# FIRING ESTONIAN OIL SHALE IN CFB BOILERS – ASH BALANCE AND BEHAVIOUR OF CARBONATE MINERALS

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The ash balance and the extent of carbonate decomposition (ECD) for circulating fluidised-bed (CFB) boilers depending on oil shale lower heating value (8.5 and 11.1 MJ/kg) were analysed. As for the ash balance, ash mass flow rates (kg/s) for each ash separation port were determined. In calculations the ECD methodology developed at the Department of Thermal Engineering (DTE) on the basis of ash composition was used. Changes in the boiler ash balance occurred when firing oil shale of different quality. Additionally, the reduction of the CO<sub>2</sub> emission by 7% and of the total ash mass flow by 23% was obtained when firing upgraded oil shale instead of low-grade oil shale.

## Introduction

Oil shale is the main energy resource in Estonia. Around 90% of the electricity in the country is produced from oil shale at the Narva Power Plants (NPP). The lower heating value (LHV) of oil shale used for electricity production is 8.3-8.4 MJ/kg. This is a low-grade fuel with a high content of carbonate minerals. Burning that kind of fuel is associated with several problems concerning dissociation of carbonate minerals, high CO<sub>2</sub> emission levels, ash handling and storing. In the context of minimising the environmental impact of power production, the question has arisen about utilisation of oil shale of higher quality. The application of upgraded oil shale with the LHV at up to 11.0 MJ/kg.

Several positive aspects of using oil shale of higher quality can be highlighted: decreased concentration of  $CO_2$  in flue gas, reduction of fuel consumption per kWh of produced power, and the improvements in ash handling and storing. Considering these aspects, the energy unit efficiency increases, which also improves cost efficiency.

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However, firing of oil shale of higher quality could cause changes in the CFB boiler operating conditions. Considering the fact that the carbonate minerals (mainly limestone) in oil shale are mechanically harder (compressive strength range of 40–80 MPa) and heavier by density (2200–2600 kg/m<sup>3</sup>) than the organic and sandy-clay part (compressive strength range of 20–40 MPa and density at 1500–1800 kg/m<sup>3</sup>), firing of oil shale containing reduced amount of carbonate minerals could cause redistribution of the CFB boiler ash mass flows and changes in the behaviour of mineral matter in the furnace during the combustion process.

To investigate the distribution of ash mass flows and the behaviour of the mineral matter depending on oil shale quality, the boiler ash balance was determined and the extent of carbonate decomposition for the boiler ash was calculated. The investigation is based on the full-scale oil shale firing tests carried out by the DTE and the NPP during 2006–2007.

#### **Experimental part**

### Arrangement of the tests and collection of the process data

The oil shale firing tests were carried out in the CFB boiler No. 1 of the Balti Power Plant energy unit No. 11. The capacity of the energy unit was 215 MW<sub>e</sub> and it was commissioned in 2004 by Foster Wheeler Energia OY. The main parameters of the boiler (Fig. 1) used were as follows:

- steam capacity (primary/secondary) 95/76 kg/s;
- primary/secondary steam pressure 12.7/2.4 MN/m<sup>2</sup>;
- steam temperature 535/535 °C.
- The detailed description of the boiler is provided in [1].

Several fuel classes of various composition and the LHV at 8.2-11.5 MJ/kg were fired. A total of 17 tests were carried out in accordance with EVS-EN 12952 – 15:2003 [2]. The upgraded oil shale fuel was specially prepared. The tests were run at boiler loads of 90% of nominal power.

During each test run several process data sets were collected. As regards the investigation of the ash mass balance and the behaviour of carbonate minerals in the CFB boiler, the fuel and ash sampling from the separation ports was performed as described below, followed by averaging and dividing procedures for achieving the representative average sample of the test run. The locations of the ports used to collect solid samples are indicated in Fig. 1. The fuel samples (A) before and (B) after the secondary fuel crusher were taken to determine the granular composition of the fuel fed into the boiler. The secondary fuel crushers are located at the end of each fuelfeeding line before fuel entering the furnace and are used to ensure the most suitable granular composition of the fuel for the CFB boiler. The fuel samples for the ultimate and proximate analysis were taken from the main fuel conveyor (not shown in Fig.1). Additionally, several ash samples were taken. The furnace ash samples were taken from the following collection ports (Fig. 1): C – bottom ash and D – reheater of the second stage (INTREX). Small and light ash particles ( $d < 50 \mu m$ ) [1] not separated by the separators of solids comprise fly ash. The fly ash samples were taken from the following collection ports: E – convective cage of superheater and reheater of first stages (SH-RH), F – economizer (ECO), G – air preheater (APH) and from four fields in the electrostatic precipitator (ESP: H, I, J, K). The fuel and ash samples were analysed by the chemistry laboratory of the DTE. The granular composition analyses of the fly ash samples were performed by ENAS OY, Finland.



Fig. 1. Oil shale-fired CFB boiler (sample ports).

1 - raw fuel silo, 2 - fuel feeder, 3 - grate, 4 - furnace chamber, 5 - separating chamber, 6 - fluidised bed internal heat exchanger (INTREX), 7 - separator of solids, 8 - convective superheater and reheater, 9 - economizer, 10 - air preheater, 11 - electrostatic precipitator, 12 - secondary fuel crusher

### **Processing test data**

#### Determination of the ash mass flow rates

The ash formed during the combustion process is removed from the boiler by several separation ports as shown in Fig. 1 (C to K). For the ash balance, the ash mass flow rates for each separation port were calculated. The ash from the separation ports is directed to the common ash silo by the ash senders via the mechanical and pneumatic conveying lines. The calculation was performed on the basis of the ash senders' operation frequency (except convective cage (E) and INTREX (D)) and the ash bulk density. The data of the ash senders' operation frequencies was registered by the data logging system of the plant. For the calculation it was assumed that 2/3 of the total ash senders' volumes was effective.

Considering the circumstance that the ash mass flow from the SH-RH (E) is directed to the bottom ash silo, a specially prepared valve was installed on the ash tube under the convective cage to determine the ash mass flow rate from SH-RH (E). The ash mass flow rate (E) was calculated on the basis of the ash bulk volume in the tube and the time spent on the tube fulfilment in the case of the closed valve. The valve was closed cyclically during the tests for measurements. The ash mass flow from the INTREX (D) is included in the bottom ash mass flow (C).

#### Determination of the extent of carbonate decomposition

Regarding  $CO_2$  emissions from the CFB boiler, the behaviour of carbonate minerals during the combustion process plays a significant role. It is well known that calcite and dolomite during the combustion process dissociate according to the following reactions [3]:

$$CaCO_3 \rightarrow CaO + CO_2$$
 (1)

$$CaMg(CO_3)_2 \rightarrow CaO + MgO + 2CO_2$$
(2)

$$CaCO_3 + SO_2 + 1/2O_2 \rightarrow CaSO_4 + CO_2.$$
(3)

Carbon dioxide formed during the dissociation (reactions 1–3) of such carbonate minerals is added to the amount of  $CO_2$  formed during the burning of carbon. It results in an increased amount of  $CO_2$  in the flue gas. The share of mineral  $CO_2$  in the total  $CO_2$  emission depends on the oil shale mineral  $CO_2$  content and the ECD.

It is possible to determine the ECD for the CFB boiler ash on the basis of the ash composition alone [4]. In order to determine the ECD, it is important to know the CaO and MgO content of the ash. The initial amount of  $CO_2$  bound with CaO and MgO before the decomposition of carbonates occurs can be established using the formulas below:

$$CO_{2 CaO} = 0.7785 CaO_{ash}$$
<sup>(4)</sup>

$$CO_{2 MgO} = 1.0555 MgO_{ash}$$
<sup>(5)</sup>

$$\mathrm{CO}_{2\,\mathrm{sum}} = \mathrm{CO}_{2\,\mathrm{CaO}} + \mathrm{CO}_{2\,\mathrm{MgO}},\tag{6}$$

where  $CO_{2 CaO}$  and  $CO_{2 MgO} - CO_2$  bound accordingly with CaO and MgO and calculated in percentages of the ash mass, and  $CaO_{ash}$  and  $MgO_{ash} - CaO$ and MgO content of ash. If the carbonaceous  $CO_2$  content of ash ( $CO_{2 ash}$ ) is also determined by the chemical analysis, the ECD is calculated with Eq. 7:

$$k_{\rm CO2} = 1 - (\rm CO_{2 \ ash} / \rm CO_{2 \ sum}).$$
 (7)

#### CO<sub>2</sub> emission from the CFB boiler

As mentioned above, the total amount of  $CO_2$  discharged into the atmosphere when firing oil shale depends on these two aspects: burning of carbon and decomposition of carbonates. The calculation of the  $CO_2$  emission per one kilogram of fuel as received is performed according to the formulas below [3]:

The amount of  $CO_2$  arising from the burning of carbon, in nm<sup>3</sup>/kg:

$$V_{\rm CO2\ carbon} = 0.01853\ {\rm C}^{\rm r},$$
 (8)

where  $C^r$  – carbon content of oil shale, %.

The amount of the  $CO_2$  arising from the decomposition of carbonates,  $nm^3/kg$ :

$$V_{\rm CO2\ carb} = 0.00509\ k_{\rm CO2}\ (\rm CO_2)^{\rm r}_{\rm c},\tag{9}$$

where  $k_{CO2}$  – extent of carbonate decomposition;

 $(CO_2)^r_c$  – content of mineral CO<sub>2</sub> in oil shale, %.

The total amount of the  $CO_2$  emission from the CFB boiler is calculated as follows, in nm<sup>3</sup>/kg:

$$V_{\rm CO2} = V_{\rm CO2\ carbon} + V_{\rm CO2\ carb}.$$
 (10)

This is the specific emission of  $CO_2$  from the CFB boiler per produced thermal energy, in t/MWh<sub>th</sub>:

$$CO_2 = 3.6 V_{CO2} \rho B / Q_{heat},$$
 (11)

where  $\rho = 1.977 - \text{density of CO}_2$ , kg/nm<sup>3</sup>;

B – fuel consumption rate, kg/s;

 $Q_{\text{heat}}$  – boiler heat output, MW<sub>th</sub>.

### **Results and discussion**

#### Investigation of the ash balance

The investigation of the CFB boiler ash balance is based on the tests in which oil shale with the LHV 8.5 MJ/kg (Test 1) and 11.1 MJ/kg (Test 2) were fired. For Test 1 the boiler operated continuously for three days and five days for Test 2. A short characterisation of the fuels is provided in Table 1.

The results for the CFB boiler ash balance when firing oil shale of different quality can be viewed in Fig. 2. As it was expected, the firing of oil shale of different quality resulted in changes in the distribution of the ash mass flows. The main difference can be noticed in the bottom ash mass flows.

Symbol	Description, unit	Test 1	Test 2
Qi <sup>r</sup>	Lower heating value, MJ/kg	8.5	11.1
$W^r$	Moisture, %	11.1	11.3
$\mathbf{A}^{\mathbf{r}}$	Ash (815 °C), %	44.1	42.3
C <sup>r</sup>	Organic carbon, %	21.1	26.1
$(CO_2)^r_c$	Mineral CO <sub>2</sub> , %	18.7	14.1
R[0.5] <sub>A</sub>	Median size of fuel before crusher (Fig. 1, A), mm	1.2	0.75
$R[0.5]_{B}$	Median size of fuel after crusher (Fig. 1, B), mm	0.57	0.41

Table 1. Characterisation of oil shale fuel as received (mass %)



Fig. 2. Ash balance for CFB boiler.

The shares of bottom and fly ash were 37% and 63% when burning lowgrade (8.5 MJ/kg) oil shale, but 30% and 70% in the case of firing upgraded (11.1 MJ/kg) oil shale. This denotes a reduced bottom ash ratio when firing upgraded fuel. One of the reasons for the reduced bottom ash mass flow when firing upgraded oil shale could be in the reduction of the content of carbonate minerals in the fuel. When firing oil shale at 8.5 MJ/kg (higher content of carbonate minerals), carbonate minerals (relatively large limestone particles) during the combustion process in the furnace subside through the fluidised bed due to their substantial density and can be removed from the boiler along with the bottom ash, resulting in a higher share of the bottom ash mass flow. On the other hand, the reduced bottom ash mass flow when firing upgraded fuel can be explained by the granular composition of the fuel. More precisely, as it can be seen in Table 1, the upgraded fuel used in Test 2 was finer, with the median size of particles at  $R[0.5]_B = 0.41$  mm. When firing low-grade oil shale, the fuel median size was  $R[0.5]_B = 0.57$  mm. The finer granular composition of the upgraded fuel in Test 2 was caused by the finer initial fuel entering the secondary fuel crusher. The finer granular

composition of the initial fuel was caused by the higher crushing rate of the fuel due to better conditions in the primary fuel crusher (not shown in Fig. 1). The primary crusher's new hammers were installed during operation one month before the firing tests with the upgraded fuel. Due to finer fuel particles, limestone decomposes to a larger extent and the organic part burns quicker, resulting in reduction of the bottom ash mass flow rate.

The firing of oil shale of higher quality also affected the boiler total ash mass flow (Fig. 2). To summarise the ash mass flows from the separation ports, the total ash mass flow discharged from the boiler was 16.3 kg/s for Test 1 and 12.6 kg/s for Test 2, meaning a reduction of the total ash mass flow by 23% when firing oil shale of higher quality. The reduction of the total ash mass flow was achieved by the reduction of both fuel consumption due to the increased LHV and ash content of oil shale (Table 1).

#### The sulphate- and carbonate-free ash balance

For estimating the accuracy of the measurements of boiler ash mass flows, the sulphate- and carbonate-free ash balance was composed. The sulphateand carbonate-free ash balance is based on the ash components which form oxides during the combustion process:  $SiO_2$ ,  $Fe_2O_3$ ,  $Al_2O_3$ , CaO, MgO,  $K_2O$ and Na<sub>2</sub>O. These components are bound totally into the ash and they do not proceed partly or totally into the combustion gases such as  $SO_2$ ,  $CO_2$  and Cl. The boiler ash which contains only these elements is called sulphate- and carbonate-free ash.

For composing the sulphate- and carbonate-free ash balance, the flow rate of sulphate-free ash mass into the boiler with the fuel was calculated. The calculation is based on the laboratory data on ash content of the fuel, fuel consumption rate (calculated via boiler heat balance) and chemical composition of the fuel ash. The sulphate- and carbonate-free ash mass flow discharged from the boiler is calculated on the basis of the ash composition and the measured ash mass flows. If the ash balance is correct, the sulphatefree ash mass flow fed into the boiler with the fuel should be equal to the sulphate- and carbonate-free total ash mass flow discharged from the boiler.

The calculation showed that the sulphate- and carbonate-free total ash mass flow discharged from the boiler was 8% greater than the sulphate-free ash mass flow fed into boiler when firing oil shale with the LHV 8.5 MJ/kg and 16% greater when firing oil shale with the LHV 11.1 MJ/kg (see also Table 2).

#### Investigation of the behaviour of carbonate minerals and CO<sub>2</sub> emissions

The results of the analyses of the ash samples and determined  $k_{CO_2}$  values are presented in Table 3. It can be seen in Table 3 that median sizes and densities of the fly ash samples (E-K) are quite similar when firing oil shale (8.5 MJ/kg or 11.1 MJ/kg). Determined  $k_{CO_2}$  values for the fly ash samples are also quite similar, being in the range of 0.70–0.88.

However, concerning the  $k_{CO_2}$  value for the bottom ash samples, it can be seen in Table 3 that when firing low-grade (8.5 MJ/kg) oil shale it is 0.47 and when firing upgraded (11.1 MJ/kg) oil shale it is 0.68. The reason for the lower  $k_{CO_2}$  value when firing low-grade fuel could be explained by the coarser granular composition of the ash. As it can be seen in Table 3, the bottom ash median size when firing the low-grade fuel is 1.13 mm and when firing the upgraded fuel it is 0.43 mm. The coarser granular composition of the bottom ash when firing low-grade fuel was caused by the coarser fuel (coarser limestone particles in the fuel) fired.

While the CFB boiler is equipped with a separator of solids, the granular composition of fly ash leaving separator does not depend on the fuel granular composition. Coarser and heavier fuel and ash particles are captured by the separator and directed to the circulating medium for burnout.

Taking into account the ash mass flow rates (kg/s) for each separation port (Fig. 2), the  $k_{CO_2}$  for the CFB boiler total ash is calculated (weighted average). It can be seen from Table 3 that the total  $k_{CO_2}$  for the CFB boiler when burning upgraded oil shale (Test 2) is 0.78 and when firing low-grade oil shale (Test 1) it is 0.69. As the boiler was operated at the same load and furnace temperatures, the reason for the higher  $k_{CO_2}$  value when firing upgraded fuel can be explained by the fuel granular composition. As mentioned above, the upgraded fuel used was finer. Indeed finer limestone particles in the fuel during the combustion process can be heated up quickly and thus decompose to a larger extent.

The specific CO<sub>2</sub> emission results for the CFB boiler's useful heat rate are presented in Table 2. According to the test results, the total CO<sub>2</sub> emission when firing low-grade oil shale was  $0.384 \text{ t/MWh}_{th}$  and when firing upgraded oil shale it was  $0.356 \text{ t/MWh}_{th}$ . When firing oil shale of higher quality, a reduction of the CO<sub>2</sub> emission by ~7% was achieved as compared to firing of low-grade oil shale. As regards the CO<sub>2</sub> emission from the decomposition of carbonates when firing low-grade fuel, it was 14.1%, and when firing upgraded fuel, it was 10.4% of the total CO<sub>2</sub> emission.

Indicator	LHV 8.5 MJ/kg	LHV 11.1 MJ/kg	
Total $CO_2$ emission, t/MWh <sub>th</sub>	0.384	0.356	
CO <sub>2</sub> emission from burning of carbon, t/MWh <sub>th</sub>	0.330	0.319	
CO <sub>2</sub> emission from decomposition of carbonates, t/MWh <sub>th</sub>	0.054	0.037	
Sulphate-free ash mass flow fed into the boiler with fuel, kg/s (1)	12.42	8.94	
Sulphate- and carbonate-free total ash mass flow from the boiler, kg/s (2)	13.51	10.68	
Difference between (1) and (2), %	8.1	16.3	

Table 2. Results for CFB boiler CO<sub>2</sub> emissions and sulphate- and carbonate-free ash balance

Separation port (Fig. 1)	LHV 8.5 MJ/kg						LHV 11.1 MJ/kg					
	Density g/cm <sup>3</sup>	R[0.5] μm	CO <sub>2</sub> %	CaO %	MgO %	k <sub>CO2</sub>	Density g/cm <sup>3</sup>	R[0.5] μm	CO <sub>2</sub> %	CaO %	MgO %	k <sub>CO2</sub> -
Bottom (C)	1.483	1133	24.04	53.55	3.00	0.47	1.647	430	14.46	50.57	5.60	0.68
INTREX (D)	1.280	108.76	1.52	53.82	4.45	0.97	1.300	118.12	1.42	47.25	6.56	0.97
SH-RH (E)	0.787	20.77	6.94	36.39	4.45	0.79	0.758	19.49	5.26	30.52	5.14	0.82
ECO(F)	0.668	-	6.24	33.93	3.60	0.80	0.710	-	4.67	29.48	4.76	0.83
APH (G)	0.841	-	5.44	38.77	5.11	0.85	0.841	-	3.95	34.41	5.36	0.88
ESP 1 (H)	0.652	10.99	5.61	32.94	3.73	0.82	0.598	10.83	4.33	25.52	4.23	0.82
ESP 2 (I)	0.666	7.93	5.04	31.84	3.36	0.83	0.565	7.99	4.01	24.88	4.51	0.83
ESP 3 (J)	0.564	-	4.29	29.43	3.49	0.84	0.515	-	3.40	22.74	4.81	0.85
ESP 4 (K)	0.431	-	5.43	31.74	3.98	0.81	0.447	-	7.36	25.73	4.34	0.70
k <sub>CO2</sub> for CFB boiler total ash (weighted average), –					0.69						0.78	

Table 3. Characteristics of the ash samples and results of ECD calculation

#### Conclusions

The following general conclusions can be drawn from the investigation of the CFB boiler ash balance and of the mineral matter behaviour when firing oil shale of different quality:

- 1. When firing low-grade oil shale, the share of the bottom ash mass flow in the total ash was 37% instead of 30% when firing upgraded oil shale. The reduced bottom ash mass flow when firing upgraded oil shale could be explained by the reduced content of the carbonate minerals in the fuel and by the finer granular composition of such fuel.
- 2. The  $k_{CO_2}$  value for the CFB boiler's total ash when firing upgraded oil shale was 0.78, and 0.69 when firing low-grade oil shale. The reason for the higher  $k_{CO_2}$  value when firing upgraded fuel could be explained by the finer granular composition of the fuel used in the test.
- 3. In the context of the environmental impact of power production, we should note the reduction of the CO<sub>2</sub> emission by ~7% achieved when firing upgraded oil shale. As CO<sub>2</sub> emissions depend on the  $k_{CO2}$  value and the latter depends on the fuel granular composition, theoretically, taking the boiler  $k_{CO2}$  value for the boiler total ash at 0.69 as it was when low-grade oil shale was fired, an additional reduction of the total CO<sub>2</sub> emission by more than 1% can be achieved when firing upgraded fuel.

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