

## SEASONAL BINDING OF ATMOSPHERIC CO<sub>2</sub> BY OIL SHALE ASH

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*The current study was focused on establishing the dynamics and extent of CO<sub>2</sub> seasonal binding from the atmosphere by oil shale ashes formed in PF and CFBC boilers and stored in open-air deposits. The effect of different kinds of ashes as well as of transportation and deposition conditions, namely the effect of conventional hydro separation or dense slurry technology on the formation and properties of ash stone was estimated.*

### Introduction

It has been established that increasing emissions of anthropogenic greenhouse gases cause climate changes [1]. Measurements confirm global growth of CO<sub>2</sub> concentration in the atmosphere as well as rise of its temperature, the data being in good correlation with intensive industrialization since the beginning of the 20th century. To limit CO<sub>2</sub> emissions, EU Parliament has worked out the guidelines for member states [2]. The requirements directly affect power production in the Republic of Estonia, as this branch of industry, based on combustion of local low-grade fossil fuel – oil shale, is the most intensive CO<sub>2</sub>-producing branch of the local economy.

Due to high mineral content of oil shale, huge amounts of ash are formed – 45–47% of oil shale burnt (dry mass basis) and removed *via* hydrotransport into deposits. Ash, which contains free Ca and Mg oxides, could be considered a CO<sub>2</sub> binder in open-air conditions. Also, as a result of hydration of free lime and clinker minerals (various silicates), so-called ash stone as the final product is formed. Progress of the above-mentioned processes is controlled largely by weather conditions – temperature, rain, wind, etc. The first theoretical estimation of CO<sub>2</sub> binding in natural conditions was made by Punning and coworkers [3]. Experimental evaluation of the CO<sub>2</sub>-binding process in model conditions showed that the relative share of CO<sub>2</sub> bound at ash deposits and ash-handling

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tract was 20.5 and 4.2 % of carbonate and total CO<sub>2</sub>, emission, respectively [4, 5]. The recommendations to increase the amount of CO<sub>2</sub> bound in natural field conditions were offered in [4] and [6].

During recent years, the Estonian oil-shale-based energy sector has been rapidly developing: novel circulating fluidized-bed boilers have been put into exploitation. The role of expired pulverized-firing TP-67 type boilers has been diminished on account of newer TP-101 type boilers [7]. Modernization of ash-handling technologies is also in progress [6]. As new equipment differs greatly by main operating regimes (temperatures, temperature profiles, grain size of fuel particles and residential times), the chemical and phase composition as well as reactivity of forming ashes differ, too [8, 13]. The reactivity of ashes has an essential impact on the processes occurring at ash fields. Therefore the goal of the current study was to estimate the dynamics and extent of CO<sub>2</sub> binding from the atmosphere by different types of ashes in conditions corresponding to different seasons, as well as to establish the formation and properties of forming ash stone.

## Materials and methods

### CO<sub>2</sub> binding

The model experiments of CO<sub>2</sub> binding in natural open-air conditions were carried out using circulating fluidized-bed combustion ashes (*CFBCA*), pulverized firing ashes (*PFA*) and their 1 : 1 mixture (Table 1). Ash samples were collected from CFBC and PF boilers at the Estonian Thermal Power Plant in 2004 and 2005. PF ash was a mixture of ashes; mass ratio furnace ash : superheater ash : cyclone ash : electrostatic precipitator ash = 15 : 15 : 60 : 10. CFBC ashes (*CFBCA04* and *CFBCA05*) were mixtures of ashes taken from ash silo. The characteristics of different kinds of ashes have been discussed in detail in our earlier publication [13].

The ashes were mixed with water (phase ratio 1 : 5 was used to imitate hydro ash removal (henceforth liquid suspension) and 1 : 0.3–0.9 to imitate

Table 1. Characterization of initial ashes

Ash	CO <sub>2</sub> , %	CaO <sub>f</sub> , %	Specific gravity, g/cm <sup>3</sup>	SSA, m <sup>2</sup> /g
PF ashes				
PFA04	0.9	20.46	1.5	0.640
PFA05	1.0	15.23	1.5	0.642
CFBC ashes				
CFBCA04	7.19–7.60	7.10–7.93	0.7	7.112
CFBCA05	10.71	4.50	0.7	7.045
Ash mixtures				
CFBCA04+PFA05; 3:1	5.95	9.13	0.9	5.495
CFBCA04+PFA05; 1:1	4.30	11.17	1.1	3.877
CFBCA04+PFA05; 1:3	2.65	13.19	1.3	2.260

dense slurry technology), and the mixture was loaded into boxes (sample holders) divided into 4×4×7-cm sections. In the case of liquid suspension (LS), the mixture of ash and water was stirred for 5 minutes and after settling the homogenized solid part was loaded into sample holders. Dense slurry (DS) was stirred intensively during 15 minutes with a mechanic stirrer before loading into sample holders. These sample bodies were held under summer ( $t = 20\text{ }^{\circ}\text{C}$ , in laboratory at room temperature), autumn/spring (October and April,  $t = 5\text{--}15\text{ }^{\circ}\text{C}$ ) and winter temperature (February,  $t = -22\text{--}3\text{ }^{\circ}\text{C}$ ) conditions and humidified weekly to keep the moisture content at 15%. In autumn/spring and winter the samples were held outside under the influence of real weather conditions: daily changes of temperature, rain, wind, etc.

After 1, 2, 4 and 8 weeks, the sample bodies were taken out of the box and divided mechanically into 6 layers using a special procedure. The layers were analyzed for the content of moisture [9],  $\text{CO}_2$  and  $\text{CaO}_f$  [10]. The data obtained were used to calculate the amounts of  $\text{CO}_2$  and free  $\text{CaO}$  bound during the experiment (Eq. (1, 2)) and the binding degree (Eq. (3)). The latter shows the degree of  $\text{CO}_2$ -binding potential basing on free  $\text{CaO}$  realization.

$$\Delta\text{CO}_2 = \text{CO}_2 - \frac{\text{CO}_2^i}{100 + \Delta\text{CaO} \cdot \frac{44}{56}} \cdot 100 \quad (1)$$

$$\Delta\text{CaO} = \frac{\text{CaO}_f^i - \text{CaO}_f}{1 + \text{CaO}_f / 56} \quad (2)$$

$$\text{BD} = \frac{\Delta\text{CO}_2}{(\text{CaO}_f^i \cdot 44 / 56) / (100 + \text{CaO}_f^i \cdot 44 / 56)} \cdot 100, \quad (3)$$

where  $\text{CO}_2$  and  $\text{CaO}_f$  are analytically determined  $\text{CO}_2$  and  $\text{CaO}_f$  content of the sample, %;  $\text{CaO}_f^i$  and  $\text{CO}_2^i$  are the content (%) of  $\text{CaO}_f$  and  $\text{CO}_2$  of the initial sample;  $\Delta\text{CO}_2$  and  $\Delta\text{CaO}$  are the amounts of  $\text{CO}_2$  and free  $\text{CaO}$  bound during the experiment, %.

### Ash stone formation

Pulverized firing ash was represented by *PFA04* and *PFA05* and circulating fluidized-bed ash by *CFBCA04* and *CFBCA05* samples (Table 1). To study the influence of different kinds of materials and the conditions of preparing suspension, both liquid and dense suspensions of both types of ashes were used for experiments. Originating from different nature of CFBC and PF ashes, their concurrence was also studied using mixtures of ashes in various proportions (1 : 3; 1 : 1; 3 : 1). Sample bodies of these mixtures were prepared imitating dense slurry method as described above.

Suspensions were loaded into 4×4×4 cm boxes and held at 20 °C under laboratory conditions (summer temperature conditions), because, supposedly, the processes of interest proceed at the optimal rate under these conditions. The sample bodies were humidified weekly to keep their moisture content at 15%. After given time intervals (from 1 week to 4 months) the sample cubes were photographed and analyzed for water absorption [11], compression strength (compression strength analysis [12] was carried out at the Laboratory of building materials) and for average content of moisture [9], CO<sub>2</sub> and CaO<sub>f</sub> [10] in the whole sample body.

## Results

### CO<sub>2</sub> binding

The dynamics and extent of CO<sub>2</sub> natural binding by different kinds of oil shale ashes (CFBC ash, PF ash and their mixture) were investigated. It was shown that the most intensive CO<sub>2</sub> binding takes place in top layers within few centimeters; while in deeper layers the binding rate is moderate (Figures 1–3). For example, in the case of sample bodies consisting of *CFBCA* and *PFA* mixture, the content of free CaO decreased by 2.2–4.9% and the content of CO<sub>2</sub> increased by 1.9–3.6% in the top layer during one month, as for the whole sample body the values of  $\Delta\text{CaO}_f$  and  $\Delta\text{CO}_2$  were within 1.2–3.2% and 1.0–2.0% after the same period (Fig. 2). The positive effect of summer temperature conditions generally manifested itself at CO<sub>2</sub> binding in top layers in the case of ash mixture (CFBC+PF 1:1): the content of CO<sub>2</sub> increased in the top layer during one month by 4.7%, 3.0–3.6% and 1.9–2.8% in summer, autumn/spring and winter conditions, respectively (Fig. 2d). Ambient temperature did not influence remarkably the process in deeper layers.

Comparison of different kinds of ashes showed that a considerable part of CO<sub>2</sub>-binding capacity of CFBC ashes could be exhausted in natural conditions – the binding degree (BD) achieved its average value of 57.5% for the entire sample and 82.6% in the top layer during 1 month of deposition. After a longer period in favorable deposition conditions (top layers), the value of binding degree, calculated basing on content of free CaO in the initial sample, could even exceed 100% (Table 2, Fig. 3a), because there can be other CO<sub>2</sub>-binding compounds present in oil shale ash of heterogeneous composition [13]. In the case of PF ashes, most of the free CaO present in the initial ash had not reacted during the given periods – the average value of BD was within 1.5–7.1% after 1 month of deposition. Distinct differences between the magnitudes of binding degrees of CFBC and PF ashes were caused by different chemical composition of the initial samples: as *CFBCA* contains considerably less free CaO, it would be exhausted during a much shorter period (Table 1, Fig. 4b).

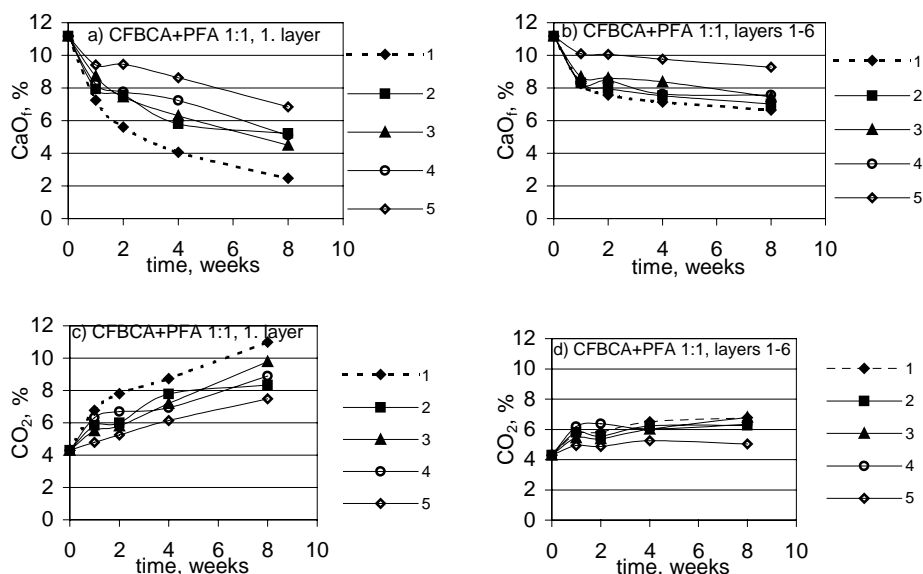


Fig. 1. Dynamics of free CaO and CO<sub>2</sub> content for CFBC and PF ash mixture: 1 – summer conditions, liquid slurry; 2 – autumn conditions, liquid slurry; 3 – autumn conditions, dense slurry; 4 – winter conditions, liquid slurry and 5 – winter conditions, dense slurry.

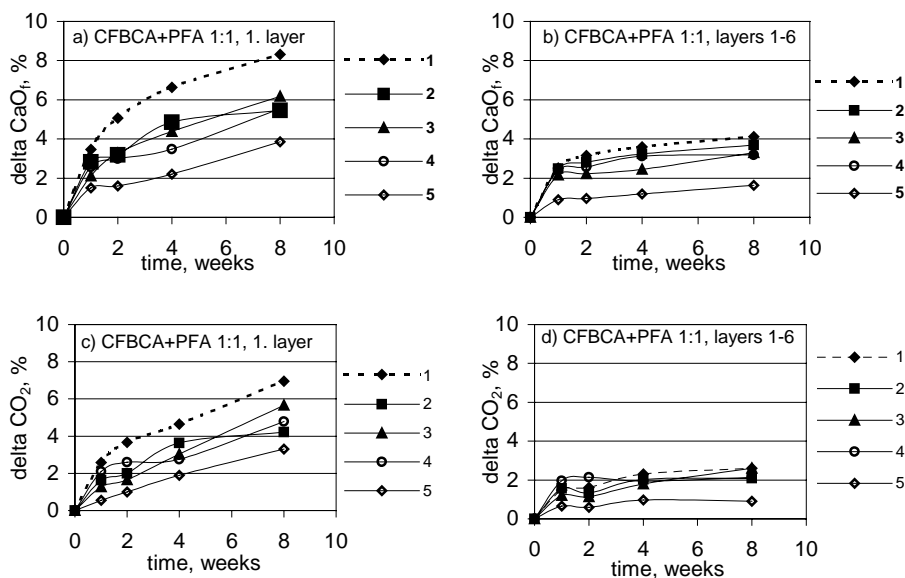


Fig. 2. Dynamics of  $\Delta\text{CaO}_f$  and  $\Delta\text{CO}_2$  for CFBCA and PFA mixture: 1 – summer conditions, liquid slurry; 2 – autumn conditions, liquid slurry; 3 – autumn conditions, dense slurry; 4 – winter conditions, liquid slurry and 5 – winter conditions, dense slurry.

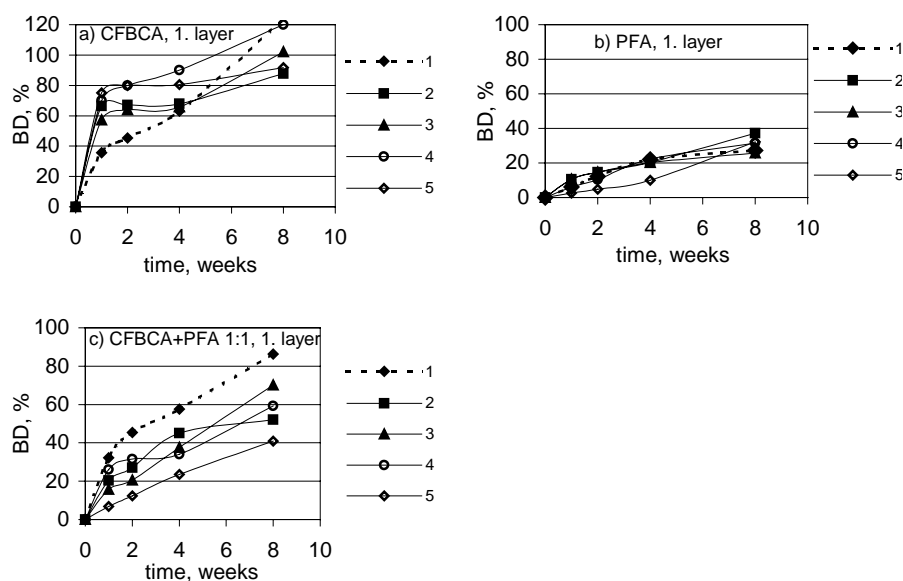


Fig. 3. Seasonal binding of atmospheric CO<sub>2</sub> by different types of oil shale ashes: 1 – summer conditions, liquid slurry; 2 – autumn/spring conditions, liquid slurry; 3 – autumn/spring conditions, dense slurry; 4 – winter conditions, liquid slurry and 5 – winter conditions, dense slurry.

Table 2. CO<sub>2</sub>-binding characteristics of different kinds of oil shale ashes in natural conditions (Average results from experiments in summer, spring/autumn and winter conditions), %

Time, weeks	CFBCA				PFA				CFBCA and PFA mixture, 1:1			
	ΔCO <sub>2</sub>		BD		ΔCO <sub>2</sub>		BD		ΔCO <sub>2</sub>		BD	
	1. layer	1–6. layers	1. layer	1–6. layers	1. layer	1–6. layers	1. layer	1–6. layers	1. layer	1–6. layers	1. layer	1–6. layers
0	0	0	0	0	0	0	0	0	0	0	0	0
1	3.33	2.98	62.20	55.89	0.89	0.28	7.89	2.5	1.71	1.39	21.18	17.25
2	4.02	3.06	74.69	57.44	1.40	0.48	12.26	4.18	2.14	1.37	26.5	16.95
4	4.55	3.11	82.60	57.50	2.20	0.54	18.98	4.54	3.41	1.89	42.3	23.38
8	5.75	3.12	105.4	58.16	3.48	0.89	30.54	7.67	5.22	2.19	64.68	27.11

Nevertheless, the experiments indicated that CFBC ashes are characterized by the most intensive binding properties – the content of CO<sub>2</sub> increased during 1 month averagely by 3.1% (Table 2, Fig. 4). For comparison, in the case of PF ashes the value of ΔCO<sub>2</sub> increased by 0.5%. It has been shown earlier that, due to higher porosity (SSA = 7.05–7.10 m<sup>2</sup>/g, Table 1) and favorable structure, the CFBC ashes are expected to be more active towards

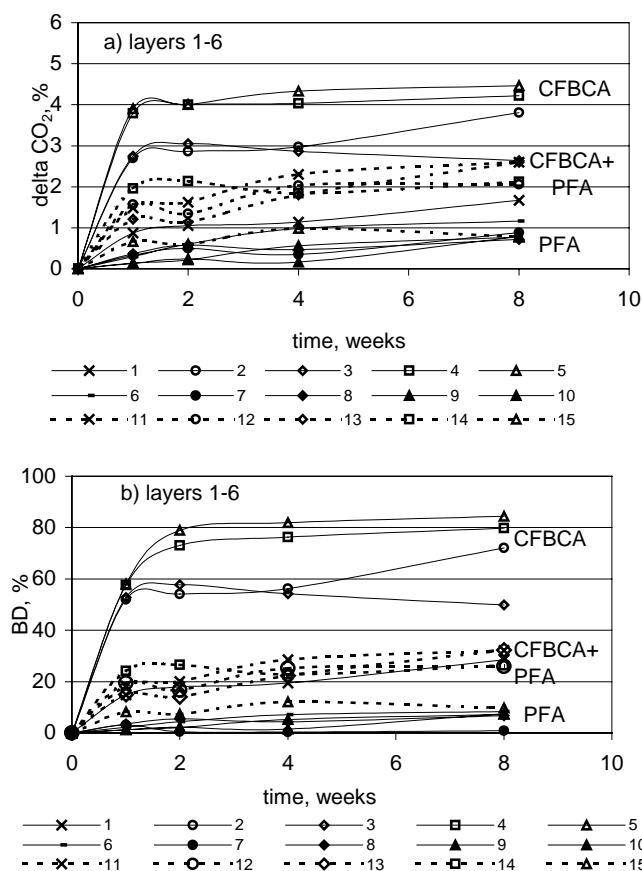


Fig. 4. Dynamics of  $\Delta\text{CO}_2$  (a) and BD (b) for sample bodies prepared from CFBCA (1 – summer/LS, 2 – autumn/LS, 3 – autumn/DS, 4 – winter/LS, 5 – winter/DS), PFA (6 – summer/LS, 7 – autumn/LS, 8 – autumn/DS, 9 – winter/LS, 10 – winter/LS) and mixture of ashes CFBCA+PFA (11 – summer/LS, 12 – autumn/LS, 13 – autumn/DS, 14 – winter/LS, 15 – winter/DS).

$\text{CO}_2$  [14, 15]. The mixture of both kinds of ashes showed medium  $\text{CO}_2$ -binding characteristics: the value of  $\Delta\text{CO}_2$  increased by 1.9%, achieving an average of 23.5% of free CaO-based  $\text{CO}_2$ -binding potential during 1 month of deposition. Differences in the reactivity of ashes are related to the structure and surface properties of ash particles [13] – for instance the specific surface area of CFBC ashes is up to ten times higher than that of PF ashes (Table 1).

Considering the conditions of ash deposition, the  $\text{CO}_2$ -binding characteristics were not systematically influenced by slurry preparation technologies. The values of  $\Delta\text{CO}_2$  for liquid and dense slurries were 3.0% and 2.9%; 0.35% and 0.41%; 2.0% and 1.8% for CFBC, PF and mixture of ashes after 1 month in autumn/spring temperature conditions.

### Ash stone formation

The influence of different kinds of ashes and slurry preparation methods with reference to the formation of ash stone – water absorption and compression strength of sample bodies – were under investigation.

Determination of CO<sub>2</sub> and CaO<sub>f</sub> during the experimental cycle confirmed the tendencies discussed in the previous chapter: natural binding of CO<sub>2</sub> was not systematically influenced by slurry preparation conditions (Fig. 5). The average binding degree BD for the whole sample body achieved its highest value in the case of CFBC ashes (50–55%) and stabilized at the 10–17% level in the case of PF ashes after two months of deposition.

Water absorption measurements indicated that the sample bodies formed from CFBCA slurries absorb considerably more water: after one month of deposition 77.8% and 60.5% in the case of liquid and dense slurries, respectively (Fig. 6a). Water absorption coefficients for the sample bodies consisting of PFA were within 30%, regardless of slurry preparation conditions. In the course of time, ability of the sample bodies to absorb water stays on an approximately same level. Water absorption coefficients of ash mixtures were within 36–48%, depending on the proportion of CFBCA in the mixture.

Compression strength of the sample bodies consisting of CFBCA dense slurries was relatively high (for CFBCA04 and CFBCA05 3.3 MN/m<sup>2</sup> and 4.2 MN/m<sup>2</sup>, respectively) (Fig. 6b). The corresponding values for the sample bodies consisting of PFA04 liquid slurry (1.2 MN/m<sup>2</sup>) and PFA05 dense slurry (0.9 MN/m<sup>2</sup>) were the lowest. In the course of time, the indicators of compression strength started to decrease in the case of the CFBCA sample bodies (after 4 months 2.4 MN/m<sup>2</sup> in the case of CFBCA04 dense slurry) and to increase in the case of the PFA sample bodies (after 4 months 2.2 MN/m<sup>2</sup> in the case of PFA04 liquid slurry). Thereby, compression strength is influenced by conditions of slurry preparation: the indicators are somewhat higher in the case of sample bodies consisting of dense slurries. Compression strength of sample bodies consisting of dense slurries of ash mixtures was determined by the share of CFBCA in the mixture – bigger percentage gave better indicators.

Visual observation indicated that the shape and volume of PFA sample bodies changed during the experimental cycle. Expanding of sample bodies even caused deformation of boxes (Fig. 7). The surface of sample bodies was bumpy and uneven, up to large cracks. Also, in the case of sample bodies consisting of PFA, the formation of a partly drifted crust could be observed. Sample bodies consisting of CFBCA were more stable during the experimental cycle: no large cracks, no unevenness of surface or deformation of boxes were observed.



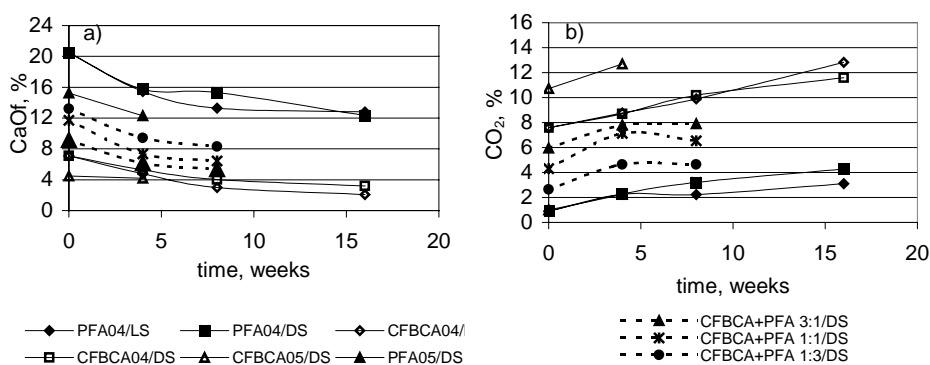


Fig. 5. Dynamics of free CaO (a) and CO<sub>2</sub> (b) content in sample bodies prepared from liquid or dense slurries of *CFBCA* and *PFA* and ash mixtures in various proportions.

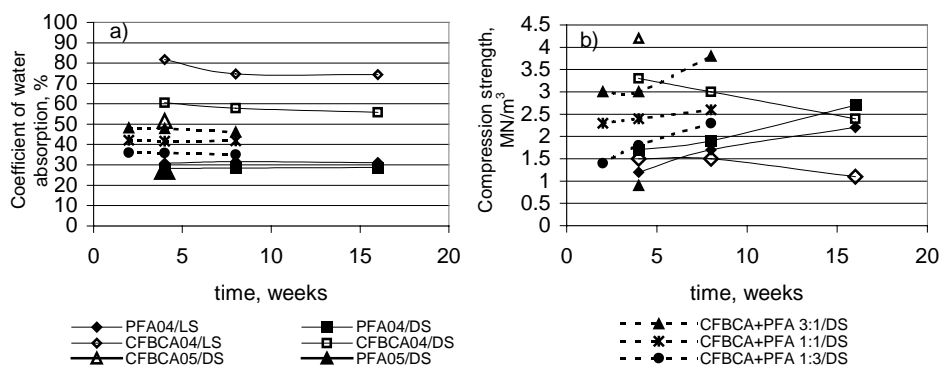


Fig. 6. Dynamics of water absorption coefficient (a) and compression strength (b) in sample bodies prepared from liquid or dense slurries of *CFBCA* and *PFA* and ash mixtures in various proportions.

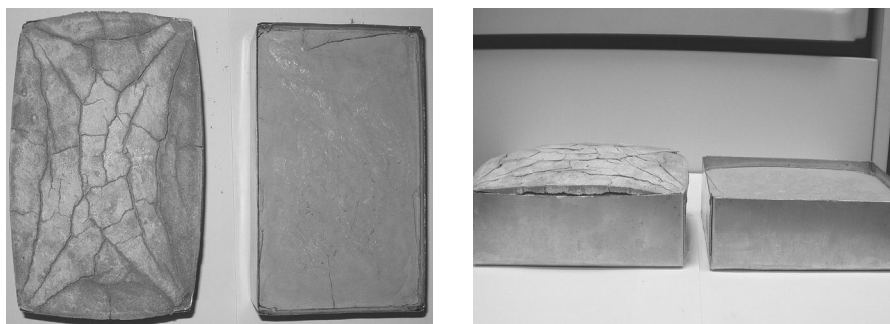


Fig. 7. Sample bodies of *PFA* (left) and *CFBCA* (right) after two months of deposition, top view (left) and side view (right).

## Discussion

### CO<sub>2</sub> binding

Considering the results of experiments in model conditions, 1 ton of ash binds 9–31 kg CO<sub>2</sub> that gives an average of ~100,000 t CO<sub>2</sub> bound by open-air ash deposits annually. By implementing simple technological means, the amount of CO<sub>2</sub> bound could be doubled [4] – about 60,000 tons of CO<sub>2</sub> bound per one million tons of ash, which forms 3.1% of the total CO<sub>2</sub> amount emitted at combustion (Table 3). The evaluation of CO<sub>2</sub> amounts bound in open-air deposits gave somewhat lower results than those calculated earlier [4]. The differences could be explained by lower content of key components like free lime and secondary silicates in the currently used samples as well as by experimental conditions. The previous experiments were carried out only in summer conditions, whereas the present average results include also the influence of seasons unfavorable for chemical transformations. As it was shown, CFBC ashes, characterized by higher reactivity towards atmospheric CO<sub>2</sub>, have relatively low binding potential due to modest content of free CaO. Also, specific surface areas of pulverized firing ashes collected at the present time are somewhat less (SSA = 0.64 m<sup>2</sup>/g, Table 1) than those of previously used ashes (SSA = 1.23 m<sup>2</sup>/g, cyclone ash collected from Estonian PP in 1998 [16]). Latter could be inflicted by differences in combustion temperature regimes which have a great influence on reactivity of ashes.

**Table 3. Amounts of CO<sub>2</sub> bound per 1 million ton of ash (A, 10<sup>3</sup>t) and ratios of CO<sub>2</sub> captured from total (B, %) and mineral part (C, %) of CO<sub>2</sub> emitted at combustion**

CO <sub>2</sub> natural open air binding by:	A, 10 <sup>3</sup> t	B, %	C, %
CFBC ash	31	1.7	12.6
PF ash	9	0.5	2.3
Mixture of ashes CFBC+PF	22	1.1	6.9
Circulating water	8.4	0.4	2.6
Total natural binding:	30.4	1.5	9.5
Total natural binding with simple technological means:	60	3.1	18.7

### Ash stone formation

Transition to the dense slurry method does not improve significantly the formation and properties of ash stone. Slow hydration rate of ashes seems to be the main problem. Although reported data generally show that the reaction between CaO and H<sub>2</sub>O is quite fast, the hydration rates of oil shale ashes proved to be much lower. The latter is attributed mainly to the slow transport of H<sub>2</sub>O molecules through the layers of other ash constituents and

reaction products ( $\text{Ca}(\text{OH})_2$ ,  $\text{CaCO}_3$ ) [17, 18]. In the case of PF ashes characterized by very low surface area values, the hydration process is particularly hindered. Consequently, the hydration of ash as a slow process is not completed during slurry preparation and goes on after deposition. Due to lower CaO content (4–8%) and higher porosity, CFBC ashes hydrate faster than PF ashes containing 15–21% lime, and the hydration process takes weeks producing heat and causing expansions, large cracks and bumps. Hardening of sample bodies is inhibited by slow and uneven hydration of lime. Although the compression strength indicators were somewhat higher in the case of ash stone formed from *CFBCA*, water absorption coefficients were very high and did not show tendencies of decreasing after longer deposition periods. High hygroscopicity of ash stone increases mobility and leaching of ash components like alkaline metals and lime, which cause high alkalinity ( $\text{pH} = 12\text{--}13$ ). Due to relatively low solubility of  $\text{Ca}(\text{OH})_2$ , the hazardous effect of forming  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions could continue for years while contacting with fresh water. At the same time natural carbonization-neutralization of alkaline drain waters by dissolved  $\text{CO}_2$  derivatives can be expected.

## Conclusions

The dynamics and extent of  $\text{CO}_2$  seasonal binding from the atmosphere by oil shale ashes formed in PF and CFBC boilers were studied under conditions corresponding to summer, autumn/spring and winter.

- It was shown that in the case of all kinds of ashes the most intensive  $\text{CO}_2$  binding takes place in top layers within few centimeters. Pileup of fresh layers of ash suspension inhibits  $\text{CO}_2$  binding into deeper layers.
- Summer temperature conditions enhance natural binding of  $\text{CO}_2$  into top layers of ash deposits, while surrounding temperature does not influence the process in deeper layers remarkably. Autumn/spring and winter conditions greatly inhibit the rate and extent of processes under discussion by worse prerequisites for chemical reactions and mass/heat transfer.
- Comparison of different kinds of ashes showed that CFBC ashes react readily with atmospheric  $\text{CO}_2$ , but their total binding capacity is quite low due to moderate content of CaO. Therefore, a substantial part (60–80%) of  $\text{CO}_2$  binding capacity of CFBC ashes could be exhausted in natural conditions. In the case of PF ashes, characterized by considerable  $\text{CO}_2$  binding potential as well as by low surface area of particles, most of the free CaO present in the initial ash remains unrealized during given periods – the average value of BD was within 1.5–7.1% after 1 month of deposition.

- CO<sub>2</sub>-binding characteristics are not systematically influenced by slurry preparation conditions – hydro-separation or dense slurry technology.
- Considering the results of the experiments in model conditions, 1 ton of ash binds 9–31 kg CO<sub>2</sub>, giving an average of ~100,000 t CO<sub>2</sub> bound by open-air ash deposits annually.

The effect of different kinds of ashes (CFBC ash, PF ash and mixtures of ashes) and deposition conditions – conventional hydro separation and dense slurry technology – on formation and properties of ash stone was estimated.

- Transition to the dense slurry method does not improve substantially the formation and properties of ash stone. Hardening of sample bodies is inhibited by slow and uneven hydration of lime.
- Compression strength of sample bodies is influenced by slurry-preparation conditions – the indicators were somewhat higher in the case of dense slurries.
- Ash stone formed from CFBC ashes is characterized by high water absorption coefficient (80%), which could enhance leaching of ash components like alkaline metals and lime into the environment.
- Water absorption coefficients and compression strength indicators of sample bodies consisting of dense slurries of ash mixtures are determined by the proportion of *CFBCA* in the mixture – bigger percentage gives higher indicators.
- Visual observation indicated that the shape (expansions, bumps and large cracks) and volume of *PFA* sample bodies changed radically during the experimental cycle. The sample bodies consisting of *CFBCA* were more stable during the experimental cycle.

## Acknowledgements

Partial funding of this study by ESF grant G6195 and *SC Narva Elektri-jaamad* as well as the performance of compression strength measurements by Department of Building Materials of Tallinn University of Technology are acknowledged.

## REFERENCES

1. Climate Change 2007: The Physical Science Basis. Summary of Policymakers. IPCC Fourth Assessment Report of the Intergovernmental Panel of Climate Change. Approved at the 10<sup>th</sup> session of working group I of the IPCC, Paris, February 2007.
2. Commission decision of 18 July 2007 establishing guidelines for the monitoring and reporting of greenhouse gas emission pursuant to Directive 2003/87/EC of

- the European Parliament and the Council (2007/589/EC) / Official Journal of the European Union. 85 pp.
3. *Punning, J.-M., Karindi, A.* Composition of Estonian Atmosphere // Estonia in the System of Global Climate Change / J.-M. Punning (ed.). Institute of Ecology. Publication, 1966. Vol. 4. P. 26–34.
  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. 2002. Vol. 18, No. 2. P. 109–122.
  5. *Uibu, M., Kuusik, R., Veskimäe, H.* Abatement of CO<sub>2</sub> emission in Estonian energy sector // VI Intern. Symp. and Exhib. on Environmental Contamination in Central and Eastern Europe and the Commonwealth of Independent States, Prague, Czech Republic, 1–4 Sept. 2003. Tallahassee, Florida State University, 2004. 5 pp.
  6. *Arro, H., Prikk, A., Pihu, T.* Reducing the environmental impact of Baltic Power Plant ash fields // Oil Shale. 2003. Vol. 20, No. 3 Special. P. 375–382.
  7. *Hotta, A., Parkkonen, R., Hiltunen, M., Arro, H., Loosaar, T., Parve, T., Pihu, T., Prikk, A., Tiikma, T.* Experience of Estonian oil shale combustion based on CFB technology at Narva Power Plants // Oil Shale. 2005. Vol. 22, No. 4 Special. P. 369–380.
  8. *Paat, A., Traksmäa, R.* Investigation of the mineral composition of Estonian oil shale ash using X-ray diffractometry // Oil Shale. 2002. Vol. 19, No. 4. P. 373–386.
  9. EVS-EN 12048:2000. Solid fertilizers and liming materials - Determination of moisture content – Gravimetric method by drying at  $(105 \pm 2)$  °C.
  10. *Reispere, H. J.* Determination of free CaO content in oil shale ash / Tallinn Polytechnical Institute. – Tallinn, 1966. No. 245. P. 73–76 [in Estonian].
  11. EVS-EN 771-2:2003. Determination of the coefficient of water absorption.
  12. EVS-EN 196-1. Methods of testing cement – Part 1: Determination of strength.
  13. *Kuusik, R., Uibu, M., Kirsimäe, K.* Characterization of oil shale ashes formed at industrial-scale CFBC boilers // Oil Shale. 2005. Vol. 22, No. 4 Special. P. 407–420.
  14. *Kuusik, R., Uibu, M., Toom, M., Muulmann, M.-L., Kaljuvee, T., Trikkel, A.* Sulphation and carbonization of oil shale CFBC ashes in heterogeneous systems // Oil Shale. 2005. Vol. 22, No. 4 Special. P. 421–434.
  15. *Uibu, M., Trikkel, A., Kuusik, R.* Transformations in the solid and liquid phase at aqueous carbonization of oil shale ash // Proc. ECOSUD VI 2007, 4–7. Sept. 2007, Coimbra, Portugal. WIT Transactions on Ecology and the Environment 2007. Vol. 106. P. 473–483. ISSN 1743-3541.
  16. *Kuusik, R., Veskimäe, H., Uibu, M.* Carbon dioxide binding in the heterogeneous systems formed at combustion of oil shale. 3. Transformations in the system suspension of ash – flue gases // Oil Shale. 2002. Vol. 19, No. 3. P. 277–288.
  17. *Wang, J., Wu, Y., Anthony, E. J.* The hydration behavior of partially sulfated fluidized bed combustor sorbent // Ind. Eng. Chem. Res. 2005. Vol. 44, No. 22. P. 8199–8204.
  18. *Kuusik, R., Paat, A., Veskimäe, H., Uibu, M.* Transformations in oil shale ash at wet deposition // Oil Shale. 2004. Vol. 21, No. 1. P. 27–42.

Presented by A. Siirde

Received December 1, 2007