

## CALCULATION OF CO<sub>2</sub> EMISSION FROM CFB BOILERS OF OIL SHALE POWER PLANTS

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*The extent of carbonate decomposition and calculation of carbon emission factor for CFB boilers of oil shale power plants are examined. The research results proved that CO<sub>2</sub> emission from CFB boilers of Estonian power plants is at least 20% less than that at pulverised firing of oil shale. It is recommended to additionally insert in the regulation of the Minister of the Environment a new value for the carbon emission factor for CFB boilers.*

### Initial position and objective of the work

The amount of carbon dioxide discharged into the atmosphere at oil shale power plants is currently determined as stipulated in the regulation of the Minister of the Environment No. 94 [1] dated July 16<sup>th</sup>, 2004. In accordance with this regulation, specific emission of carbon  $q_{c\ OS}$  is calculated using the following formula:

$$q_{c\ OS} = 10[C_t^r + k(CO_2)_M^r \cdot 12/44]/Q_i^r, \text{ tC/TJ}, \quad (1)$$

where  $C_t^r$  – carbon content in oil shale, %,  $(CO_2)_M^r$  – content of mineral CO<sub>2</sub> in oil shale, %,  $Q_i^r$  – lower heating value of oil shale, MJ/kg, and  $k$  – factor taking into account the extent of carbonate decomposition (ECD) and CO<sub>2</sub> binding at ash fields (the aforementioned values are calculated for fuel as received).

The formula provided in the regulation [1] uses the value of  $k$  0.64. In case this value is used at the calculation, specific emission of carbon from Estonian oil shale is 27.85 tC/TJ, on the basis of which the actual amounts of carbon and CO<sub>2</sub> emissions are established. CO<sub>2</sub> emission (in gigagrams) is calculated using the following formula:

$$M_{CO_2} = 10^{-3} \cdot B^1 \cdot q_{c\ OS} \cdot K_c \cdot 44/12, \text{ Gg CO}_2, \quad (2)$$

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where  $B^1$  – fuel consumption calculated for heat, TJ, and  $K_c$  – the share of oxidised carbon, the value of which for solid fuels, in accordance with the regulation of the Minister of the Environment [1], is 0.98.

Actually factor  $k$  in Formula (1) does not represent ECD in the direct meaning of this term, although applied so in the regulation of the Minister of the Environment. Considering the essence of the issue, it can be said that in reality the value of  $k$  is a multiplication of two factors, one of which is ECD in boilers ( $k_{CO_2}$ ), and the other ( $k_{not\ bound}$ ) takes into account the relative share of CO<sub>2</sub> that remains unbound at ash fields in the carbon dioxide discharged from power plant funnels into the atmosphere. Thus, the value of  $k$  is determined using the formula

$$k = k_{CO_2} \cdot k_{not\ bound}. \quad (3)$$

The value of  $k$  was established on the basis of the research made at the Laboratory of Inorganic Materials of the Tallinn University of Technology (TUT). In that research we used the value of ECD in pulverised firing (PF) boilers  $k_{CO_2} = 1$ . As the general value of  $k$  based on the results of this research is 0.64, the value of  $k_{not\ bound}$ , basing on Formula (3), is 0.64 as well. As a matter of fact, the results of the long-term research carried out at the Department of Thermal Engineering (DTE) of TUT indicate that the average value of  $k_{CO_2}$  in PF boilers is approximately 0.97. In this case the actual value of  $k_{not\ bound} = 0.66$ . The binding of CO<sub>2</sub> at ash fields needs future investigations because of different properties of CFB ash and application of new ash handling technology. Therefore the value of  $k_{not\ bound}$  should be established.

With the introduction of new power units with circulating fluidised-bed (CFB) boilers at Eesti and Balti power plants, the situation concerning ECD and  $k_{CO_2}$  has changed. Firing temperatures in CFB boilers are substantially lower than those in PF boilers. As shown by the corresponding measurements carried out in new boilers, temperature of flue gases in the furnaces of these boilers never exceeds 850 °C, usually staying at 780–820 °C (in PF boilers the furnace temperature is >1400 °C). This circumstance exerts a considerable influence on the intensity of carbonate decomposition.

The warranty trials conducted by the Finnish company Electrowatt-Ekono OY at the 8<sup>th</sup> power unit (with CFB boilers) of Eesti Power Plant in October of 2004 at loads 216.3–218.4 MW that exceed the normal load of the unit (215 MW) showed ECD in the boilers fluctuating during the trials in the range of  $k_{CO_2} = 0.706–0.771$  (average 0.728) [2]. The trials were carried out with a certain oil shale of lower heating value that fluctuated in the range of  $Q_i^f = 7.86–8.54$  MJ/kg. The obtained result demonstrates that calculations of carbon and CO<sub>2</sub> emissions from the CFB boiler using Formula (1) do not justify the use of the value of  $k$  stipulated in the regulation [1] of the Minister of the Environment as it gives a higher result than it should do.

Proceeding from the facts given above, DTE of TUT suggested to conduct a research consisting of a review of the research materials already

existing and additional experiments with the aim of determining ECD in CFB boilers in their usual operating conditions and of explaining how the changes in boiler load and fuel composition influence ECD. This article presents the results of the completed research.

### Method used in experiments

The method used for carrying out the intended experiments was an important aspect of this research – what data should be used as the basis for determining ECD to ensure as accurate results as possible.

In theory, there are several ways of establishing ECD of carbonate-rich fuels, in practice in most cases this process involves quite extensive boiler experiments. Such experiments in large boilers, in which case boiler dimensions make the taking of samples and measurements often rather difficult, often do not provide data that are sufficiently representative. In the particular case of the new CFB boilers installed at the power plants at Narva and considering specific composition of Estonian oil shale, widely acceptable results can indeed be achieved by using a much simpler method than those conventionally employed, and this method does not require special, precisely timed sampling and analysis of fuel, of flue gases, etc. The method described below was developed at DTE of TUT.

As we know, the average chemical composition of main ingredients of Estonian oil shale (organic, carbonaceous and sandy-clay parts) is quite stable [3, 4]. Therefore, it is completely justified to use the average composition for characterising the fuel over a longer working period. Proceeding from the average chemical composition and content of the basic part of the main ingredients, as given in reference sources and calculated using the method given in [3] basing on heating value  $Q_i^f = 8.00\text{--}8.60$  MJ/kg that is in accordance with the data on oil shale currently used at power plants, it was found that the carbonaceous part contains on average 99.2% of all CaO in oil shale, and 96.7% of all MgO. Such a result allows to use the data on CaO and MgO content determined at ash analysis for establishing the initial amount of CO<sub>2</sub> bound in these ingredients before decomposition of carbonates. The following formulas were used:

$$\text{CO}_{2\text{CaO}} = \text{CaO}_{\text{ash}} \cdot 0.992 \cdot 44.01 / 56.08 \quad (4)$$

$$\text{CO}_{2\text{MgO}} = \text{MgO}_{\text{ash}} \cdot 0.967 \cdot 44.01 / 40.32 \quad (5)$$

$$\text{CO}_{2\text{sum}} = \text{CO}_{2\text{CaO}} + \text{CO}_{2\text{MgO}} \quad (6)$$

where  $\text{CO}_{2\text{CaO}}$  and  $\text{CO}_{2\text{MgO}}$  – CO<sub>2</sub> bound with CaO and MgO, respectively, calculated as percentage of the ash mass.

FeCO<sub>3</sub> content of the carbonaceous part of oil shale is so small (~0.3% [3, 4]) that in practice it can be excluded from calculations. In case the

content of carbonaceous CO<sub>2</sub> in ash (CO<sub>2,ash</sub>) is also determined by chemical analysis, ECD is calculated using formula

$$k_{\text{CO}_2} = 1 - \text{CO}_{2,\text{ash}}/\text{CO}_{2,\text{sum}} \quad (7)$$

As it is evident from the aforementioned facts, ECD of an ash fraction can easily be calculated basing on the content of CaO, MgO and carbonaceous CO<sub>2</sub> determined by chemical analysis. Thus the decisive issue in our case is obtaining of representative ash samples.

This problem is also relatively easily solved when dealing with CFB boilers of the power plants at Narva (the power unit No. 8 of Eesti Power Plant and the power unit No. 11 of Balti Power Plant). Namely, practically all ash from these boilers is sent to a common ash silo. Only a quite small part of the ash is carried out of the boilers with flue gas, and the relative importance of this ash is not as large as to influence the results considerably. For instance, the amount of the ash discharged with flue gas in the course of the experiments conducted by DTE of TUT was merely 0.03-0.04% of the total ash amount. It can therefore be stated that practically all CaO and MgO present in the ash goes to the ash silo.

Four samples were to be taken at sampling the ash from the CFB boiler ash silo because such an ash silo has four outlets, and grain composition of the ash flowing out of these outlets slightly differs. Certain volumes of the ash samples were taken at equal time intervals after the rotation speeds of all outlet rotary valves were adjusted to a common value. Volume mass of the samples was measured and the analysis results are given per volume mass.

### **ECD in CFB boilers determined on the basis of ash composition**

The data on the ECD in CFB boilers presented below are based on the results of the analysis of the ash samples taken during various experiments carried out at the power unit No. 8 of Eesti Power Plant and the power unit No. 11 of Balti Power Plant in 2004–2006. Ash samples were analysed at the chemistry laboratory of DTE. Some of these experiments were related to general studies of CFB boiler operations, while some others were aimed at obtaining data about ash composition and properties to solve the problems related to ash removal from CFB boiler, and there were also some special experiments to establish ECD in CFB boilers.

Calculation of ECD on the basis of ash sample analysis using the method described above (formulas 4-7) demonstrates that ECD in CFB boilers depends to a large extent on fuel particle size and boiler load. The dependence of ECD on particle size is illustrated by data of an ash sample taken from the ash silo of the power unit No. 8 of Eesti Power Plant (Table 1). The sample was sieved, the fractions analysed for ingredient content and, basing on these data, ECD of each fraction was calculated.

Low values of ECD in thicker pieces of ash indicate that most likely larger and heavier pieces of fuel, consisting mainly of carbonaceous minerals, relatively quickly fall out of the fluid bed, which is why the process of carbonate decomposition in such pieces cannot be completed.

**Table 1. Composition of fractions (%) of the sample taken from ash silo of a CFB boiler on 22.10.2004. Calculated values of ECD**

Ingredient	Total ash	Ash fraction		
		< 4 mm	4-8 mm	> 8 mm
SiO <sub>2</sub>	25.35	27.06	5.82	5.51
Fe <sub>2</sub> O <sub>3</sub>	4.06	4.20	2.59	1.94
Al <sub>2</sub> O <sub>3</sub>	6.38	6.80	1.43	2.02
CaO	36.81	36.00	45.81	46.78
CaO <sub>free</sub>	9.44	10.13	1.54	1.30
MgO	5.51	5.57	5.12	4.20
K <sub>2</sub> O	2.79	2.98	0.70	0.54
Na <sub>2</sub> O	0.20	0.21	0.08	0.10
SO <sub>3</sub> general	7.11	7.49	3.15	2.20
SO <sub>3</sub> sulphate	6.98	7.43	2.00	1.41
CO <sub>2</sub>	11.78	9.69	35.31	36.71
Total:	100.00	100.00	100.00	100.00
<b>Extent of carbonate decomposition</b>				
CO <sub>2</sub> CaO	28.66	28.02	35.66	36.41
CO <sub>2</sub> MgO	5.82	5.88	5.41	4.43
CO <sub>2</sub> summ	34.47	33.91	41.07	40.84
k <sub>CO2</sub>	0.658	0.714	0.140	0.101

Special experiments were also carried out at the power unit No. 8 of Eesti Power Plant with the aim of assessing how a decreased load of the boilers (the power unit) influences the composition and properties of ash. The experiments were made at three loads of the power unit – 215, 160 and 120 MW<sub>el</sub>. The results of chemical analysis of ash samples taken during these experiments are presented in Table 2. It should be noted that sieve analysis of the ash samples did not reveal any special and distinct changes in the grain composition of the ash samples obtained at different loads of the boiler. Yet the results of chemical analysis show that if the load decreases, ECD of the samples decreases as well. Here we can also note that ECD of coarser ash samples (silo outlets 13 and 14) is generally less than that of finer ash samples (outlets 11 and 12). As for the decrease in ECD with the decrease in boiler load, it is definitely at least partially caused by lower temperatures in boiler furnace at lower loads. This is illustrated by the data in Fig. 1 on the temperature of flue gas entering the crossover duct of the boiler at different loads of the energy unit.

Table 2. ECD in CFB boilers depending on boiler load (ash samples from the total ash silo of power unit No. 8 of Eesti Power Plant)

Unit load, MW	215				160				120						
	11	12	13	14	4 outlets	11	12	13	14	4 outlets	11	12	13	14	4 outlets
<b>Chemical analysis, %</b>															
CaO	45.28	45.87	56.53	50.40	49.52	40.67	39.07	55.55	46.22	45.38	40.28	36.77	55.03	47.28	44.84
MgO	4.82	4.01	4.54	3.53	4.23	4.51	3.43	4.63	4.97	4.39	2.85	4.08	4.11	3.90	3.73
CO <sub>2k</sub>	10.89	10.52	19.42	15.32	14.04	12.44	19.60	24.70	16.54	18.32	16.03	12.88	26.85	21.30	19.27
S <sub>total</sub>	2.32	2.16	2.63	2.38	2.37	2.12	2.12	2.61	2.44	2.32	2.19	2.46	2.66	2.31	2.41
S <sub>sulphate</sub>	2.31	2.16	2.54	2.30	2.33	2.12	2.12	2.49	2.43	2.29	2.18	2.23	2.60	2.24	2.31
CaO <sub>v</sub>	7.66	8.32	7.38	7.09	7.61	4.16	4.39	3.50	4.14	4.05	2.54	2.85	1.64	1.65	2.17
<b>Extent of carbonate decomposition</b>															
CO <sub>2-Ca</sub>	35.25	35.71	44.01	39.24	38.55	31.67	30.41	43.24	35.98	35.33	31.36	28.63	42.84	36.81	34.91
CO <sub>2-Mg</sub>	5.09	4.23	4.79	3.73	4.46	4.76	3.62	4.88	5.25	4.63	3.01	4.30	4.34	4.11	3.94
CO <sub>2 total</sub>	40.34	39.94	48.80	42.96	43.01	36.42	34.03	48.13	41.23	39.95	34.37	32.93	47.18	40.92	38.85
k <sub>CO2</sub>	<b>0.73</b>	<b>0.74</b>	<b>0.60</b>	<b>0.64</b>	<b>0.68</b>	<b>0.66</b>	<b>0.42</b>	<b>0.49</b>	<b>0.60</b>	<b>0.54</b>	<b>0.53</b>	<b>0.61</b>	<b>0.43</b>	<b>0.48</b>	<b>0.51</b>

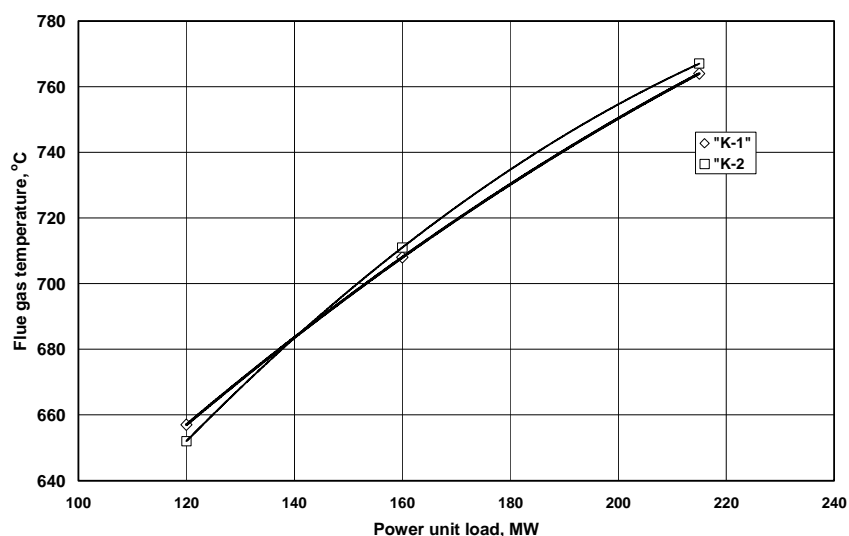


Fig. 1. Flue gas temperature in crossover duct of boilers of the power unit No. 8 of Eesti Power Plant at different loads

Examining all data on ECD determined during various experiments described above, one can see that ECD in ash samples taken from different outlets of the ash silo never exceeded 0.75,  $k_{CO_2}$  fluctuating between 0.42 and 0.75. Fine fractions are characterized by the highest ECD. As for ECD of the total ash, its average value at the nominal load of the boiler fluctuated between 0.51 and 0.68. As shown by last measurements, in most cases the value of ECD did not exceed 0.6.

### Calculation of specific emission of carbon

The data presented above demonstrate that the formula included in the regulation of the Minister of the Environment for calculating specific emission of carbon needs to be corrected for the use for CFB boilers operating on Estonian oil shale. At first in Formula (1) ECD value  $k$  is to be corrected. DTE of TUT recommends to proceed as follows: as the actual ECD value  $k_{CO_2}$  established for the total ash was mainly below 0.60, this number can be initially used as the basis for calculating the value of  $k$  in Formula (1) using Formula (2). This guarantees that the real amount of  $CO_2$  will by no means be underestimated. After all, the power units equipped with CFB boilers are currently set to be operated mainly at their nominal load. At lower loads, as proved above, ECD does not increase – it decreases.

As for the  $CO_2$  binding at ash fields and sedimentary ponds with alkaline water, in view of the fact that the ash of CFB boilers, as demonstrated by its chemical analysis, contains on average 7–10% free lime ( $CaO_{free}$ ), such an

amount is sufficient for saturating, with Ca(OH)<sub>2</sub>, a 3–4 times greater volume of water than actually used in the hydro ash removal process. This allows to conclude that the alkalinity of the water circulating in the hydro ash removal of the CFB boiler ash will remain unchanged. This, in its turn, means that the degree of CO<sub>2</sub> binding by the CFB boiler ash in the hydro ash removal process at ash fields will also remain at the current level. Therefore, the value of  $k_{\text{not bound}}$  should be the already determined figure 0.66.

Proceeding from the data given above, the new value of  $k$  to be used in Formula (1) for CFB boilers instead of the previously used 0.64 is

$$k = k_{\text{CO}_2} \cdot k_{\text{not bound}} = 0.60 \cdot 0.66 = 0.40.$$

Apparently it would be practical to correct the regulation [1] of the Minister of the Environment, and in the future specific emission of carbon and, accordingly, emission of CO<sub>2</sub> from PF and CFB boilers must be calculated separately.

Thus, also the table of specific emissions  $q_c$  in the regulation [1] needs correcting and adding of a separate value of specific emission  $q_c$  for CFB boilers. Researchers of DTE of TUT recommend to use the value  $q_c = 26.94$ . This was calculated proceeding from the data provided below. Heating value of oil shale, basing on the average heating value of the fuel currently used at Narva power plants,  $Q_i^r = 8.40$  MJ/kg. The average content of carbonaceous CO<sub>2</sub> in this fuel  $(\text{CO}_2)_M^r = 17.7\%$  is in accordance with the method [3], and carbon content  $C^r = 20.7\%$ . Introducing the obtained initial data into Formula (1) gives

$$q_c = \frac{10 \cdot (20.7 + 0.40 \cdot 17.7 \cdot 12 / 44)}{8.40} = 26.94, \text{ tC/TJ.}$$

Therefore specific emission of carbon in the CFB boiler is less than that in oil shale boilers stipulated in the regulation [1] by  $\Delta q_c = 27.85 - 26.94 = 0.91$  tC/TJ.

Proceeding from the new value of  $q_c$ , the rated decrease in CO<sub>2</sub> emission is established in comparison with the rated emission currently determined on the basis of the regulation [1]. The estimated number of working hours of the power unit per annum, as set in the delivery contract of the power unit,  $T = 8000$  h/a, and the rate of fuel feed into the boilers of the power unit  $m = 67.3$  kg/s (calculated in accordance with specific heat consumption). The value of the share of oxidised carbon ( $K_c = 0.98$ ) is in compliance with the regulation [1] – the actual  $K_c$  value for oil shale is about 0.99.

Annual fuel consumption of the power unit is determined first

$$B = 8000 \cdot 3.6 \cdot 67.3 = 1938240, \text{ t/a,}$$

or expressed in heat units

$$B^1 = 1938240 \cdot 10^3 \cdot 8.40 \cdot 10^6 \cdot 10^{-12} = 16281, \text{ TJ.}$$



Proceeding from the established value of  $\Delta q_c$ , the difference between the amounts of CO<sub>2</sub> emission  $q_c$  for one power unit of the CFB boiler calculated as prescribed by the regulation [1] and that calculated on the basis of this research (the suggested corrected value)

$$\Delta\text{CO}_2 = 16281 \cdot 0.91 \cdot 0.98 \cdot 44 / 12 = 54324, \text{ t/a.}$$

Totally for the two (Eesti and Balti) power plants the annual amount of CO<sub>2</sub> emission from operating CFB power units would thus in fact be more than 108,000 tons less than the amount calculated currently.

### Comparison of the amounts of CO<sub>2</sub> emission from PF and CFB boilers

In order to paint a more detailed picture of how much the implementation of CFB boilers at oil shale power plants decreases CO<sub>2</sub> emissions, Table 3 gives the results of comparative calculations for PF and CFB boilers on the amounts of CO<sub>2</sub> discharged into the atmosphere per the same electricity output 1 GWh. Specific heat consumption for CFB boilers is equal or less than 9471 kJ/kWh. The value of specific heat consumption for PF boilers was determined on the basis of the conditional specific fuel consumption that, according to the data in [5], was 400.5 g/kWh in 2002 at the power units of Eesti Power Plant equipped with TP-101 boilers. The values of specific emission of carbon  $q_c$  for PF and CFB boilers are taken from the data given in this article.

Table 3. Comparison of the amounts of CO<sub>2</sub> emission from PF and CFB boilers

Indicator	Unit	PF boiler	CFB boiler
Specific heat consumption	kJ/kWh	11738	9471
Specific heat consumption	TJ/GWh	11.738	9.471
Specific emission of carbon, $q_c$	tC/TJ	27.85	26.94
CO <sub>2</sub> emission per GWh	t/GWh	1199	936
Percentage of PF boiler emission	%	100.0	78.1

As one can see, the adoption of CFB boilers reduces CO<sub>2</sub> emission by over 20% (in this particular case:  $100 - 78.1 = 21.9\%$ ). In practice, as shown by the warranty trials [2], specific heat consumption of power units with CFB boilers was between 9181–9280 kJ/kWh, and this allows us to assume that the actual decrease in CO<sub>2</sub> emission in CFB boilers compared to PF definitely exceeds 20%.

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