

Mineral sequestration of CO₂ by carbonation of oil shale ash

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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 producing 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 determining the binding ability of CFBC and PC boiler OS ash 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, it is found that approximately 8% of the CO₂ emitted is bound by OS CFBC and approximately 4% is bound by PC boiler ash in an ash field.

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

Keywords:

Oil Shale, CFBC, 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 NPP). 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 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 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 NPP in 2004 put into commercial operation two CFBC units with total output 430 MW_{el}. According to [3] the CO₂ emission from CFBC unit is at least 20% less compare to PC units. With CFBC technology, there is another aspect of OS usage that has not been thoroughly studied and that decreases the overall CO₂ emission: the binding ability of the ash fields and settling ponds. Laboratory investigations focused on CO₂ binding at oil shale ash deposits have been conducted by [4]. Anthony et al. [5] conducted a long-term study of the behavior of CFBC ash – water systems in which a reduction in landfill chemical reactivity and free lime carbonation were observed. An estimation of residues CO₂ absorption potential has been analyzed by [6]. Preliminary results for CFBC boiler ash CO₂ binding properties has been analyzed by [7].

The current study has been focused on *in situ* investigations in which the increases in the CO₂ content in ash and transportation water are determined from samples taken from an ash field. The samples are 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 have been studied, taking into consideration the conditions of different seasons. CO₂ absorption by transportation water in

sediment ponds have been studied 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 (PP) was determined and generalized on the basis of the results from field sample analyses and calculations.

2. System description

The total areas of the ash fields, settling ponds and open return flow channels of the ash handling systems for the two power plants are 5,088,000 m² (Balti PP) and 9,800,000 m² (Eesti PP). The ash deposit areas are 2,200,000 m² (Balti PP) and 4,900,000 m² (Eesti PP) accordingly. The amount of system water is estimated to be approximately 6,000,000 m³ at the Balti PP and 14,000,000 m³ at the Eesti PP.

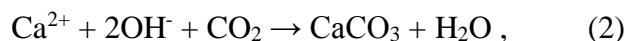
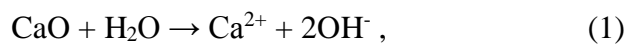
The ash handling system is hydraulic, with ash and slag transportation to the ash field. The ash from the boilers is mixed with water (in a mass ratio up to 1:20) and the formed ash/water mix is pumped through the pipes into the ash field. Flowing along the slightly inclined ash field surface, the ash separates from the mix, and the water collects in the upper sediment pond where the final separation from the fine ash particles takes part. 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 ash transport water circulates between the power plant and the ash field. Because the Balti PP runs primarily on CFBC technology, the Balti PP ash field was chosen for the CFBC ash studies. Since Eesti PP runs primarily on PC technology, the Eesti PP was chosen for the PC ash studies.

3. Materials and methods

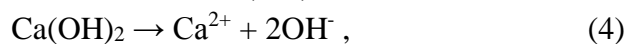
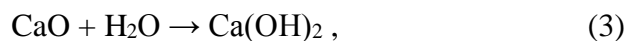
From the CO₂ absorption point of view, the ash field can be divided into three sections—the dry section of the ash field, the wet section of the ash field and the settling ponds. The dry section of the ash field is in a stationary state and has no binding properties. The primary binding material in the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

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.

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

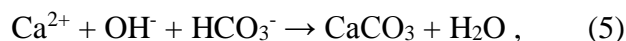


Between these two reactions, there is an intermediate process of Ca(OH)₂ accumulation:



In a similar way, ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) 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 CFBC oil shale ash has been studied by [8].

Formed CaCO_3 does not settle down at the point at which the reaction between Ca(OH)_2 and CO_2 takes place. The settling occurs along the ash/water mixture flow path. 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.

To calculate the amount of CO_2 absorbed by ash in the dry ash field section, the CO_2 content for ash coming out of the boiler and the CO_2 content 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 type of combustion technologies used. The ash CO_2 content is different in PC and CFBC technologies. CO_2 content depends on decomposition of carbonate minerals, as found by [9]. In PC boilers, the extent of carbonate minerals decomposition is in the range of 0.93-0.97, and in CFBC boilers, the extent is considerably lower at the range of 0.60-0.69 largely because of the lower temperature in the furnace. According to [10], PC boiler ash going to the ash field contains approximately 2% CO_2 , and CFBC boiler ash contains considerably more, approximately 10-14% CO_2 . 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 CO_2 content in ash field material. The chemical analysis results of drilling samples are on a dry basis, meaning water- and CO_2 -free ash material. The difference (gap) between the CO_2 content (ΔCO_2) in the ash field material and in the total ash from the boiler shows the quantity of CO_2 bound from the surrounding air.

The ash field is not a uniform body. Its chemical and mineralogical composition differs because of different landfilling times, seasons and combustion technologies. 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 presented in Figure 1. The sampling locations for PC ash samples are presented in Figure 2.

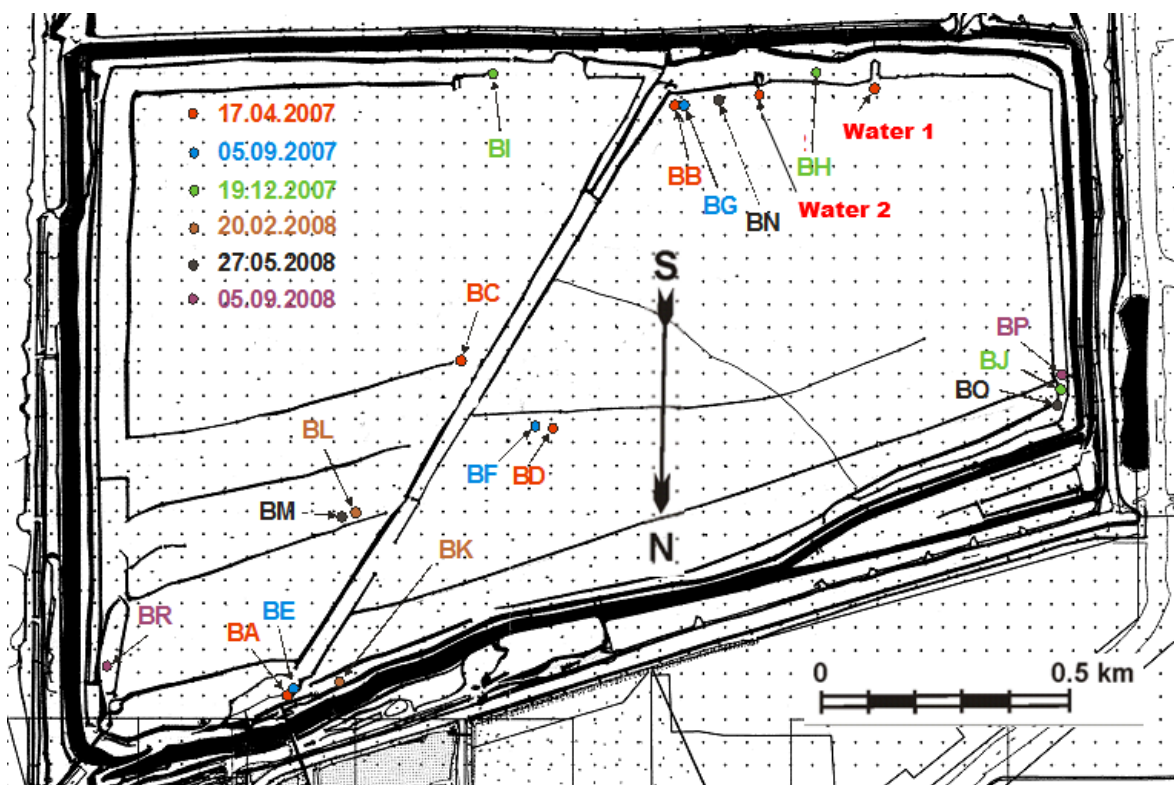


Figure 1. Sampling locations at the Balti PP ash field

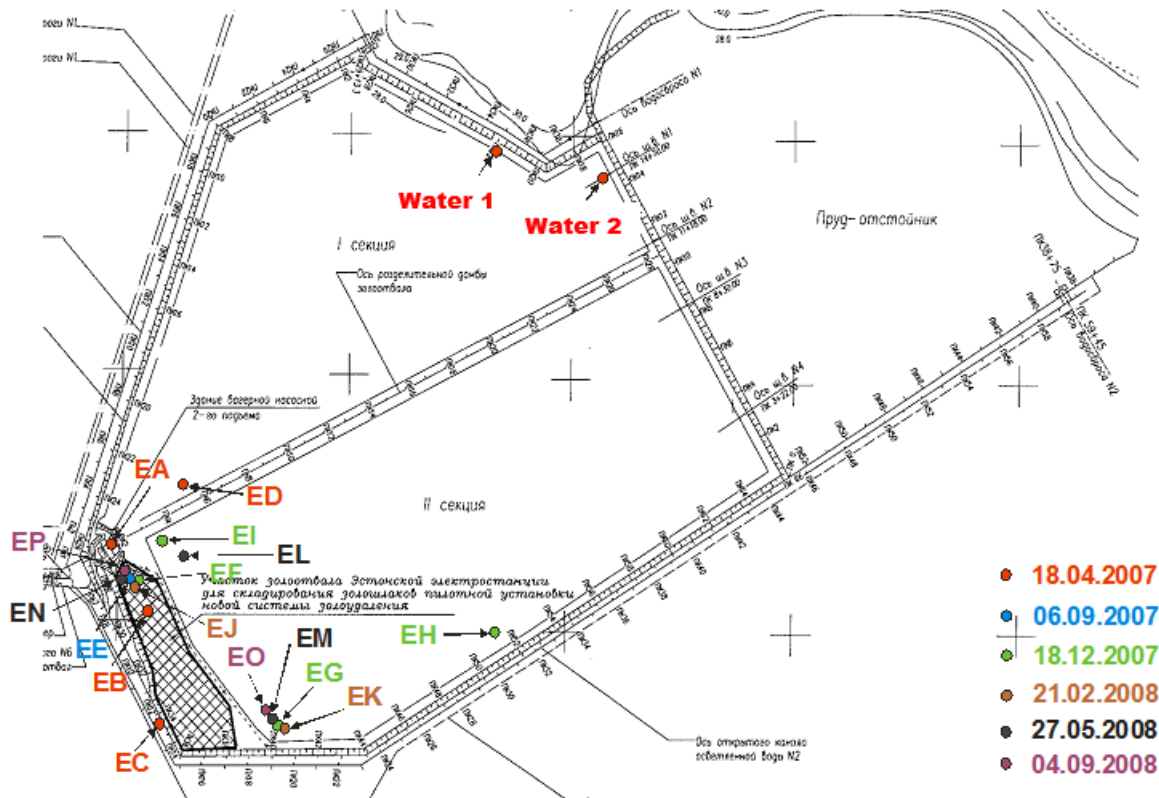


Figure 2. Sampling locations at the Eesti PP ash field

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 Σ_{comp} , mineral (CO₂)_M and the amount of water bound (H₂O)_M with the 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.

Calculations:

1. Water-free CO₂ content in ash:

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

2. With the average OS net calorific value, the (CO₂)_M^d and A^d dry content were calculated according to the method described by Arro et al. (2003).
3. Taking into account the average extent of carbonate decomposition (k_{CO2}), the average content of CO₂ in 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 (ΔCO₂) 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 ash 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 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 (CO₂)_{M average} = 21.2%, the loss on ignition LOI = 27.59% and the water content H₂O_{M average} = 6.39% (Table 1). Using the method of [11], the following fuel parameters were found: (CO₂)_M^d=19.99% and dry fuel carbonate-

free ash content $A^d_{\text{carbonate-free}}=52.72\%$. According to the calculations, the amount of CO_2 absorbed per ton of fuel is $0.066 \text{ tCO}_2/\text{t}_{\text{fuel}}$ in the case of the CFBC boiler.

Ash from PC boilers is mainly deposited in the Eesti PP ash field, the studies were conducted in locations where OS PC boiler ash had previously been landfilled. 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 CO_2 content $(\text{CO}_2)_M \text{ average} = 10.92\%$, the loss on ignition $\text{LOI} = 14.09\%$ and the water content $\text{H}_2\text{O}_M \text{ average} = 6.68\%$ (Table 1). Using the method of [11], the following fuel parameters were found: $(\text{CO}_2)^d_M=18.84\%$ and dry fuel carbonate-free ash content $A^d_{\text{carbonate-free}}=46.30\%$. According to the calculations, the amount of CO_2 absorbed per ton of fuel is $0.043 \text{ tCO}_2/\text{t}_{\text{fuel}}$ in the case of the PC boiler. The calculations are presented in table 1.

Table 1. Amount of CO_2 absorbed by PC and CFBC boiler ash in the Eesti PP and Balti PP ash field, respectively

Variable	Symbol	Unit	Values	
Calculation of mean constituents of fuel and ash			PC	CFBC
Heating value of fuel as received	Q^r_i	MJ/kg	9.20	8.45
Calculated content of CO_2 for dry fuel	$(\text{CO}_2)^d_M$	%	18.84	19.99
Extent of carbonate decomposition	k_{CO_2}		0.95	0.60
Undecomposed carbonates (dry fuel)	$\text{CO}_2^d_{\text{undecomposed}}$	%	0.94	8.00
Moisture content of fuel as received	W^r_t	%	12.10	11.57
Amount of formed carbonate-free ash for dry fuel	$A^d_{\text{carbonate-free}}$	%	46.30	52.72
Chemical composition of dry ash samples taken from the ash field				
Amount of carbonate CO_2	$(\text{CO}_2)^d_{M \text{ ash field}}$	%	10.92	21.20
Loss on ignition	$\text{LOI}_{815^\circ\text{C}}$	%	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)	$\text{CO}_2_{M \text{ ash field}}$	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)	$\Delta\text{CO}_2_{M \text{ ash field}}$	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	$\text{CO}_2_{k \text{ ash field}}$	$\text{tCO}_2/\text{t}_{\text{fuel}}$	0.043	0.066

According to studies, PC and CFBC boiler ash binds 0.043 and 0.066 tons of CO_2 per ton of fuel, respectively.

The CO_2 content in ash field ash depending on the sampling depth and time is shown in Figure 3 and 4. Samples were taken in the time period from 17.04.07 to 5.09.08. B and E indicate the overall average of CFBC and PC ash CO_2 content in Balti and Eesti PP ash field.

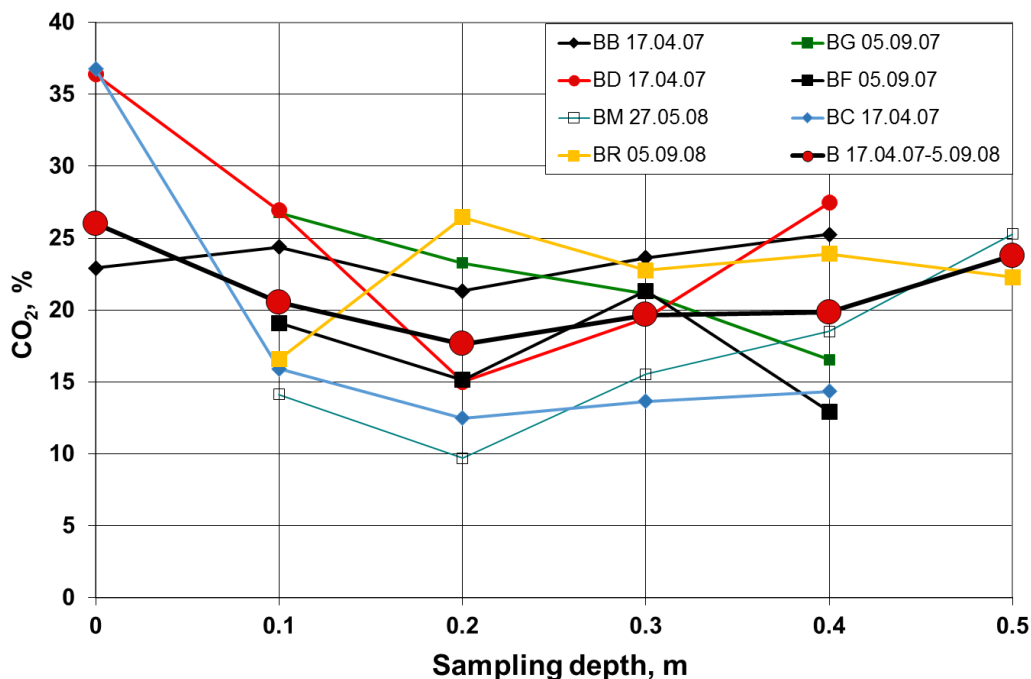


Figure 3. Balti PP ash field (generated primarily with CFBC technology)

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

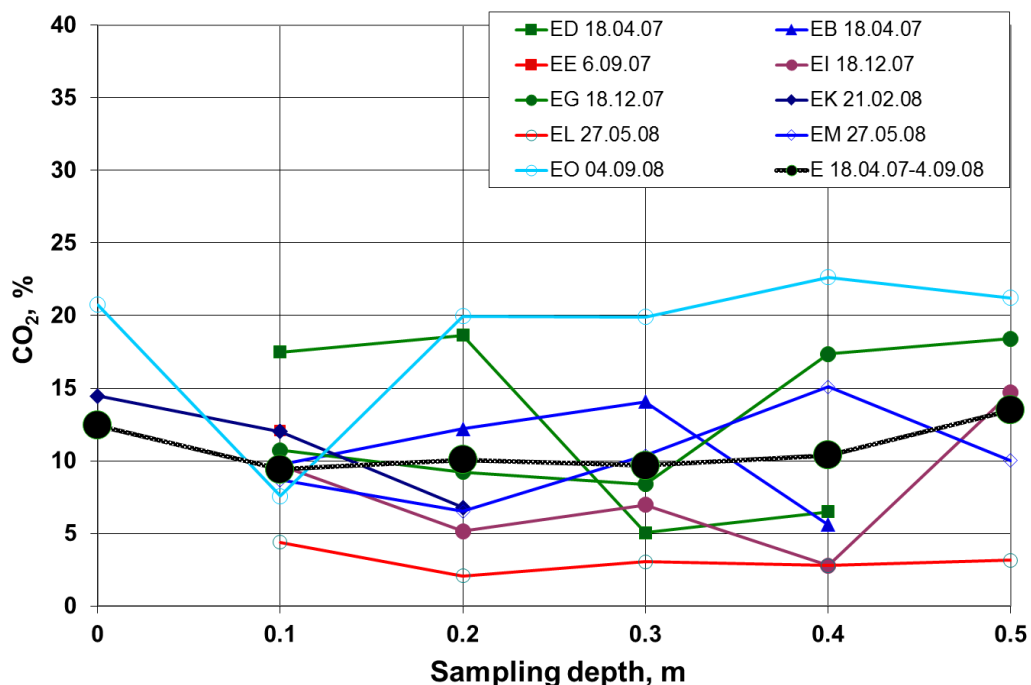


Figure 4. Eesti PP ash field (generated primarily with PC technology)

5. Amount of CO₂ absorbed by PC and CFBC boiler ash in the ash field each year

The conducted in situ study on PC and CFBC boiler ash to determine the CO₂ binding rate in the ash field provided a good overview of where and when the binding takes place. The main CO₂ binding with PC and CFBC ash occurs 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. Calculations were based on the method of [11], where an average OS lower heating value of 9.20 and 8.45 MJ/kg for PC and CFBC boiler was used, respectively. According to 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 the PC and CFBC boiler, respectively.

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

Conclusion

According to the *in situ* studies that were conducted, OS PC and CFBC ash has tremendous CO₂ binding capabilities. These capabilities are due to the high free-CaO content that remains in the ash. The main CO₂ binding takes place in the ash field surface layer and in 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:

- OS CFBC boiler ash binds 0.066 tons of CO₂ per ton of OS fuel used or approximately 8% of the emitted CO₂ content.
- OS PC boiler ash binds 0.043 tons of CO₂ per ton of OS fuel used or approximately 4% of the emitted CO₂ content.
- 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 we increase the ash contact time with ambient air.

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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 Processing Technology*.
- [3] Arro H., Prikk A., Pihu T., Calculation of CO₂ emission from CFB boilers of oil shale power plants. *Oil Shale* 2006;23:356-365.
- [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;18:109-122.
- [5] Anthony E.J., Bulewicz E.M., Dubek K., Kozak A., The long term behaviour of CFBC ash-water systems. *Waste Manage* 2002;22:99-111.
- [6] 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;88:246-254.
- [7] Konist A., Pihu T., Reducing CO₂ emissions with oil shale circulating fluidized bed boiler ash. *Proceeding of The 21st international conference on Fluidized Bed Combustion, 2012 Jun 3-6, Naples, Italy. EnzoAlbanoEditore:1117-22.*
- [8] Pihu T., Arro H., Prikk A., Rootamm R., Konist A., Kirsimäe K., Liira M., Mõtlep R., Oil shale CFBC ash cementation properties in ash fields. *Fuel* 2012;93:172-180.
- [9] 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 Engineering* 2011;44:382-385.
- [10] 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;28:58-67.
- [11] 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; 82:2179-2195.