CARBON DIOXIDE BINDING IN THE HETEROGENEOUS SYSTEMS FORMED AT COMBUSTION OF OIL SHALE 3. TRANSFORMATIONS IN THE SYSTEM SUSPENSION OF ASH – FLUE GASES

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Power production based on oil shale combustion is accompanied by high carbon dioxide emissions and by the formation of alkaline waste ash. A set of laboratory experiments was carried out in order to investigate the interactions in the heterogeneous system: water suspension of ash – flue gases. Suspensions of ash were treated with model gases imitating the content of CO_2 and SO_2 in flue gases and air. Comparative experiments were carried out using the model system: suspension of pure CaO – flue gases. The aim of the experiments was to achieve the complete carbonation of oil shale ash by CO_2 from flue gases.

Experiments indicated that ash can be completely carbonated if the pH value of suspensions decreases to 9–7. The total amount of bound CO_2 reached up to 153.8 kg per ton of oil shale ash or 70.8 kg per ton of oil shale burnt for electricity production. The part of bound CO_2 formed 35.6 and 7.3 % from the carbonate and total emission of CO_2, respectively. Due to carbon dioxide binding, alkaline ash will be chemically stabilized and its hazardous environmental effect decreased.

Introduction

The main part of total CO_2 emitted in Estonia results from power industry based on combustion of oil shale [1]. As oil shale contains more mineral CO_2 than the other fuels, its carbon emission factor is higher, too. The solid combustion product is ash, 42–48 % of the oil shale mass burned. Decomposition products of carbonates include free Ca and Mg oxides, whose content in the ashes reaches up to 30 %. Ca and Mg oxides can be the binders of acidic gases (CO_2 and SO_2). Usability of the ashes as dry sorbents for binding SO_2 has been discussed in the articles [2–4].

Table 1. **Main Characteristics of Ashes**

Ash type	Content, %		Specific surface area, m²/g	Screenings, mm						
	CaO_{free}	CO_2		+0.63	+0.40	+0.16	+0.1	+0.071	+0.045	−0.045
Bottom ash	22.21	2.25	2.02	8.67	9.00	32.00	11.67	23.66	7.33	7.67
Bottom ash, ground	21.87	2.60	2.31	–	–	–	–	–	56.7	43.3
Cyclone ash	22.94	0.08	1.23	–	–	6.50	9.00	28.00	38.50	18.00
Cyclone ash, ground	22.83	1.66	–	–	–	–	–	–	28.0	72.0
Electrostatic precipitator ash	14.74	1.83	1.53	–	–	0.50	1.00	3.00	3.50	92.00
Pure CaO, reference sample	93.22	0.48	5.50	–	–	–	–	–	59.9	40.1

Table 2. **Composition and Characteristics of the Liquid Phase**

N	Ca^{2+}, g/l		pH		Alkalinity, mmol/l									
					A_p		A_t		HCO_3^-		CO_3^{2-}		OH^-	
	Ash	CaO	Ash	CaO	Ash	CaO	Ash	CaO	Ash	CaO	Ash	CaO	Ash	CaO
0	1.091	0.822	13.1	13.1	54.0	42.8	54.0	44.4	0	0	0	3.20	54.0	41.2
1	0.85	0.83	12.61	12.62	33.0	38.25	35.75	40.5	0	0	5.50	4.50	30.25	36.0
2	0.63	0.61	12.27	12.24	25.0	29.50	27.5	30.5	0	0	5.0	2.0	22.5	28.5
3	0.26	0.08	9.4	11.3	2.5	2.50	4.00	3.50	0	0	3.0	2.0	1	1.5
4	0.33	0.15	7.92	7.25	1.0	0	2.00	6.50	0	6.50	2.0	0	0	0
7	0.47	0.18	7.07	7.04	0	0	7.50	7.50	7.50	7.50	0	0	0	0
10	0.53	0.17	7.04	7.02	0	0	9.00	8.50	9.0	8.50	0	0	0	0

Introduction

The combustion-related CO_2 emission of the Estonian power industry based on the combustion of oil shale [1]. As the content of mineral matter in oil shale is higher, its carbon emission factor is higher, too. The solid combustion product is ash, 42–48 % of the oil shale mass burned. Decomposition products of carbonates include free Ca and Mg oxides, whose content in the ashes reaches up to 30 %. Ca and Mg oxides can be the binders of acidic gases (CO_2 and SO_2). Usability of the ashes as dry sorbents for binding SO_2 has been discussed in the articles [2–4].

Carbonation of lime is well studied [5], but the data on the reactivity of oil shale ash with CO_2 are incomplete. It has been presumed [6] and demonstrated [7, 8] that oil shale ash binds air CO_2 intensively during its transportation and storage in natural conditions. Under these conditions the amount of CO_2 bound by ash and the binding rate are moderate due to poor interfacial contact and low driving force (low CO_2 concentration in the gaseous phase).

The aim of the current work was to investigate the possibility of maximizing the amount of CO_2 to be bound by suspensions formed during hydraulic transport of ash and flue gases (content of CO_2 12–15 %).

Materials and Experimental Methods

Ashes (Table 1) formed at the Estonian Thermal Power Plant (TPP) were used for preparing the suspensions of ash (5 g ash + 100 ml distilled water, mole ratio of CaO_{free}/H_2O 0.0033). The ratio of solid phase to liquid phase was chosen to be equal to 1 : 20, which is similar to that formed during hydrotransport. Pure CaO ($CaCO_3$ was decomposed to CaO at 900 °C) was used for preparing the model suspensions (1 g CaO + 100 ml distilled water, mole ratio of CaO_{free}/H_2O 0.0030).

Two model gases were used for simulating the flue gases: gas I (85 % air + 15 % CO_2) and gas II (84.965 % air + 15 % CO_2 + 0.035 % SO_2). The extent of carbonation was described by index N, which indicates how many times the amount of CO_2 entrained into suspensions exceeds the stoichiometric ratio calculated according to Eq. (1):

$$CaO^{(s)} + CO_2^{(g)} \rightarrow CaCO_3^{(s)} \tag{1}$$
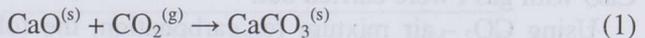
Carbonation of suspensions was carried out in an absorber (diameter 55 mm, height of water column 60 mm) equipped with a magnetic stirrer for achieving better interfacial contact and a sintered glass gas distributor (diameter of pores 100 μm) (Fig. 1).
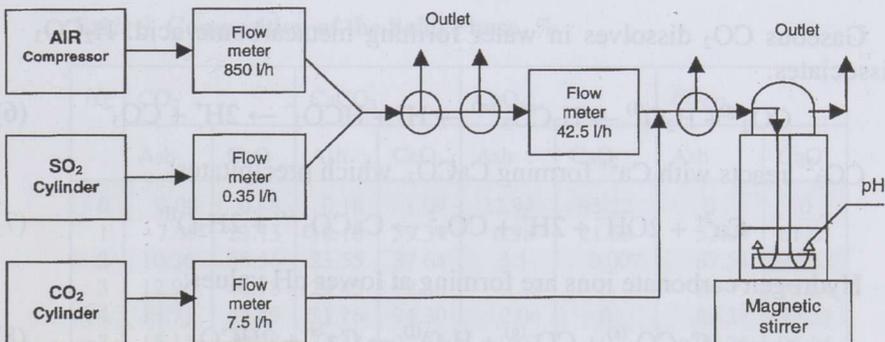
Fig. 1. Flow-sheet of the experimental device

The suspension was filtered and solid residue dehumidified at 105 °C. For the liquid phase, the content of Ca^{2+}, SO_3^{2-} and alkalinity [9, 10] were determined. The content of free CaO [11], CO_2 and SO_3^{2-} [9, 12] were determined in the solid residue. The effectiveness of carbonation process was described by the CO_2-binding degree (BD_{CO_2}). BD_{CO_2} expresses which part of the theoretical binding capacity of ash is employed. It was calculated on the basis of changes in CO_2 content:

$$BD_{CO_2} = \frac{CO_2}{CO_{2\,max}} *100 \ (\%) \tag{2}$$

where CO_2 is analytically determined CO_2 content of the sample, %;

CO_{2max} is maximum possible CO_2 content of the sample, %, calculated on the basis of free CaO content of the initial sample as follows:

$$CO_{2\,max} = \frac{CaO_{free}^i * M_{CO_2} / M_{CaO} + CO_2^i}{100 + CaO_{free}^i * M_{CO_2} / M_{CaO}} *100 \tag{3}$$

where CaO_{free}^i and CO_2^i are the content, %, of free CaO and CO_2 in the initial sample, respectively.

Results and Discussion

Carbonation of Suspensions Using Gas I

Laboratory experiments for treating the suspensions of cyclone ash and pure CaO with gas I were carried out.

Using CO_2 – air mixture for carbonation, the following reactions were presumed:

$$CaO^{(s)} + H_2O^{(l)} \rightarrow Ca(OH)_2^{(s)} \tag{4}$$
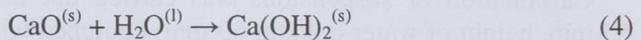
$Ca(OH)_2$ dissociates in aqueous solution:

$$Ca(OH)_2^{(aq)} \rightarrow CaOH^+ + OH^- \rightarrow Ca^{2+} + 2OH^- \tag{5}$$
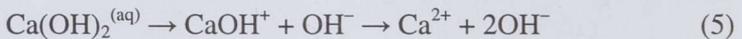
Gaseous CO_2 dissolves in water forming metacarbonic acid. H_2CO_3 dissociates:

$$CO_2^{(g)} + H_2O^{(l)} \rightarrow H_2CO_3^{(aq)} \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \tag{6}$$
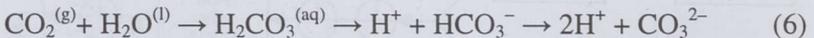
CO_3^{2-} reacts with Ca^{2+} forming $CaCO_3$, which precipitates:

$$Ca^{2+} + 2OH^- + 2H^+ + CO_3^{2-} \rightarrow CaCO_3^{(s)} + 2H_2O^{(l)} \tag{7}$$

Hydrogen carbonate ions are forming at lower pH values:

$$CaCO_3^{(s)} + CO_2^{(g)} + H_2O^{(l)} \rightarrow Ca^{2+} + 2HCO_3^- \tag{8}$$
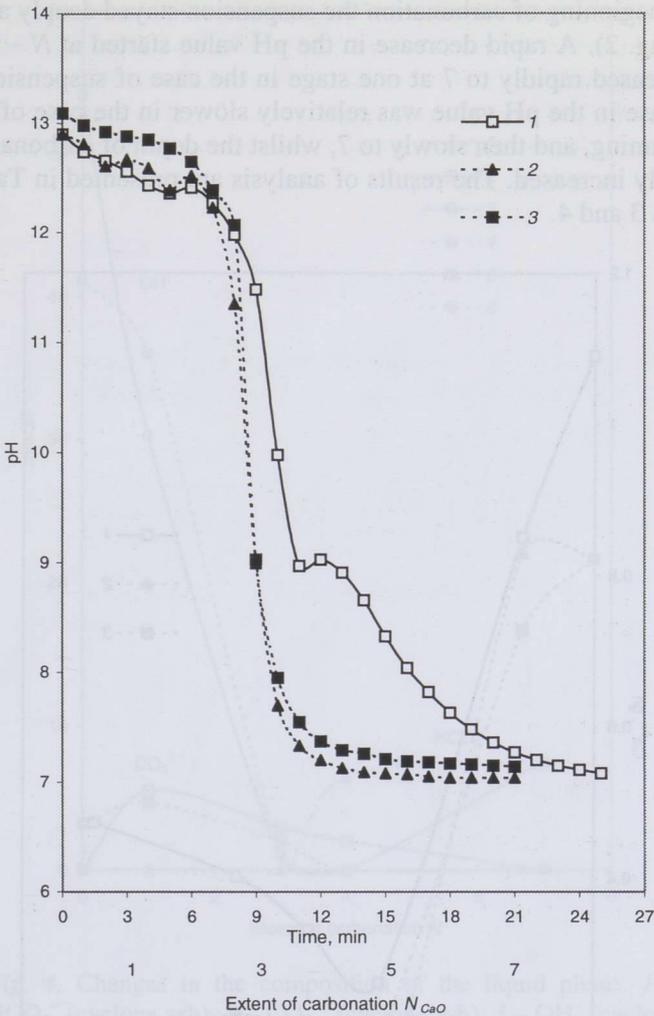
Fig. 2. Changes in pH during carbonation time: *1* – cyclone ash
(gas I), *2* – CaO (gas I), *3* – CaO (gas II). $N_{\text{cyclone ash}} = 1.23 N_{\text{CaO}}$

Table 3. **Composition of the Solid Phase, %**

N	CO_2		$CaCO_3$		CaO_{free}		BD_{CO_2}	
	Ash	CaO	Ash	CaO	Ash	CaO	Ash	CaO
0	0.08	0.48	0.18	1.09	22.94	93.22	0	0
1	7.99	23.13	18.16	59.39	6.98	21.63	52.09	61.41
2	10.36	38.56	23.55	87.64	3.1	0.007	67.54	90.62
3	12.96	40.78	29.45	92.68	2.22	0	84.49	95.84
4	13.71	41.49	31.16	94.30	2.06	0	89.37	97.51
7	15.15	40.78	34.43	92.68	0.93	0	98.76	95.84
10	15.34	41.64	34.86	94.64	0.37	0	100.0	97.86

At the beginning of carbonation the suspension stayed deeply alkaline for a while (Fig. 2). A rapid decrease in the pH value started at $N \sim 3$. The pH value decreased rapidly to 7 at one stage in the case of suspension of lime. The decrease in the pH value was relatively slower in the case of ash: to ~9 at the beginning, and then slowly to 7, whilst the depth of carbonation N was significantly increased. The results of analysis are presented in Tables 2 and 3, and Figs 3 and 4.
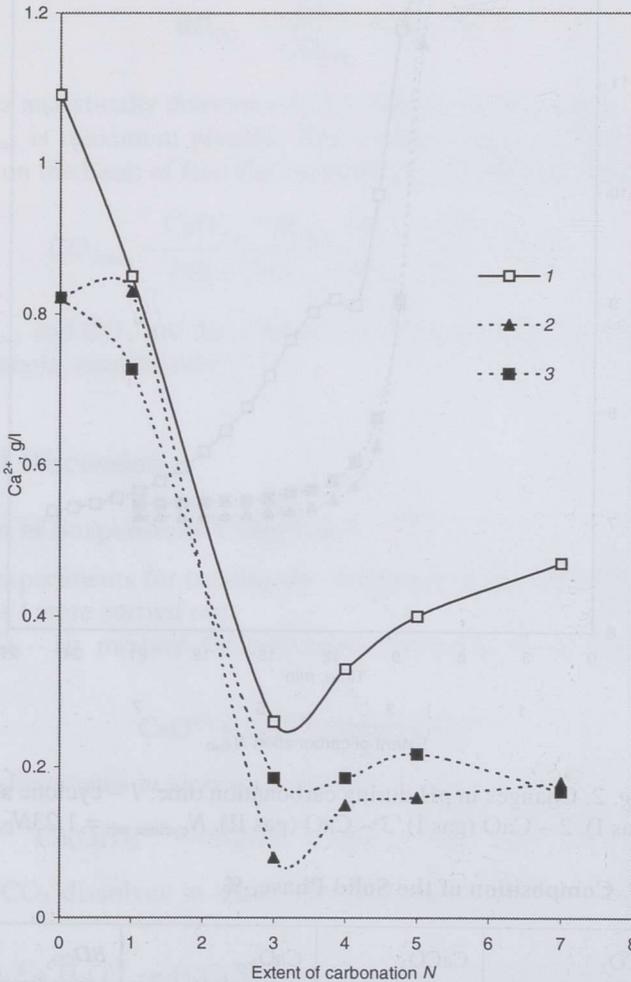
Fig. 3. Dependence of Ca^{2+} content on the extent of carbonation N: 1 – cyclone ash (gas I), 2 – CaO (gas I), 3 – CaO (gas II)
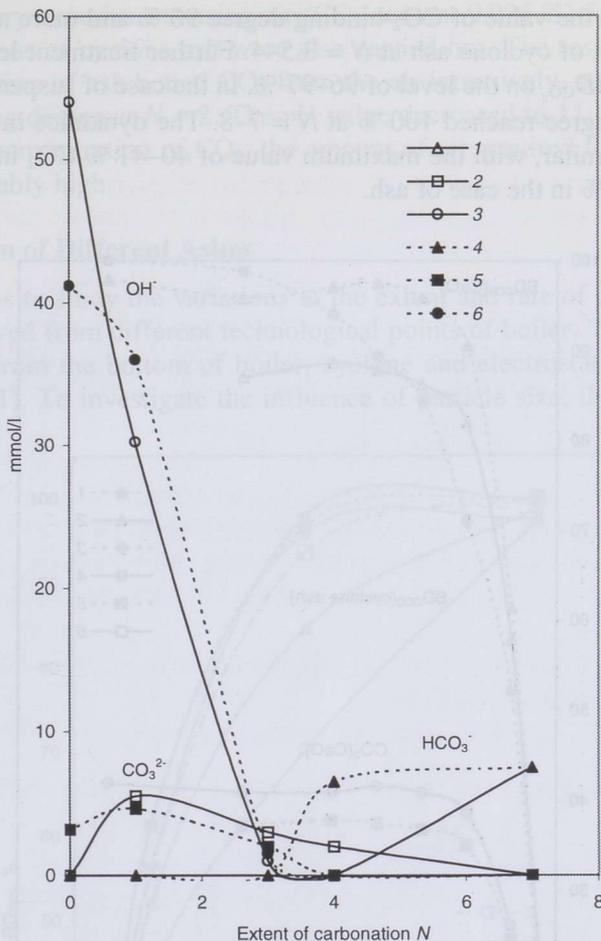
Fig. 4. Changes in the composition of the liquid phase: *1* – HCO_3^- (cyclone ash), *2* – CO_3^{2-} (cyclone ash), *3* – OH^- (cyclone ash), *4* – HCO_3^- (CaO), *5* – CO_3^{2-} (CaO), *6* – OH^- (CaO)

The experiments indicated that the content of Ca^{2+} ions changed similarly in both cases during carbonation, but the initial content of Ca^{2+} ions was lower in the case of lime suspension. Probably, some components of the system: oil shale ash – water promote saturation of the solution with Ca^{2+} ions. The content of Ca^{2+} ions decreased during carbonation synchronously with the content of OH^- ions and the pH value, but it started to increase again at pH values ~ 7.5–7 (see Fig. 3). Formation of hydrogen carbonate ions started at lower pH values (see Fig. 4), resulting in the increase in the content of Ca^{2+} ions.

Based on the results of chemical analysis of the solid phase it can be concluded that the carbonation of the suspension of lime occurs faster than the carbonation of the suspension of cyclone ash (Fig. 5). The suspension of

CaO achieved the value of CO_2-binding degree 90 % and more at $N = 2$, but the suspension of cyclone ash at $N = 3.5$–4. Further treatment led to stabilization of the BD_{CO_2} on the level of 96–97 %. In the case of suspension of ash, the binding degree reached 100 % at $N = 7$–8. The dynamics in the content of CO_2 was similar, with the maximum value of 40–41 % CO_2 in the case of lime and ~15 % in the case of ash.
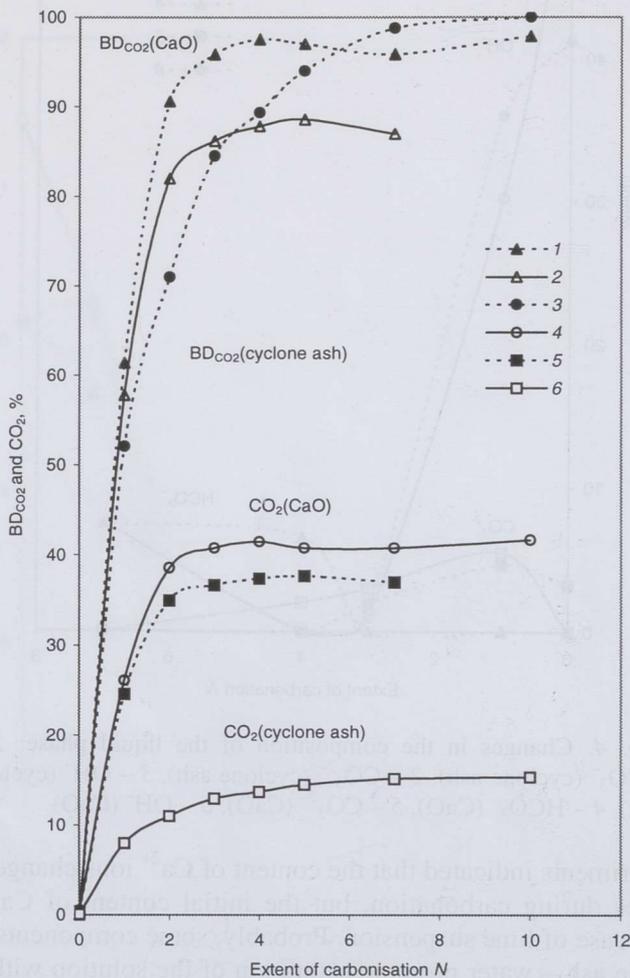
Fig. 5. Dependence of CO_2 content (CO_2, %) and CO_2-binding degree (BD_{CO_2}) on the extent of carbonation N: 1–3 – BD_{CO_2}: 1 – for CaO in gas I, 2 – for CaO in gas II, 3 – for cyclone ash in gas I; 4–6 – CO_2: 4 – for CaO in gas I, 5 – for CaO in gas II, 6 – for cyclone ash in gas I

Laboratory experiments using air (CO_2 content 0.036 %) for carbonation of suspensions of cyclone ash were also carried out. The results confirmed that suspension of ash bound CO_2 from the air intensively, achieving maximum binding degree at $N = 2$. The pH value decreased to 11. However, due to the low concentration of CO_2, the amount of air required for carbonation was remarkably high.

Comparison of Different Ashes

The aim was to study the variations in the extent and rate of carbonation of ashes removed from different technological points of boiler. The ashes used originated from the bottom of boiler, cyclone and electrostatic precipitator (see Table 1). To investigate the influence of particle size, the experiments
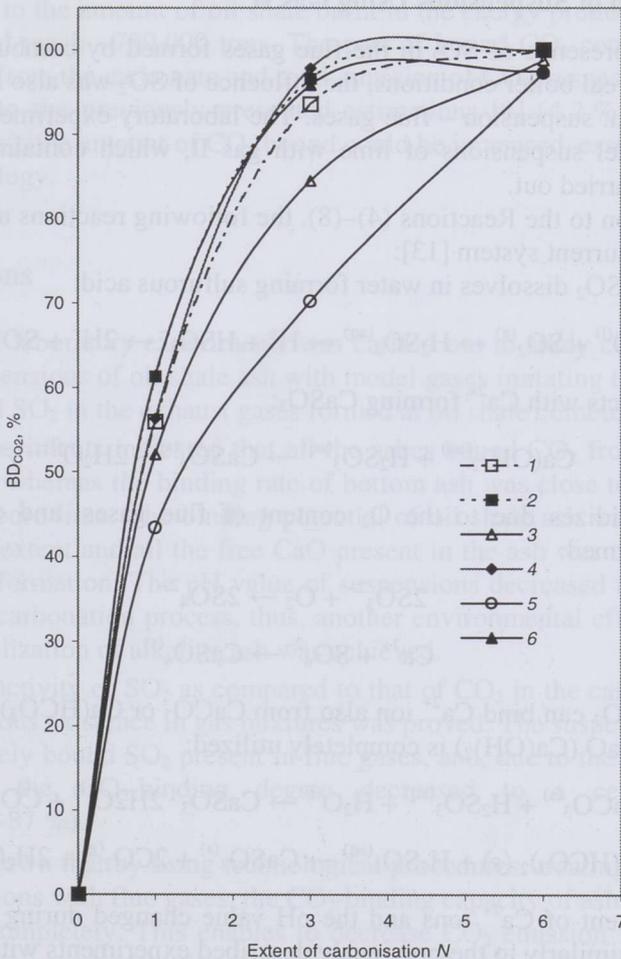
Fig. 6. Dynamics of BD_{CO_2} depending on the kind of ash: *1* – bottom ash, *2* – bottom ash (ground), *3* – cyclone ash, *4* – cyclone ash (ground), *5* – electrostatic precipitator ash, *6* – CaO

using ground bottom and cyclone ash (size fraction –0.071 mm) were carried out. Gas I was used for treating the suspensions.

The results of the experiments indicated that the binding potential of different ashes can be realized to the full extent, but at different rates (Fig. 6). The CO_2-binding degree increased fastest in the case of bottom ash and slowest in the case of electrostatic precipitator ash. This can be explained by differences in the structure (porosity, surface area) and in the glass phase content of ashes. This phase retards hydration process. The content of glass phase is highest in electrostatic precipitator ash and lowest in bottom ash. The binding dynamics of bottom ash was closest to the lime because of its porous structure and minimum content of glass phase. The binding dynamics of the ground bottom ash, the ground cyclone ash and lime were alike.

Carbonation of Suspensions Using Gas II

Due to the presence of SO_2 in the flue gases formed by combustion of oil shale under real boiler conditions, the influence of SO_2 was also investigated in the system: suspension – flue gases. The laboratory experiments of treating the model suspensions of lime with gas II, which contained 0.035 % SO_2, were carried out.

In addition to the Reactions (4)–(8), the following reactions are also possible in the current system [13]:

Gaseous SO_2 dissolves in water forming sulfurous acid:

$$H_2O^{(l)} + SO_2^{(g)} \leftrightarrow H_2SO_3^{(aq)} \leftrightarrow H^+ + HSO_3^- \leftrightarrow 2H^+ + SO_3^{2-} \tag{9}$$

SO_3^{2-} reacts with Ca^{2+} forming $CaSO_3$:

$$Ca(OH)_2^{(aq)} + H_2SO_3^{(aq)} \rightarrow CaSO_3^{(s)} + 2H_2O^{(l)} \tag{10}$$
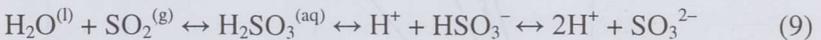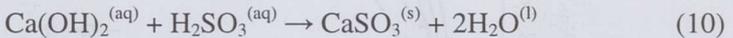
SO_3^{2-} oxidizes due to the O_2 content of flue gases, and calcium sulfate is formed:

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \tag{11}$$

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4^{(s)} \tag{12}$$
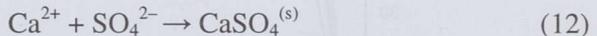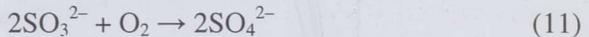
Active SO_2 can bind Ca^{2+} ion also from $CaCO_3$ or $Ca(HCO_3)_2$, especially when free CaO ($Ca(OH)_2$) is completely utilized:

$$CaCO_3^{(s)} + H_2SO_3^{(aq)} + H_2O^{(l)} \rightarrow CaSO_3 \cdot 2H2O^{(s)} + CO_2^{(g)} \tag{13}$$

$$Ca(HCO_3)_2 \, (s) + H_2SO_3^{(aq)} \rightarrow CaSO_3^{(s)} + 2CO_2^{(g)} + 2H_2O^{(g)} \tag{14}$$
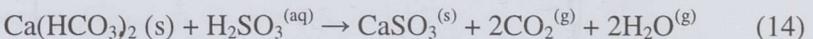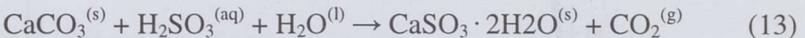
The content of Ca^{2+} ions and the pH value changed during carbonation with gas II similarly to the previously described experiments with gas I (Figs 2 and 3). The results of analysis confirmed that in addition to CO_2, the suspension also binds actively SO_2 from the gas mixture. At $N = 7$, the content of SO_2 rose up to 2 % in the solid phase and up to 90 mg/l in the liquid

phase. It was deduced from the values of SO_2-binding degree (BD_{SO_2}) (expresses which part of the contacted SO_2 was bound by suspension) that all SO_2 contacted with the suspension was bound by solid and liquid phases of the suspension. Due to the formation of $CaSO_3$, CO_2 content of the solid phase stayed lower and the CO_2-binding degree did not exceed 87 %. The CO_2-binding degree could even decrease during further treatment due to the Reactions (13) and (14). So, the binding reactions with CO_2 and SO_2 are competitive ones, and due to the goal of maximizing the BD_{CO_2}, the index N can have an optimum value that should not be exceeded.

The calculations based on the results of chemical analysis of the products obtained at laboratory experiments indicated that the amount of bound CO_2 could reach 153.8 kg per ton of oil shale ash or 70.8 kg per ton of oil shale burnt for electricity production. The annual amount of CO_2 bound by ash (according to the amount of oil shale burnt in the energy production in 2000 [14]), could reach ~730,000 tons. The part of bound CO_2 could form 35.6 and 7.3 % from the carbonate and total emission of CO_2, respectively. So, as compared to the previously presented estimations [8] (4.2 % and 20.5 %, respectively), the amount of CO_2 bound could be increased, essentially using this technology.

Conclusions

1. A set of laboratory experiments was carried out to study carbonation of the suspensions of oil shale ash with model gases imitating the content of CO_2 and SO_2 in the exhaust gases formed at oil shale combustion.

2. The experiments indicated that all the ashes bound CO_2 from flue gases actively whereas the binding rate of bottom ash was close to the binding rate of pure lime. The binding potential of oil shale ash was realized to the full extent and all the free CaO present in the ash was consumed for $CaCO_3$ formation. The pH value of suspensions decreased to 7.5–7 during the carbonation process, thus, another environmental effect – chemical stabilization of alkaline ash was achieved.

3. High reactivity of SO_2 as compared to that of CO_2 in the case of their simultaneous existence in gas mixtures was proved. The suspension of lime completely bound SO_2 present in flue gases, and, due to the formation of $CaSO_3$, the CO_2-binding degree decreased to a certain extent (BD_{CO_2} ~87 %).

4. It was shown that by using technological procedures: treating ash – water suspensions with flue gases, the CO_2-binding capacity of ashes can be put to use completely. This enables to decrease CO_2 emission level considerably as compared to the current situation. Besides, chemical stabilization of the ashes can be achieved.

Acknowledgements

REFERENCES

1. Possible Energy Sector Trends in Estonia. Context of Climate Change / T. Kallaste, O. Liik, A. Ots (eds.). – Tallinn, Estonia, 1999.
2. *Kaljuvee, T., Trikkel, A., Kuusik, R.* Reactivity of oil shale ashes towards sulfur dioxide. 1. Activation of high-temperature ashes // Oil Shale. 1997. Vol. 14, No. 3. P. 393–407.
3. *Kuusik, R., Kaljuvee, T., Trikkel, A., Arro, H.* Reactivity of oil shale ashes towards sulfur dioxide. 2. Low-temperature ashes formed by using CFBC technology // Oil Shale. 1999. Vol. 16, No. 1. P. 51–63.
4. *Kuusik, R., Kaljuvee, T., Veskimäe, H., Roundygin, Yu., Keltman, A.* Reactivity of oil shale ashes towards sulfur dioxide. 3. Recurrent use of ash for flue gas purification // Oil Shale. 1999. Vol. 16, No. 4. P. 303–313.
5. *Oates, J. A. H.* Lime and Limestone: Chemistry and Technology, Production and Use. – Weinheim etc.: Wiley – VCH, USA, 1998.
6. *Punning, J.-M., Karindi, A.* Composition of Estonian atmosphere // Estonia in the System of Global Climate Change / Institute of Ecology. Publications. 1996. Vol. 4. P. 26–34.
7. *Kuusik, R., Veskimäe, H., Kaljuvee, T., Keltman, A.* Oil shale ash deposits as natural CO_2 binders // Proc. 5th Intern. Symp. and Exhibition on Environmental Contamination in Central and Eastern Europe. Prague, 2000.
8. *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. Vol. 18, No. 2. P. 109–122.
9. *Vilbok, H., Ott, R.* Mahtanalüüs. Praktiliste tööde juhend (Volumetric Analysis. Instruction for Practical Works) / Tallinn Polytechnical Institute. – Tallinn, 1977.
10. Water Quality. Determination of Alkalinity. International Standard ISO 9963-1:1994(E).
11. Lendtuha katsemeetodid. Osa 1: Vaba kaltsiumoksiidi sisalduse määramine (Test methods of fly-ash. Part 1: Determination of free CaO content), EVS-EN 451-1, 1999-11-23.
12. Tahkekütused. Väävlisisaldus (Solid fuels. Sulfur content). Eesti Standart (Estonian Standard), EVS 664: 1995.
13. *Boyton, R.* Chemistry and Technology of Lime and Limestone. – John Wiley & Sons. Inc.
14. Keskkonnaaruanne 2000 (Environment Report 2000). *Eesti Energia* (SC Estonian Energy). http://www.energia.ee