

MINERAL SEQUESTRATION OF CO₂ BY CARBONATION OF Ca-RICH OIL SHALE ASH IN NATURAL CONDITIONS

ALAR KONIST^{(a,b)*}, BIRGIT MAATEN^(b), LAURI LOO^(b),
DMITRI NESHUMAYEV^(b), TÕNU PIHU^(b)

^(a) School of Engineering, Brown University, 182 Hope St., Providence, RI, USA, 02912

^(b) Department of Thermal Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Abstract. Oil shale (OS) is an unconventional low-calorific-value fossil fuel, the usage of which is increasing due to increasing energy demand. Today, Estonia's OS usage is the largest in the world. Approximately 90% of the electricity consumed is produced from Ca-rich OS. Most of the OS, approximately 12 million tons yearly, is used for power generation utilizing pulverized combustion (PC) and circulating fluidized bed combustion (CFBC) technologies that produce nearly 6 million tons of ash. As a result, Estonia has one of the world's highest CO₂ emission rates per capita.

The current study is focused on determination of the amount of CO₂ bound by CFBC and PC boiler OS ashes in an ash field. The binding ability toward CO₂ of the ash stored in an ash field is observed. Based on the in situ experimental data, when looking the binding abilities of ashes from both the technologies separately, it is found that approximately 9.7% of the CO₂ emitted is bound by the CFBC ash and about 3.4% by the PC boiler ash in an ash field.

On the basis of experimental data it is found that approximately 5–6% of the CO₂ emitted is bound back by oil shale power plant ash fields and sediment ponds.

Keywords: oil shale ash, circulating fluidized bed combustion, pulverized combustion, CO₂, free lime carbonation, ash field.

1. Introduction

The largest air pollution emitter in Estonia is the power company Eesti Energia Narva Power Plants (EE Narva PPs). More than 90% of Estonia's electricity is produced from OS [1]. OS is known as a fuel with a low heating value (8.0–9.2 MJ/kg) and a high ash content (43–53%). OS dry

* Corresponding author: e-mail alar_konist@brown.edu; alar.konist@ttu.ee

matter consists of three components: organic, carbonate and sandy clay [2]. The main components in the carbonate part of OS are calcium carbonate and dolomite. During OS combustion, a considerable amount of CO₂ is produced by the decomposition of carbonate minerals. This high level of CO₂ production is the reason why the OS-specific carbon emission factor is high. Therefore, OS usage for energy production is considered environmentally unfriendly. To decrease the CO₂ emission, EE Narva PPs put in 2004 into commercial operation two CFBC units with a total output of 430 MW_{el}. According to [3] the CO₂ emission from the CFBC unit is at least 20% less compared to PC units. With the CFBC technology, there is another aspect of OS usage that has not been thoroughly studied and that decreases the overall CO₂ emission: the CO₂ binding ability of ash fields and settling ponds. Laboratory investigations on CO₂ binding at oil shale ash deposits have been conducted by several researchers [4–7]. Anthony et al. [8] carried out a long-term study of the behavior of CFBC ash-water systems in which the reduction in landfill chemical reactivity and free lime carbonation were observed. The CO₂ absorption potential of residues has been estimated by Vassilev et al. [9]. Preliminary results for the CO₂ binding properties of the CFBC boiler ash have been analyzed by Konist and Pihu [10].

The current study was focused on the in situ determination of the increase of the CO₂ content in ash and transportation water in the samples taken from an ash field. The samples were taken over a long time period. The dynamics and amount of CO₂ absorbed from the atmosphere by OS ashes formed in PC and CFBC boilers were studied, taking into consideration the conditions of different seasons. CO₂ absorption by transportation water in sediment ponds was investigated in laboratory conditions. Finally, the total quantity of CO₂ bound in the ash fields and sediment ponds of OS from the Eesti and Balti power plants (PPs) was determined and generalized on the basis of the results from field sample analyses and calculations.

The total CO₂ emissions from OS power plants have changed due to the fact that some of the old PC energy units have been closed for power production and a 300 MW_{el} CFBC unit is under commissioning. The reference fuel for a new CFBC unit is OS with a heating value of 8.2 MJ/kg. The heating value of OS used nowadays for PC units is 7.6 MJ/kg. Taking into account these changes, the share of the emitted CO₂ bound back by ash fields and sediment ponds has risen by approximately 1%.

2. System description

The total area of ash fields, settling ponds and open return flow channels of the ash handling system of the Balti Power Plant (Balti PP) is 5,088,000 m² and of the Eesti Power Plant (Eesti PP) 9,800,000 m². The ash deposit areas are 2,200,000 m² and 4,900,000 m², respectively. The amount of the system

water is estimated to be approximately 6,000,000 m³ at the Balti PP and 14,000,000 m³ at the Eesti PP.

The ash handling system is hydraulic, with ash and slag transportation to the ash field. The ash from the boilers is mixed with water (in a ratio up to 1:20) and the formed ash/water mix is pumped through the pipes into the ash field. Flowing along the slightly inclined ash field surface, the ash separates from the mix, and the water collects in the upper sediment pond where the final separation from the fine ash particles takes place. From the upper sediment pond, the water flows into the lower sediment pond and then through the collecting channels that return it to the power plant; the whole process is then repeated. Therefore, this is a system in which the ash transport water circulates between the power plant and the ash field. Because the Balti PP runs primarily on the CFBC technology, its ash field was chosen for CFBC ash studies. For PC ash studies the Eesti PP ash field was chosen since the plant employs chiefly the PC technology. The conceptual diagram of the hydraulic ash removal system is shown in Figure 1 [11].

From the CO₂ absorption point of view, the ash field can be divided into three sections: the dry section of the ash field, the wet section of the ash field and the settling ponds. The dry section of the ash field is in a stationary state and has no binding properties. The primary binding material in the wet section of the ash field is the flowing ash slurry. The main carbon dioxide

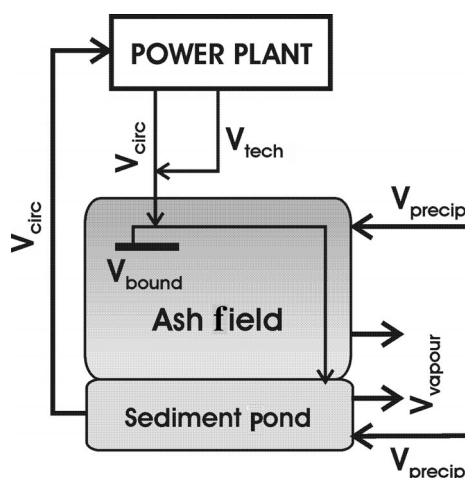


Fig. 1. Conceptual diagram of the ash field water balance. V_{circ} – water used for ash handling which together with the ash is returned to the ash field; V_{tech} – water given to the ash fields through different technological proceedings (e.g. chemical treatment) and other sewage; V_{bound} – water bound with ash; V_{precip} – water fallen on the fields in the form of precipitation; V_{vapour} – water that has evaporated from the ash fields, the surface of the sediment pond and the ash handling system.

Note: There are two sediment ponds in the working ash field – the upper and lower ponds.

binder in the settling ponds is the continuously moving water. The CO₂ absorption is influenced by several factors.

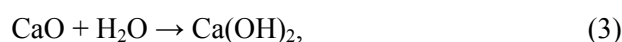
The ash fields exploitation experience has shown the ash to bind water (V_{bound}) in a quantity of 0.6–0.7 m³ per ton of ash and this water is carried out from the system. Thus, the quantity of water bound depends on the quantity of ash stored in the ash field. The water balance of the ash field is affected by weather conditions. The evaporation (V_{vapour}) decreases from and precipitations (V_{precip}) add water to sediment pond and ash field surfaces. Depending on weather conditions the water amounts may from year to year fluctuate greatly. If the ash is disposed of in a dry or partly wetted state, the crystallization reactions that occur over the long term destroy the initial hardening and lead to swelling and the formation of cracks. The other important issue is the reaction of the ash minerals with atmospheric CO₂. This reaction has a bilateral benefit to the environment: it consumes atmospheric CO₂ and transfers alkaline minerals into carbonates, decreasing the potential of alkaline leaching.

3. Materials and methods

Under atmospheric conditions, the transformation of free CaO into CaCO₃ is realized through the water phase only:



Between these two reactions, there is an intermediate process of Ca(OH)₂ accumulation:



In a similar way, ettringite dissolution will also lead to CO₂ removal.

In addition, it should be noted that CO₂ is also removed by the dissolution of calcium hydroxide and the mixing of Ca-rich alkaline water with groundwater:



Therefore, the content of free lime (CaO) in the dry ash presents the maximum potential for CO₂ removal from the atmosphere: 78.6% of the mass of free CaO in the ash (based on the stoichiometry and molecular weight of CaCO₃). Until portlandite Ca(OH)₂ and ettringite Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O are present in the ash, the CO₂ removal potential is not fully achieved. The physical and mineral properties of the CFBC oil shale ash have been studied by Pihu et al. [11].

The formed CaCO_3 does not settle down at the point at which the reaction between $\text{Ca}(\text{OH})_2$ and CO_2 takes place. The settling occurs along the flow path of the ash/water mixture. Some of the formed CaCO_3 can be found in the settling pond. Therefore, that part is taken as the amount of CaCO_3 formed in the settling pond.

The transportation water circulating in the closed cycle has been analyzed for chemical composition, the results are presented in Table 1 [11].

Table 1. Chemical composition (mg/l) and pH range of operating sediment ponds water

Component	Value
pH	12.2–13
Na^+	100–180
K^+	3000–4765
Ca^{2+}	400–800
NH_4^+	0–1
Cl^-	720–1070
SO_4^{2-}	1043–2960
CO_3^{2-}	1–360

The K/Ca ratio expresses the dominance of longer-term reactions over fresh ash dissolution reactions and actually proves that water is efficiently circulating in the hydro-transport system (if the fresh water would have been used for transport, the concentration of K^+ would be low and the concentration of Ca^{2+} high). The concentration of CO_3^{2-} shows that the system is opened to the atmosphere and removal of CaCO_3 occurs in the system (e.g. in sedimentation ponds).

The binding of CO_2 by the alkali transport water was studied in laboratory conditions by using the water from the hydraulic ash removal system.

The tests of CO_2 absorption by alkali water show that the total surface of sediment ponds can absorb up to 50 thousand tons of CO_2 annually.

To calculate the amount of CO_2 absorbed by ash in the dry ash field section, the CO_2 content in the ash coming out of the boiler and in the ash field material must be known. The differences between these values give us the amount of CO_2 bound by OS ash.

The difficulty of the calculations is increased by considering the fuel properties and two types of combustion technologies used. The CO_2 content of ashes in PC and CFBC technologies is different. CO_2 content depends on the decomposition of carbonate minerals, as found by Neshumayev et al. [12]. In PC boilers, the extent of carbonate minerals decomposition is in the range of 0.93–0.97, being in CFBC boilers considerably lower, in the range of 0.60–0.69, largely because of the lower temperature in the furnace. According to Plamus et al. [13], the PC boiler ash going to the ash field contains approximately 2% CO_2 , while the CFBC boiler ash contains con-

siderably more, approximately 10–14% CO₂. This is the main information that must be known to obtain accurate results from the calculations.

The baseline data for the calculations are taken from the sampling and determination of the CO₂ content in the ash field material. The chemical analysis results of drilling samples are on a dry basis, meaning water- and CO₂-free ash material. The difference (gap) between the CO₂ contents (ΔCO_2) in the ash field material and the total ash from the boiler shows the quantity of CO₂ bound from the surrounding air.

It is important to note that the samples had been packed air tight immediately after sampling to minimize additional carbonation prior to analysis.

The ash field is not a uniform body. Its chemical and mineral compositions vary depending on landfilling time, season and combustion technology. The sampling locations were chosen according to that knowledge. Samples were taken with a dry-type drill in 10 cm steps up to 60 cm. To obtain representative data and draw accurate conclusions, the samples were taken over a period of two years while keeping in mind the different seasons. The sampling locations for CFBC ash samples are shown in Figure 2 and those for PC ash samples in Figure 3.

The amount of CO₂ absorbed by ash in the ash field can be determined as follows. Using chemical analyses, we can determine the quantity of chemical components \sum_{comp} , mineral (CO₂)_M and the amount of water bound (H₂O)_M with ash. To determine the amount of water (H₂O)_M bound with ash, the amount of CO₂ was subtracted from the loss on ignition at 815 °C.

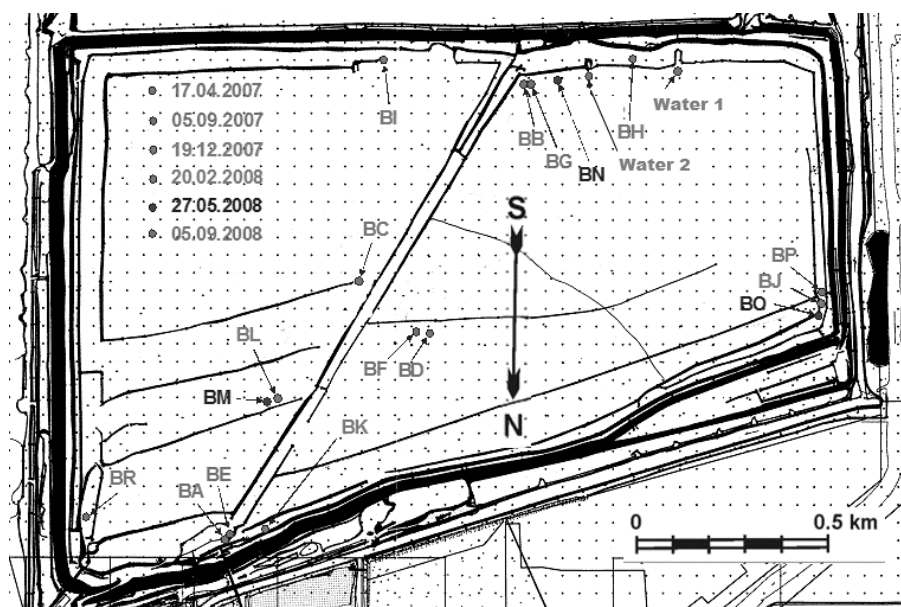


Fig. 2. Sampling locations in the Balti PP ash field.

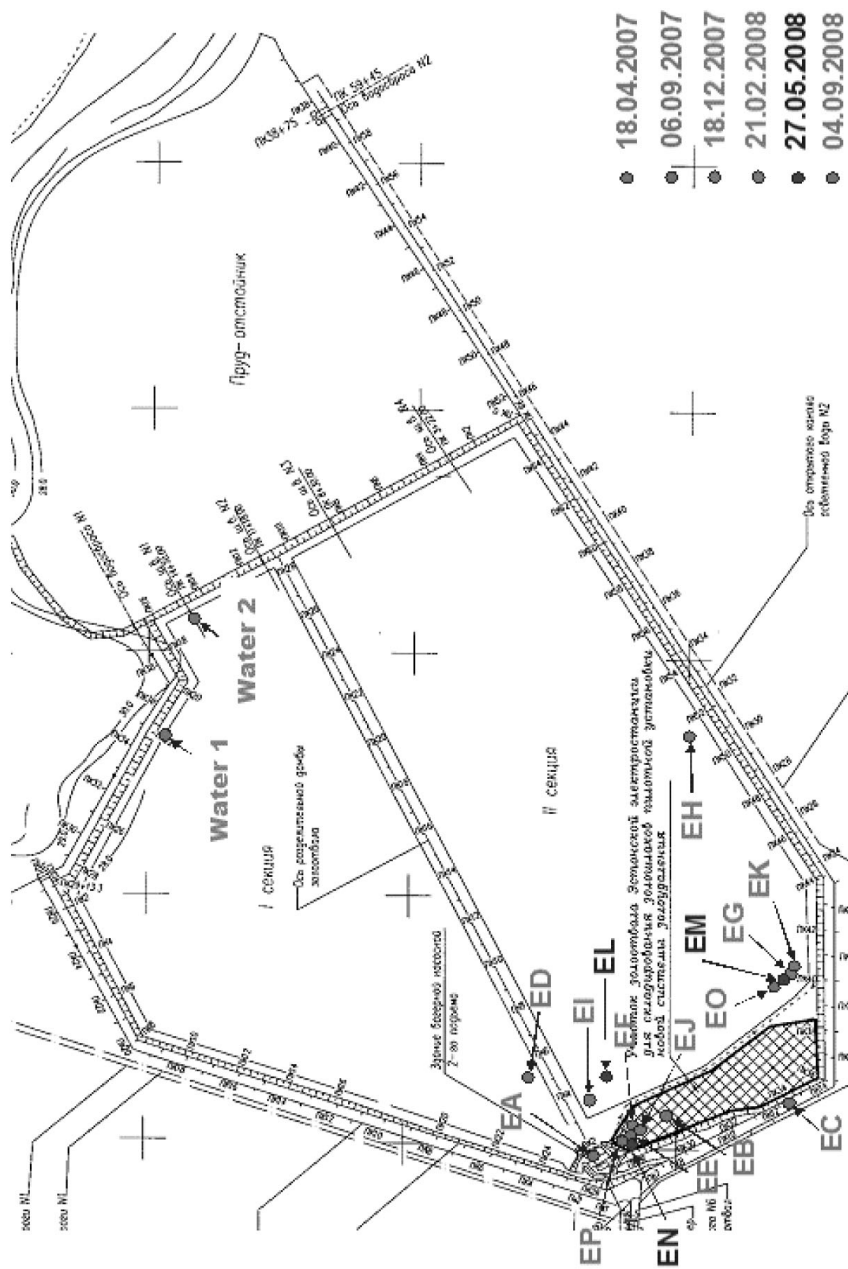


Fig. 3. Sampling locations in the Eesti PP ash field.

Calculations were as follows:

1. Water-free CO₂ content in ash:

$$(\text{CO}_2)_{\text{M water-free}}^{\text{d}} = (\text{CO}_2)_{\text{M}} \cdot 100 / (\sum_{\text{comp}} - \text{H}_2\text{O}_{\text{M}}). \quad (6)$$

2. With the average OS net calorific value, the $(\text{CO}_2)_{\text{M}}^{\text{d}}$ and A^{d} dry content were calculated according to the method described by Arro et al. [14].
3. Taking into account the average extent of carbonate decomposition (k_{CO_2}), the average content of CO₂ in the ash field ash can be found accordingly:

$$(\text{CO}_2)_{\text{M in ash field}}^{\text{d}} = (1 - k_{\text{CO}_2}) \cdot (\text{CO}_2)_{\text{M}}^{\text{d}} \cdot 100 / A^{\text{d}}. \quad (7)$$

4. The amount of CO₂ absorbed from the atmosphere (ΔCO_2) by ash in the ash field is thus calculated:

$$\Delta\text{CO}_2 = (\text{CO}_2)_{\text{M water-free}}^{\text{d}} - (\text{CO}_2)_{\text{M in ash field}}^{\text{d}} / (100 - (\text{CO}_2)_{\text{M water-free}}^{\text{d}} + (\text{CO}_2)_{\text{M in ash field}}^{\text{d}}). \quad (8)$$

4. Amount of CO₂ absorbed by PF and CFBC ashes in the ash field

Because ash from CFBC boilers is mainly deposited in the Balti PP ash field, the studies were conducted in locations where the OS CFBC boiler ash had previously been landfilled. Therefore, the calculations are presented on the basis of samples taken from the Balti PP ash field that were chemically analyzed. According to those results, the average CO₂ content $(\text{CO}_2)_{\text{M average}} = 21.2\%$, the loss on ignition LOI = 27.59% and the water content $\text{H}_2\text{O}_{\text{M average}} = 6.39\%$ (Table 2). Using the method of [14], the following fuel parameters were found: $(\text{CO}_2)_{\text{M}}^{\text{d}} = 19.99\%$ and dry fuel carbonate-free ash content $A^{\text{d}}_{\text{carbonate-free}} = 52.72\%$. According to the calculations, the amount of CO₂ absorbed per ton of fuel is 0.066 $t_{\text{CO}_2}/t_{\text{fuel}}$ in the case of the CFBC boiler.

Ash from PC boilers is mostly deposited in the Eesti PP ash field, the studies were carried out in locations where the OS PC boiler ash had earlier been disposed of. Therefore, the calculations are presented on the basis of samples taken from the Eesti PP ash field that were chemically analyzed. According to those results, the average CO₂ content $(\text{CO}_2)_{\text{M average}} = 10.92\%$, the loss on ignition LOI = 14.09% and the water content $\text{H}_2\text{O}_{\text{M average}} = 6.68\%$ (Table 2). Using the method of [14], the following fuel parameters were found: $(\text{CO}_2)_{\text{M}}^{\text{d}} = 18.84\%$ and dry fuel carbonate-free ash content $A^{\text{d}}_{\text{carbonate-free}} = 46.30\%$. According to the calculations, the amount of CO₂ absorbed per ton of fuel is 0.043 $t_{\text{CO}_2}/t_{\text{fuel}}$ in the case of the PC boiler. The calculations are presented in Table 2.

According to studies, PC and CFBC boiler ashes bind 0.043 and 0.066 tons of CO₂ per ton of fuel, respectively.

Table 2. Amount of CO₂ absorbed by PC and CFBC boiler ashes in the Eesti PP and Balti PP ash fields, respectively

Variable	Symbol	Unit	Values	
			PC	CFBC
Calculation of the mean constituents of fuel and ash				
Heating value of fuel as received	Q_i^r	MJ/kg	9.20	8.45
Calculated content of CO ₂ for dry fuel	$(CO_2)_M^d$	%	18.84	19.99
Extent of carbonate decomposition	k_{CO_2}		0.95	0.60
Undecomposed carbonates (dry fuel)	CO_2^d undecomposed	%	0.94	8.00
Moisture content of fuel as received	W_t^r	%	12.10	11.57
Amount of formed carbonate-free ash for dry fuel	A^d carbonate-free	%	46.30	52.72
Chemical composition of ash samples taken from the ash field				
Amount of carbonate CO ₂	$(CO_2)_M^d$ ash field	%	10.92	21.20
Water content	H_2O_M average	%	6.68	6.39
Loss on ignition	$LOI_{815^\circ C}$	%	14.09	27.59
Calculated values				
Amount of carbonate-free CO ₂ in total ash	CO_2_M	t/t	0.020	0.152
Amount of carbonate CO ₂ in the ash field sample (calculated from the carbonate- and water-free content)	CO_2_M ash field	t/t	0.127	0.293
Amount of CO ₂ absorbed in the ash field (calculated from the CO ₂ and water-free ash flow)	ΔCO_2_M ash field	t/t	0.107	0.141
Amount of CO ₂ absorbed in the ash field				
Amount of CO ₂ absorbed in the ash field per ton of fuel as received	CO_2_k ash field	t_{CO_2}/t_{fuel}	0.043	0.066

The CO₂ content in the ash field ash depending on the sampling depth and time is shown in Figures 4 and 5. Samples were taken in the time period

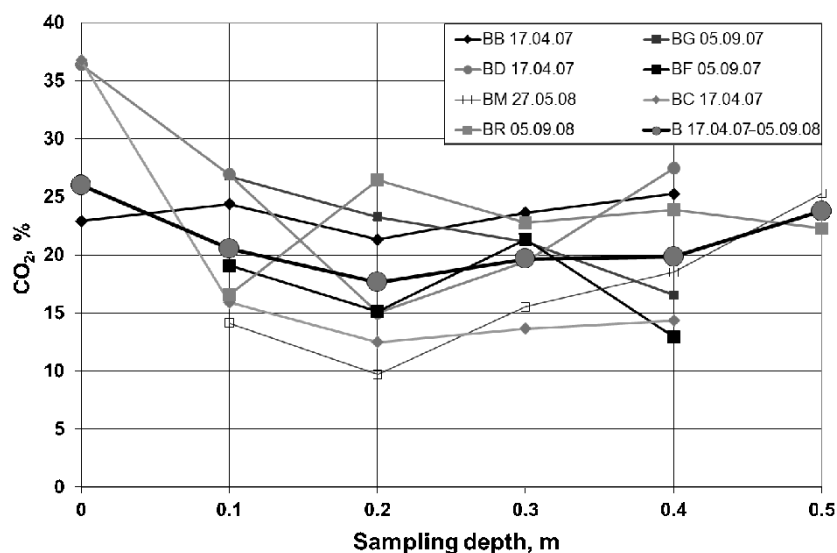


Fig. 4. Balti PP ash field (generated primarily with the CFBC technology).

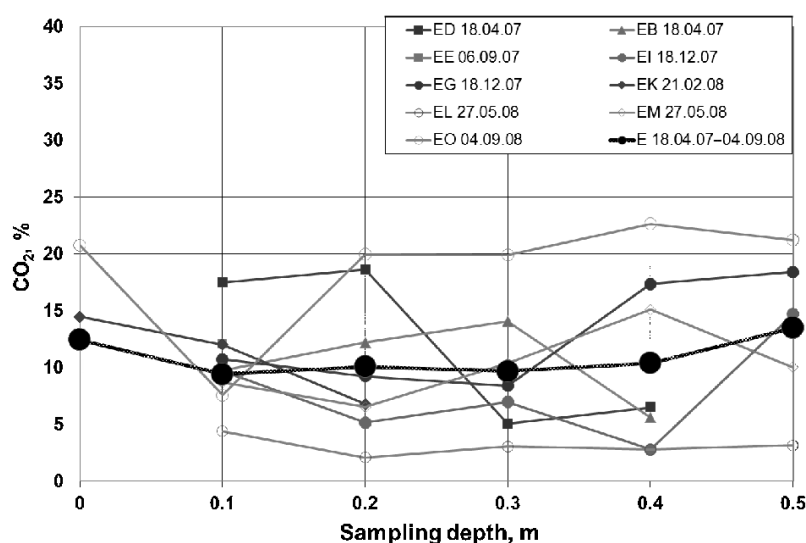


Fig. 5. Eesti PP ash field (generated primarily with the PC technology).

from 17.04.07 to 05.09.08. B and E indicate the overall average CO₂ content of CFBC and PC ashes in the Balti and Eesti PP ash fields, respectively. The average amount of carbonate CO₂ is calculated as in-depth average per sampling location, excluding the loose surface ash layer.

As a reminder, the CO₂ content in the OS CFBC boiler ash varies from 10 to 14%, depending on the boiler load and fuel granular composition. The CO₂ content in the OS PC boiler is around 2%.

The conducted in situ study on PC and CFBC boiler ashes to determine the CO₂ binding rate in the ash field provided a good overview of where and when the binding takes place. The CO₂ binding with PC and CFBC ashes occurs mainly in the ash/water flowing channels and on the surface of the moist ash field. The CO₂ absorption stops when ash has lost contact with ambient air. Therefore, the calculations can be made on the basis of the amount of ash transported to the ash field. The calculations were based on the method of [14], where an average OS lower heating value of 9.20 and 8.45 MJ/kg for the PC and CFBC boiler was used, respectively. According to the calculations, the amount of CO₂ bound in the ash field per ton of fuel is 0.043 and 0.066 t_{CO2}/t_{fuel} in the case of PC and CFBC boilers, respectively.

Based on EE Narva PPs data, the OS CFBC boiler fuel consumption in 2008 was 3.498 million tons. On the basis of this known fuel consumption, we can calculate the CO₂ emission to the atmosphere. In 2008, the CO₂ emissions were 2.844 million tons.

By multiplying the fuel amount of 3.498 million tons with the CO₂ binding rate of 0.066 t_{CO2}/t_{fuel}, we obtain the amount of CO₂ bound in the ash field by the CFBC boiler ash – 0.231 million tons annually. This value is 8.1% of the annual CO₂ emissions from CFBC boilers.

The fuel consumption of the PC boiler in 2008 was 8.530 million tons. By multiplying this fuel amount with the CO₂ binding rate of 0.043 t_{CO2}/t_{fuel}, we obtain the amount of CO₂ bound in the ash field by the PC boiler ash – 0.367 million tons annually. This value is 4.3% of the annual CO₂ emissions from PC boilers.

These in situ study values are somewhat higher compared to the laboratory test results given by Uibu et al. [6], who found the CO₂ natural open air binding to be 3.1% [6].

5. Conclusions

According to the in situ studies conducted, OS PC and CFBC ashes have tremendous CO₂ binding capabilities. These capabilities are due to the high free CaO content that remains in the ashes. The main CO₂ binding takes place in the ash field surface layer and the ash-water flow channels. However, not all of the formed Ca(OH)₂ is bound to CO₂, some of it remains as it is, and it may be potentially hazardous to the environment. To conclude, we can say the following:

- The OS CFBC boiler ash binds 0.066 tons of CO₂ per ton of OS fuel used or approximately 8% of the emitted CO₂ amount.
- The OS PC boiler ash binds 0.043 tons of CO₂ per ton of OS fuel used or approximately 4% of the emitted CO₂ amount.
- The alkali water of sediment ponds can absorb up to 50 thousand tons of CO₂ annually, which is approximately 1% of the emitted CO₂ amount.
- The main binding takes place in the surface layer. If the ash loses contact with ambient air, the CO₂ binding stops.
- The CO₂ binding rate can be increased if the contact time of ash with ambient air is increased.

Acknowledgments

The authors are grateful to the helpful personnel of Eesti Energia Narva Power Plants, especially to the Development Manager, Rain Veinjärv.

REFERENCES

1. Konist, A., Valtsev, A., Loo, L., Pihu, T., Liira, M., Kirsimäe, K. Influence of oxy-fuel combustion of Ca-rich oil shale fuel on carbonate stability and ash composition. *Fuel*, 2015, **139**, 671–677.
2. Loo, L., Maaten, B., Siirde, A., Pihu, T., Konist, A. Experimental analysis of the combustion characteristics of Estonian oil shale in air and oxy-fuel atmospheres. *Fuel Process. Technol.*, 2015, **134**, 317–324.

3. Arro, H., Prikk, A., Pihu, T. Calculation of CO₂ emission from CFB boilers of oil shale power plants. *Oil Shale*, 2006, **23**(4), 356–365.
4. Kuusik, R., Veskimäe, H., Kaljuvee, T., Parts, O. Carbon dioxide binding in the heterogeneous systems formed by combustion of oil shale - 1. Carbon dioxide binding at oil shale ash deposits. *Oil Shale*, 2001, **18**(2), 109–122.
5. Kuusik, R., Paat, A., Veskimäe, H., Uibu, M. Transformations in oil shale ash at wet deposition. *Oil Shale*, 2004, **21**(1), 27–42.
6. Uibu, M., Kuusik, R., Veskimäe, H. Seasonal binding of atmospheric CO₂ by oil shale ash. *Oil Shale*, 2008, **25**(2), 254–266.
7. Uibu, M., Uus, M., Kuusik, R. CO₂ mineral sequestration in oil-shale wastes from Estonian power production. *J. Environ. Manage.*, 2009, **90**(2), 1253–1260.
8. Anthony, E. J., Bulewicz, E. M., Dudek, K., Kozak, A. The long term behaviour of CFBC ash-water systems. *Waste Manage.*, 2002, **22**(1), 99–111.
9. Vassilev, S. V., Vassileva, C. G., Baxter, D., Andersen, L. K. A new approach for the combined chemical and mineral classification of the inorganic matter in coal. 2. Potential applications of the classification systems. *Fuel*, 2009, **88**(2), 246–254.
10. Konist, A., Pihu, T. Reducing CO₂ emissions with oil shale circulating fluidized bed boiler ash. In: *Proceedings of the 21st International Conference on Fluidized Bed Combustion* (Editore, E. A., ed.), Naples, 2012, **2**, 1117–1122.
11. Pihu, T., Arro, H., Prikk, A., Rootamm, R., Konist, A., Kirsimäe, K., Liira, M., Mõtsep, R. Oil shale CFBC ash cementation properties in ash fields. *Fuel*, 2012, **93**, 172–180.
12. Neshumayev, D., Ots, A., Parve, T., Pihu, T., Plamus, K., Prikk, A. Combustion of Baltic oil shales in boilers with fluidized bed combustion. *Power Technology and Engineering*, 2011, **44**(5), 382–385.
13. Plamus, K., Ots, A., Pihu, T., Neshumayev, D. Firing Estonian oil shale in CFB boilers – ash balance and behaviour of carbonate minerals. *Oil Shale*, 2011, **28**(1), 58–67.
14. Arro, H., Prikk, A., Pihu, T. Calculation of qualitative and quantitative composition of Estonian oil shale and its combustion products. Part 1. Calculation on the basis of heating value. *Fuel*, 2003, **82**(18), 2179–2195.

Presented by A. Siirde

Received December 23, 2015