absorption of heating surfaces at the needed level, frequent or continuous cleaning is recommended.
3. The deposits on low-temperature heating surfaces of FB boilers contain much chlorine, and they are corrosively active like the deposits on PF boiler heating surfaces. As the corrosive activity of deposits containing chlorine decreases at metal temperatures below 450 °C, there is hardly a chance for intensive corrosion of heating surfaces.

4. Fly ash deposits on FB boiler heating surfaces may be easily removed using a nonextensive cleaning method. It avoids destruction of oxide layer protecting the heating surface tubes and diminishes corrosive wear of heating surfaces.
5. The fine-grained fly ash of FB boilers will probably not cause erosive wear of heating surfaces of these boilers.

Summarizing this study, working conditions of oil shale boiler heating surfaces considering fouling and corrosion will improve considerably while replacing PF with FB technology. A part of FB boiler low-temperature heating surfaces will be fouled and needs some cleaning. These deposits are easily removable, and using an appropriate cleaning technology will cause no intensive wear of heating surfaces.

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