## ON THE FOULING MECHANISM OF NON-BOUNDED OIL SHALE ASH DEPOSITS ON BOILER HEAT-TRANSFER SURFACES<sup>\*</sup>

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> As shown by preliminary pilot-scale experiments on oil shale combustion in circulating fluidized bed, deposition of very fine particles in the convective part of boiler takes place. Assuming a quite complete binding of sulphur in CFB combustor and taking into account low-temperature level of this combustion process, there will not be adequate conditions for formation of bounded deposits on convective boiler surfaces and the fouling process will be controlled mainly by thermophoretic, diffusion and adhesion forces. That might invoke a forced increase in deposits with high thermal resistance. The prognosis of that process is presented in the given paper.

### Introduction

Arro, Prikk *et al.* [1] have experimentally shown that on burning oil shale in pilot plants of circulating fluidized-bed (CFB) technology very fine particles may appear in flue gas after the main cyclone. By the size those particles belong to aerosols, which can form ash deposits with high thermal resistance on convective heating surfaces of the boiler.

Some results of estimating ash particle size after cyclone at a test rig of the Estonian Energy Research Institute (EERI) of Tallinn Technical University (TTU) are presented in Fig. 1. Those data are compared with experimental results obtained at Lurgi and Ahlstrom pilot plants for oil shale burning by CFB technology [2]. The probe (curve 1 in Fig. 1) for sampling of ash deposits was located in the convective pass after cyclone. It was cooled by heat pipe cross-flow tube with outer diameter of 35 mm. Flue gas velocity around that probe was about 3 m/s. Curve 2 obtained in the region of probe location at the same test device by laser Doppler anemometer tuned for measuring the concentration of particles with size between 4–70  $\mu$ m.

<sup>&</sup>lt;sup>\*</sup> Presented at the 2nd International Symposium on Oil Shale, Tallinn, Nov. 2002.

Investigations on oil shale combustion in CFB test devices [3] confirmed high capture of sulphur in fluidized bed. Due to that, there is no noticeable sulphating processes after the cyclone. The multiple ash circulation in CFB technology "generates" finest particles whose capturing by the cyclone is not possible, and flue gas in the convective duct will carry mainly aerosol particles. The fouling of those particles has a character quite different from that on fouling in the presence of chemically active particles. The situation of fouling and thermal resistance dynamics of surfaces after cyclone of oilshale CFB boiler for 215 MW<sub>e</sub> unit of Narva Power Plant will be analyzed considering the above-mentioned conditions of fly ash formation.



*Fig. 1.* Particle size distribution in flue gas after the cyclone of different CFB test devices burning oil shale: 1 - deposits on cross-flow probe at EERI test device; 2 - fly ash measured by LDA diagnostics at EERI device; 3 - fly ash in baghouse filter of Lurgi test device [2]; 4 - the same, calculated [2]; 5 - fly ash in Ahlstrom Pyroflow test rig [2]

# Possible Structure and Thermal Properties of Non-Bounded Ash Deposits

Aerosol particles deposited mainly by thermophoretic forces can form spatial structures with extraordinary high porosity. Due to intensive sulphur binding in the combustion process of CFB technology, there is no noticeable chemical binding of particles in the mentioned deposits. On the other hand, due to the low temperature level the sintering is also minimal. Due to the facts mentioned above, the structure of the formed ash deposits will be very rigid and similar to aerogel structures. The image of possible structure of that kind of deposits is presented in Fig. 2 [4]. Due to the recarbonation process activated by excess CaO, the deposit particles may become stronger and agglomerate [5]. It is, perhaps, one of the reasons of higher median particle size for deposits on the probe as compared with fly ash deposits characterized in Fig. 1.



*Fig. 2.* Possible structures of deposits with different porosity P formed by loose layer of solid particles

For estimating the real (bulk) density of structures described in Fig. 2 by particles of fly ash from oil shale combustion in CFB furnace after the main cyclone, the pure densities of main components of ash particles are required. Some approximations on that case look like that:

#### Composition of Oil Shale Fly Ash

Component	Approximate content, %	Density of crystals, kg/m <sup>3</sup>
CaO	37	3370
CaSO <sub>4</sub>	8	2600
CaCO <sub>3</sub>	18	2940
SiO <sub>2</sub>	30	2400
$Al_2O_3$	6	3990

#### Some Characteristics of Loose Deposits

Porosity	Possible bulk density, kg/m <sup>3</sup>
0.3	2060
0.4	1766
0.5	1471
0.6	1177
0.7	883

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Based on these data, the weighted pure density of ash particles is  $2940 \text{ kg/m}^3$  and on this basis the values of bulk densities at different porosities were calculated.

It is a quite complicated technical problem to perform direct measurement of the thermal conductivity or thermal resistance of that kind of deposits due to their very brittle structure.

Thermal conductivity of porous layers is effective thermal conductivity made up of the conductivities of solid frame and gas in pores. The radiation component of thermal conductivity will be noticeable at temperatures over 800 °C and pore measure larger than 10  $\mu$ m [6]. Modeling of thermal conductivity is concentrated mainly on the effect of porosity, shape of pores or solid grain and pore size distribution. Existing models of effective thermal conductivity can be subdivided into two types:

- 1. Models where exact or approximate solutions for idealized systems are provided.
- 2. Empirical and semi-empirical models.

Examples for the first type are models of parallel or series onedimensional many-phase structures, which represent bounds of thermal conductivity of a porous body with a given fractional composition, or:

$$k_{ef} = k_g P + k_s (1 - P) \text{ parallel - upper bound}$$

$$k_{ef} = \frac{k_s k_g}{k_s P + k_g (1 - P)} \text{ series - lower bound}$$
(1)

Another example is an exact solution of Maxwell equation for low concentration of inclusions of one phase in a continuous matrix of another phase. To this type of model, one can relate those based on statistical analysis using variational theorems. In these studies, the bounds for thermal conductivity are narrower than those defined by parallel and series structures. In general, as shown in [7], the real thermal conductivity of porous structures lies between the upper and lower limits, and for chaotic structures (random orientation of particles with uniform shape and size) semi-analytical models are proposed.

Käär *et al.* [8] proposed the following model of effective thermal conductivity for two-component mixture:

$$k_{ef} = k_2 \left\{ 0.75 + A^2 \left[ \frac{v - 1}{v - A(v - 1)} \right] + \frac{v}{v + 1} \left[ 0.5 + A^2 (v - 1) \right] \right\}$$
(2)

where 0.75  $k_2$  is thermal conductivity coefficient of component 2;

 $v = k_1/k_2;$ 

structural dimensionless parameter  $A = \sqrt{2(m_1 - 0.125)/3}$ ;

*m* is volume concentration of correspondent component.

Equation is true within  $0.125 < m_1 < 0.5$  and 0 < A < 0.5. That equation is modified for calculations of high porous materials and it has now the form

$$k_{ef} = k_g \left( 1 + (1.5(1-P) + 11(1-P)^2) (A(A\ln V - 1) - 0.5) \right)$$
(3)

where  $V = \frac{k_s}{k_g}$  and  $A = \frac{V}{V-1}$ ;

*P* is porosity of the structure;

 $k_g$  is thermal conductivity of flue gas in pores, W/(m · K);

 $k_s$  is thermal conductivity of solid frame, W/(m · K).

If the thermal conductivity coefficient of the solid fraction (frame material) equals to 1 W/( $m \cdot K$ ), then its effective thermal conductivity at different porosities of ash deposit layer depends on the temperature as shown in Fig. 3.



*Fig.* 3. Effective thermal conductivity of ash deposits at different porosities:  $\Diamond P = 0.4$ ;  $\Box P = 0.5$ ;  $\bigcirc P = 0.6$ ;  $\bigtriangleup P = 0.7$ ; — flue gas

For estimating thermal resistance of ash deposits and dynamics of its growth during the fouling process, the data on fouling intensity, i.e. the deposit layer growth rate are needed.

#### Fouling of Fine Particles from Flue Gas

As a rule, thermal resistance (fouling factor) of ash deposits on heating surfaces of boilers burning pulverized solid fuel is calculated taking into account possible sintering and chemical processes during the fouling process.

As for fine particles, at flue gas low velocities the fouling process takes mainly place by diffusion and thermophoretic forces, and the fouling possibility is estimated by critical Stokes number [9]:

$$Stk = \frac{\Delta^2 \rho_p w}{18 \rho_g v d} \tag{4}$$

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where  $\Delta$  is particle median size, m;

 $\rho_p$ ,  $\rho_g$  are densities of particles and flue gas, kg/m<sup>3</sup>;

v is kinematic viscosity of flue gas,  $m^2/s$ ;

d is outer diameter of cross-flow tube, m;

w is flue gas velocity, m/s.

The Stokes number depends on the gas temperature and particle size as shown in Fig. 4.



*Fig. 4.* Stokes number dependence on the flue gas temperature under cross-flow conditions of the tube with outer diameter of 42 mm at different median particle size ( $\bigcirc$  15,  $\diamondsuit$  10 and  $\square$  5 µm) and flue gas velocity in the range of 3 m/s (smaller shapes) or 5 m/s (larger shapes)

Due to intensive sulphur binding in the combustion process of CFB technology, there is no noticeable chemical binding of particles in deposits fouled on heating surfaces after the cyclone. Fine particles will schedule the streamlines of gas flow, and there is lack of inertial impact by coarse particles to destruct the deposits. Inertial impact is estimated by Stokes number: at  $Stk_{crit} < 1/16...1/8$  there is no inertial impact and fouling goes on by thermophoretic and adhesion forces.On the basis of well-known data on fouling in boilers and last investigations on deposition of extra-fine particles (with size of 4–30 µm), an empirical relationship for the growth rate of weakbounded ash deposit is offered:

$$h = 20 \frac{w\chi}{\Delta_m^{1.75}} \text{ (mm/h)}$$
(5)

Deposition of fine particles with weak bound depends on the flue gas velocity *w*, m/s, fly ash concentration in flue gas  $\chi$ , g/m<sup>3</sup>, and the particle median size  $\Delta_m$ ,  $\mu$ m. The latter has an inversely proportional effect on the growth rate of deposits. The results calculated by that equation for particle concentration of 5–15 g/m<sup>3</sup> are presented in Fig. 5.



*Fig. 5.* Fouling rate at different median particle size and fly ash concentration (O 15,  $\diamond$  10 and  $\Box$  5 g/m<sup>3</sup>), and flue gas velocity 3 m/s (smaller shapes) or 5 m/s (larger shapes)



*Fig. 6.* Bounded ash deposit growth rate as a function of flue gas velocity: curves *I* and *2* – average (*I*) and local (*2*) maximum deposit growth intensity, curve *3* – results of the same kind of experiments with the particles of median size 5  $\mu$ m, maximum size 35  $\mu$ m and ash concentration 12 g/m<sup>3</sup>, flue gas temperature 550–1100 °C.

The estimation of possible rate of deposit layer growth in a CFB boiler convective duct is given in Fig. 6. It characterizes the growth of different ash deposits on the basis of numerous experimental studies [10]. Curve *1* shows the average and curve *2* the local maximum deposit growth intensity. This result was obtained when the median particle size was 35  $\mu$ m, the maximum size – 250  $\mu$ m and ash concentration in flue gas 10 g/m<sup>3</sup>. Curve *3* shows the results of the same kind of experiments with the particles of median size 5  $\mu$ m, maximum size 35  $\mu$ m and ash concentration 12 g/m<sup>3</sup>, flue gas temperature was 550–1100 °C.

Taking into account the design parameters of oil shale CFB boiler superheater (flue gas velocity 3.7–5 m/s; temperature at entering 759 °C; median particle size 15  $\mu$ m and fly ash concentration 15 g/m<sup>3</sup>), the possible deposition intensity will be in the region marked by dashed lines in Fig. 6.

Thermal resistance growth dynamics calculated for given conditions is presented in Fig. 7 where also the data calculated by N. Kuznetsov's equation (Eq. (6)) for stabilized deposits in the case of in-line tube bank [11] are given:

$$\varepsilon = 0.0336 \left( 1 - 1.7 \lg \frac{R_{30}}{33.7} \right) \left( 1 + 3.3 \lg \frac{d}{38} \right) 10^{-0.08w} \text{ (m}^2 \cdot \text{K/W)}$$
(6)

where *d* is outer diameter of cross-flow tube, mm;

w is velocity of flue gas, m/s;

 $R_{30}$  is residue on 30-µm sieve, %.



*Fig.* 7. Dynamics of thermal resistance. Stabilization limits for fouling factor for different-size particles calculated by Eq. (6) are shown by bold lines

Taking into account the rise in thermal resistance, the dynamics of relative thermal efficiency (for the initial taken for 1, i.e. clean surface conditions) of convective superheater after cyclone for oil shale CFB boiler is predicted (Fig. 8).



*Fig. 8.* The predicted dynamics of superheater relative thermal efficiency at described fouling conditions:  $\blacksquare P=0.4$ ;  $\blacktriangle P=0.5$ ;  $\blacklozenge P=0.6$ 

An extremely high decrease of thermal efficiency of superheater is the result of high fouling rate. During first 10 minutes that parameter decreases about 20 %. Using the data on thermal resistance growth the outer surface temperature of ash deposits is calculated. That calculation shows the rise in that temperature up to 530  $^{\circ}$ C.

The nearly linear growth of thermal resistance, i.e. thickness of deposit layer in given conditions, can be stopped by crushing that layer by gravity forces. Measured cohesive force between fine particles (including ash samples from pressurized fluidized-bed combustion systems) under elevated temperatures [12] showed the tensile strength about 200 Pa. It means that the layer of deposits with thickness of about 15 mm can be crushed by its own weight. After detaching of some amount of deposit, there will remain an initial bounded layer of deposits. The real dynamics of thermal resistance in the described case can be characterized as for convective parts of conventional solid fuel boilers [13] – periodical process with logarithmic growth of the baseline.

## Conclusions

Thermal conductivity coefficient of high-porosity non-bounded deposit layer computed by different models is lower than thermal conductivity of chemically bounded deposits. Those results are in a good agreement with the data from [7]. The growth of deposit layer thickness is estimated by the deposition model. In the worst case there is no limits to deposit layer growth due to the absence of coarse particles in the flue gas flow.

The results of model calculations give the dynamics of thermal resistance of deposits during the fouling process in convective superheater of oil shale CFB boiler. As shown, thermal resistance in certain conditions may have a catastrophic growth. Therefore, the cleaning apparatus in convective gas duct must operate very often. The possible solution is to use sonic cleaning with quite weak effect to tube metal, which, however, can be used very often.

Predicted fouling mechanism and the dynamics of thermal resistance (fouling factor) must be approved in real working conditions of full-scale CFB oil shale boilers. It is very important to obtain weakly bound ash deposit samples with real structure for complete laboratory investigations (SEM pictures, chemical-mineralogical composition and thermal properties).

#### Acknowledgements

The research was supported by Estonian Science Foundation (grant No. 5179).

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Received December 2, 2002