SULPHATION AND CARBONIZATION OF OIL SHALE CFBC ASHES IN HETEROGENEOUS SYSTEMS

R. KUUSIK[*(a)], M. UIBU[(a)], M. TOOM[(a)] M.-L. MUULMANN[(a)], T. KALJUVEE[(a)], A. TRIKKEL[(b)]

[(a)] Laboratory of Inorganic Materials
[(b)] Department of Inorganic Chemistry
   Tallinn University of Technology,
   5 Ehitajate Rd., 19086 Tallinn Estonia

To explain chemical reactivity of oil shale ashes formed in circulating fluidized bed boilers towards SO_2 and CO_2, heterogeneous gas–solid and gas–solid–water model systems were studied. For comparison, the ashes from boilers of pulverized firing were used. The effect of pre-treatment conditions, differences in chemical and phase composition as well as physical properties of the ashes on the binding parameters were estimated.

Introduction

In the course of combustion, fuel inorganic part undergoes several chemical transformations, from decomposition processes to formation of new secondary mineral compounds and phases at higher temperatures. Inorganic matter (about 70% of oil shale mass) of the Estonian oil shale consists mainly of two components: carbonate matter and sandy-clay matter [1].

The mechanism of the processes that take place during pulverized firing (PF) of oil shale is thoroughly examined including the formation of ash deposits at heat-transfer surfaces [1, 2]. Investigations of fly ash composition and reactivity brought about developing and introducing ash-recycling processes like production of various building materials, cement with special properties and other products [3]. Ash is also utilized as an expedient material in road construction as well as soil conditioner in agriculture [4] and neutralizing additive in the production of mineral fertilizers [5]. In addition, it could be used as a SO_2 sorbent [6, 7].

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[*] Corresponding author: e-mail *rein.kuusik@ttu.ee*

Table 1. **Chemical Composition and Physical Properties of CFBC and PF Ashes**

Ash	Fraction	Content, %								d_{mean}, μm	SSA, m²/g
		CaO_t	CaO_f	MgO_t	CaO_{fc}^*	CO_2	S_t	$S_{sulphate}$	$S_{sulphide}$		
CFBC/BA	Initial	49.39	12.48	9.25	37.41	15.14	4.53	4.32	0.10	197	2.06
	−45 μm		14.79		32.74	11.22					4.77
CFBC/INT	Initial	47.59	18.87	13.65	20.69	1.23	7.76	7.70	0.02	95	2.61
	−45 μm		18.29		20.69	1.62					4.16
CFBC/ECO	Initial	32.84	10.40	9.50	18.38	5.48	2.32	2.22	0	27	6.89
	−45 μm		10.58		17.27	4.63					7.50
CFBC/PHA	Initial	35.17	12.26	10.77	18.52	4.30	3.31	3.27	0.0013	32	5.40
	−45 μm		12.47		18.51	4.14					5.89
CFBC/ESPA1	Initial	29.52	8.45	8.33	14.99	4.60	1.71	1.71	0	25	8.00
	−45 μm		8.15		13.56	3.84					8.63
CFBC/ESPA4	Initial	28.88	2.82	9.35	7.96	3.80	2.23	2.21	0	23	7.92
CFBC/Mix	Initial	33.28	10.33	9.50	19.75	6.41	2.46	2.43	0.03	28	7.11
	−45 μm		9.31		17.37	5.57					8.23
PF/BA	Initial	50.75	24.84	15.19	29.14	2.75	1.27	1.27	0	115	1.75
	−45 μm		25.92		30.40	2.84					2.58
PF/SHA	Initial	54.71	23.08	7.81	24.53	0.96	1.98	1.93	0	105	0.50
PF/ECO	Initial	48.00	16.04	8.24	19.71	2.50	2.52	2.52	0.006	53	0.44
PF/CA	Initial	49.39	22.52	14.19	23.58	0.70	1.33	1.33	0	48	0.36
	−45 μm		22.79		24.14	0.89					1.45
PF/ESPA1	Initial	36.08	13.56	11.26	15.21	1.16	2.74	2.74	0	24	0.61
PF/ESPA3	Initial	26.85	5.98	5.98	7.05	0.80	3.67	3.67	0	23	1.09

* – calculated on the basis of CO_2 and CaO_f content.

Compared to PF, in the case of circulating fluidized bed combustion (CFBC) operating temperatures are considerably lower. Consequently, chemical and phase composition of CFBC waste ashes differ noticeably [8], and that is why the differences in chemical reactivity can also be expected.

The aim of the current study was to elucidate chemical reactivity of CFBC ashes compared to PF ones in the systems that are important in the formation of ash deposits in a boiler, at ash deposition at landfill, at flue gas desulphurization as well as at reducing CO_2 emissions.

Materials and Methods

Ash samples used were collected from different points of the ash-separation systems of CFBC and PF boilers at the Eesti Thermal Power Plant. The CFBC ashes studied were bottom ash (CFBC/BA), intrex ash (CFBC/INT), economizer ash (CFBC/ECO), air preheater ash (CFBC/PHA), electrostatic precipitator ash from fields 1 and 4 (CFBC/ESPA 1 and 4) and mixture of ashes (CFBC/Mix) taken from a common ash silo where the ash from different units is collected before landfilling on ash fields. The PF ashes used were bottom ash (PF/BA), superheater ash (PF/SHA), economizer ash (PF/ECO), cyclone ash (PF/CA) and electrostatic precipitator ash from fields 1 and 3 (PF/ESPA 1 and 3). Chemical composition and physical properties of these ashes are presented in Table 1 and discussed in more detail in paper [8].
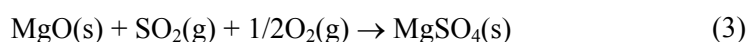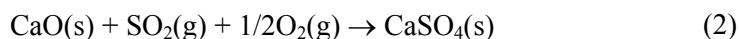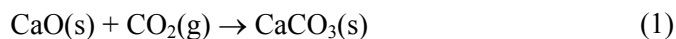
Reactivity of ashes towards SO_2 or CO_2 was tested in a heterogeneous gas-solid system using thermogravimetric equipment (Q-derivatograph, MOM) under isothermal conditions. In both cases the temperature of the isothermal experiment was 700 °C, partial pressure of SO_2 or CO_2 was 190 and 144 mm Hg, respectively. The samples (100 ± 0.5 mg) were heated up to 700 °C in the air with heating rate of 10 K/min. Gas mixture was then fed into the furnace with the rate of 270 ml/min. Thickness of sample layer in multiplate Pt crucibles was about 0.2–0.3 mm. To study the effect of grinding on SO_2 and CO_2 binding, the initial samples (except for CFBC/BA, which was slightly crushed to pass the 630 μm sieve) and the ground ones were used. Samples were ground in an one-ball vibration mill until its most part (approx 85–100%) passed through the 45-μm sieve. In some experiments with CO_2, samples were heated up to 900 °C to achieve full decomposition (FD) of carbonates and then cooled to 700 °C to perform isothermal binding.

To characterize high-temperature binding of SO_2 and CO_2 by ashes, the following parameters were calculated:

- SO_2- or CO_2-binding capacity (*BC*; weight of SO_2 or CO_2 bound by 100 mg of sample),
- SO_2- or CO_2-binding rate (*W*; mg SO_2 or CO_2 per mg sample·min^{-1}),

- SO_2- or CO_2-binding efficiency, (*BE*, %) showing the extent of utilization of CaO and MgO contained in the sample

The parameters were calculated on the basis of experimental and analyses data and the following summary binding reactions:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \tag{1}$$

$$CaO(s) + SO_2(g) + 1/2O_2(g) \rightarrow CaSO_4(s) \tag{2}$$

$$MgO(s) + SO_2(g) + 1/2O_2(g) \rightarrow MgSO_4(s) \tag{3}$$

Carbonization of aqueous suspensions of ash with model gas, whose composition (10% CO_2 and 90% air) simulated CO_2 content of flue gases formed at oil shale combustion, was carried out in an absorber (diameter 55 mm, water column height 500 mm) equipped with magnetic stirrer for achieving a better interfacial contact and a sintered glass gas distributor (pore diameter 100 μm). The experiment was carried out until suspension pH reached 7.5. Then the suspension was filtered and solid residue dehumidified at 105 °C. For the liquid phase, Ca^{2+} content [9], TDS (total dissolved solids) and alkalinity [10] were determined. Content of free CaO [11], pH of aqueous suspension of solid residue [12] and CO_2 were determined in the solid residue.

Results and Discussion

Free CaO is the main binder of SO_2 and CO_2 in the ashes (Reactions (1) and (2)). Although MgO does not take part in CO_2 binding under these conditions [13], it has a certain role in SO_2 binding [13, 14]. Hence, the negative influence of coarser fractional composition of the samples and, correspondingly, the lower level of specific surface area (SSA) in the case of, for example, CFBC/BA (mean particle size 197 μm; SSA 2.1 m^2/g) and CFBC/INT (95 μm; 2.6 m^2/g) should be compensated by higher level of free CaO content – 11.9 and 18.9%, respectively (see Table 1).

PF/BA and PF/CA are both characterized by a quite high content of free CaO (23–25%), but they differ noticeably (5 times) in their SSA. PF/ESPA1 is characterized by fine fractional composition ($d_{mean} = 24$ μm), low content of free CaO, but despite small particle size by a low value of SSA (0.61 m^2/g) and should show a modest binding activity. CFBC/ECO and CFBC/PHA are somewhere in the middle of the scale considering these parameters.

Comparing chemical composition of ground to –45 μm samples and initial samples (see Table 1) one can notice that content of free CaO in initial and ground samples in most cases is similar being slightly higher for ground ones. The difference was 1–10%, except for CFBC/BA (20%). CO_2 content was slightly less in ground CFBC ashes and higher in PF ones. SSA

increased noticeably during grinding for PF/CA, CFBC/BA, CFBC/INT and PF/BA (1.6–4 times). For the other ashes the increase was about 10%.

Transformations in the Gas–Solid System SO_2–Ash

After 30 minutes of the contact between solid and gaseous phases, SO_2-binding capacity of different CFBC ashes was about 26–30 mg SO_2 per 100 mg sample. 55–70% of this value was achieved during the first 2-min contact already (Fig. 1).
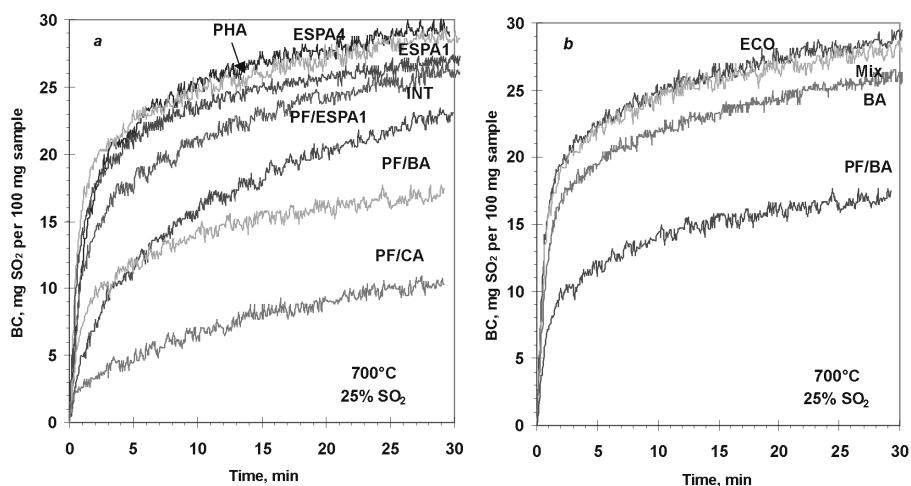

Fig. 1. SO_2-binding capacity (*BC*) of the ashes (for comparison, PF/BA is presented in both diagrams). Pulverized firing ashes marked by PF

BC values for PF ashes differed from each other more considerably – from 10.4 to 23.1 mg SO_2 per 100 mg sample – being the highest for PF/ESPA1. During a 2-min contact, PF/BA bound 58%, while PF/ESPA1 and PF/CA only 33% of the total amount of bound sulphur dioxide. This data correspond to the data obtained in our earlier research [13, 14] and can be explained by the differences in chemical and fractional composition as well as in physical and chemical properties of the ashes. Thus, CFBC/BA and CFBC/INT have coarser fractional composition and lower SSA level, but higher free CaO content, while CFBC/ESPA has fine fractional composition (and high level of SSA), but low content of free CaO (see Table 1). Differences in *BC* values for PF/BA and PF/CA can be explained by their different SSA values (1.75 and 0.36 m^2/g, respectively).

During the initial period of the contact (first 30 sec), ECO, PHA, ESPA1 and Mix were the most active among CFBC ashes, having average SO_2-binding rate *W* 0.20–0.23 mg SO_2 per mg sample·min^{-1}. The *W* values for INT, BA and ESPA were 4, 0.16 and 0.13 mg SO_2 per mg sample·min^{-1}, respectively.

In the experiments of SO_2-binding MgO, free CaO and, partially, Ca-silicates can take part in the reactions with SO_2. So, in this case binding efficiency *BE* was calculated on the basis of total content of CaO and MgO in the sample – *BE(CaO·MgO)*. *BE(CaO·MgO)* values indicated the highest level of utilization of both oxides for ESPA4 (74%) and the lowest for BA and INT – about 41% (Fig. 2) BA was the most active among PF ashes, having an average SO_2-binding rate 0.10 mg SO_2 per mg sample·min^{-1}. Like other indicators of SO_2-binding ability, the values of *BE(CaO·MgO)* for PF ashes were much less than those for CFBC ashes: 46.9% (the highest) for ESPA1, 25.7% for BA and 15.4% for CA (Fig. 2).
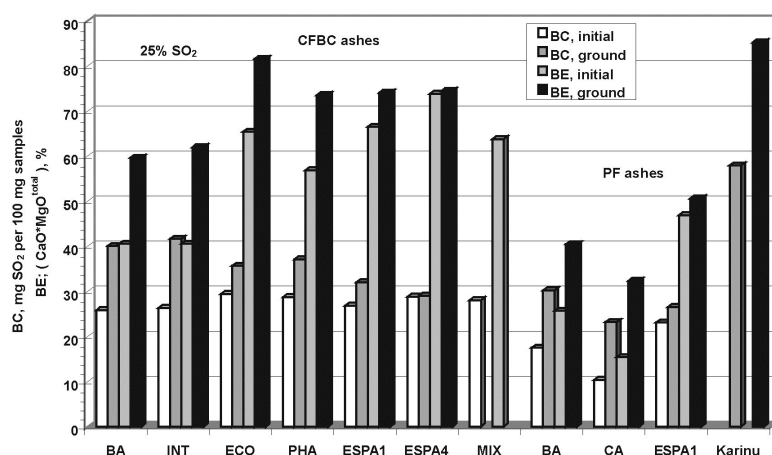

Fig. 2. The influence of grinding on SO_2-binding capacity (*BC*) and efficiency (*BE/CaO·MgO)* at 700 °C after 30-min contact

For all the ashes studied preliminary grinding increased their binding ability. To most extent it was noticed for the ashes characterized by coarse fractional composition (CFBC/BA, CFBC/INT, PF/BA) and/or those having been allocated to high temperatures at PF (especially PF/CA) resulting in the formation of liquid phases hindering further diffusion of SO_2 into the particles.

Thus, grinding increased the *BC* and *BE* values for PF/CA 2.2 times, for CFBC/BA, CFBC/INT and PF/BA 55–70%, for CFBC/ECO and CFBC/PHA 20–30%, for CFBC/ESPA1 and PF/ESPA1 10–20%, and for CFBC/ESPA4 there was no change in these values. Among ground CFBC ashes, *BC* value was the highest for BA and INT (40–42 mg SO_2 per 100 mg sample), *BE* value for ECO – 81.5% (Fig. 2). Among PF ashes, *BC* value was the highest for BA – 30.2 mg SO_2 per 100 mg sample and *BE* value for ESPA1 – 50.6 % (see Fig. 2).

These results are in good correlation with the increase in the SSA of the samples: for PF/CA 4.4 times (from 0.36 m^2/g to 1.45 m^2/g), for CFBC/BA, CFBC/INT, and PF/BA 1.5–2.3 times, for the other ashes on the level of 1.1

times, except for CFBC/ESPA4 and PF/ESPA1, for which even a small decrease in the SSA was observed. Comparing these results with those obtained with Karinu limestone, the *BC* values of the more active ashes (CFBC/BA and INT) were only 1.4 times less, but the *BE* value of CFBC/ECO was on the same level than that of Karinu limestone (see Fig. 2).

An essential increase in the average SO_2-binding rate in the initial period of the contact was fixed for CFBC/BA and INT – 1.75 and 1.5 times, respectively. But for CFBC/ECO and PHA it was noticeably lower as compared to the initial samples – 75% and 20%, respectively. For PF ashes the average SO_2-binding rate increased 1.4–2.6 times, being the highest for CA. This phenomena with CFBC/ECO and PHA need an additional study, but it could probably be explained by the negative influence of grinding in the ball mill on structural properties of ashes, for example, the decrease of porosity of the samples or partial closing of the pores on the surface of ash particles.

Transformations in the Gas–Solid System CO_2–Ash

CO_2-binding capacities of the ashes stay between 1 and 13 mg CO_2/100 mg (Fig. 3). Among CFBC samples, the highest binding capacity was calculated for bottom ash. Binding capacities of ECO, PHA and Mix were about 5 mg CO_2/100 mg, the lowest *BC* values were of INT and ESPA. Bottom ash of pulverized firing bound also about 5 mg of CO_2 per 100 mg sample, binding capacities of PF/CA and PF/ESPA were low.

Grinding of CFBC samples decreased their binding capacities noticeably, except for INT. Decrease in *BC* was from 12% (BA) to 60–70% (ECO, PHA and ESPA). This phenomenon is specific of CFBC samples, because *BC* of ground PF samples is about 75–85% higher as compared to the initial ones. This correlates with the increase in specific surface area, which is 4 times higher for ground PF/CA and 1.5 times higher for ground PF/BA. However, grinding increased also SSA of CFBC ashes. The decrease in *BC* was less for BA and INT, also the increase in SSA during grinding was higher for these samples – 2.3 and 1.6 times, respectively.

Unlike in the reactions with SO_2, MgO should not take part in CO_2-binding under these experimental conditions, so, binding efficiency *BE* was calculated on the basis of the content of free CaO and CaO formed at decomposition of carbonates during heat-up of the samples – *BE(CaO$_{fc}$)*. Besides, recarbonization extent – *X(CO$_2$)* as the ratio of the amount of CO_2 bound to the amount present in the sample was used to characterize CO_2-binding.

The values of binding efficiencies *BE(CaO$_{fc}$)* reached 40–50% (Table 2), being the highest for the initial samples of CFBC/BA, CFBC/ECO, CFBC/PHA and CFBC/Mix. The changes in binding efficiencies followed the same trend as in the case of binding capacities. They decreased noticeably for the ground CFBC ash samples remaining below 10–20%,

except for BA, and increased for the ground PF ash samples being 40% for PF/BA as compared to 25% for the untreated sample.
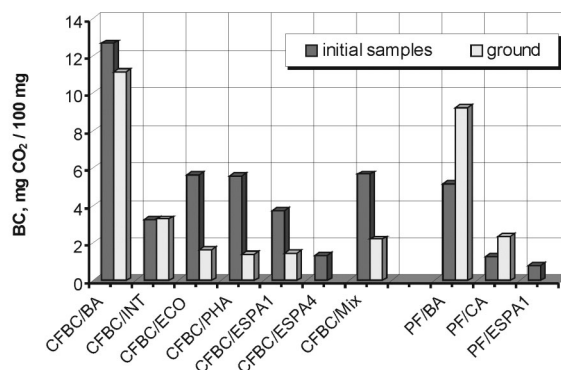

Fig. 3. CO_2-binding capacities (*BC*) of the initial and ground
to particle size less than 45 μm ash samples after 30-min binding

Recarbonization extent $X(CO_2)$ over 100% (see Table 2) indicates that in addition to free CaO formed during decomposition of carbonates at heating, also free CaO present in the initial samples participates in CO_2 binding. $X(CO_2)$ was high for CFBC/INT (265%) and pulverized firing samples – PF/BA (189%) and PF/CA (181%). High content of free CaO (19–25%) and low (<1%) CO_2 content were specific of these samples. As for the other untreated samples, their $X(CO_2)$ was in the range of 70–130%. Most probably, the fresh CaO formed during decarbonization at heating is more active in CO_2 binding than the free CaO present in initial samples.

The effect of pre-treatment and some experiment conditions on binding capacities are presented in Fig. 4. One can see that grinding of CFBC/PHA sample for 30 minutes in the ball mill decreased *BC* from 5.5 to 2.3 mg CO_2/100 mg. The effect of decarbonization temperature is even more severe – the decrease in *BC* for the samples heated before binding to 700 °C and 900 °C (marked by FD) is from 5.5 to 1.8 mg CO_2/100 mg.

Table 2. **$BE(CaO_{fc})$ and $X(CO_2)$ Values of the Initial and Ground Samples, %**

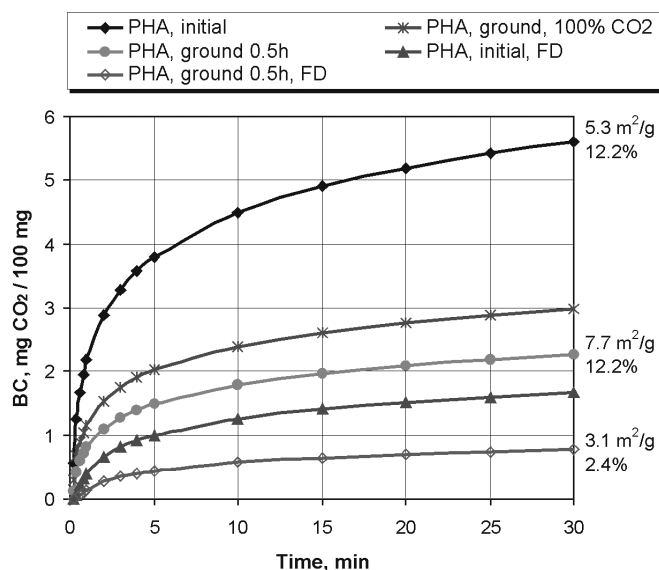| Sample	Fraction	$BE(CaO_{fc})$	$X(CO_2)$
CFBC/BA	Initial	52.3	83.7
	-45 μm	48.9	99.4
CFBC/INT	Initial	21.1	265.6
	-45 μm	20.6	203.2
CFBC/ECO	Initial	42.6	103.5
	-45 μm	12.8	35.7
CFBC/PHA	Initial	42.6	130.2
	-45 μm	10.2	34.3
CFBC/ESPA1	Initial	34.5	81.8
	-45 μm	14.4	38.3
CFBC/ESPA4	Initial	23.5	35.1
CFBC/Mix	Initial	42.9	88.6
	-45 μm	17.2	39.7
PF/BA	Initial	25.3	188.8
	-45 μm	39.9	325.3
PF/CA	Initial	7.6	180.7
	-45 μm	12.6	265.4
PF/ESPA1	Initial	7.9	67.9

Fig. 4. CO$_2$-binding capacities of PHA depending on binding duration and pre-treatment conditions. Numbers indicate SSA and CaO$_f$ content before binding

Separate experiments were performed to estimate changes in SSA and CaO$_f$ content during pre-treatment. It can be seen that a 30-min grinding increased SSA from 5.3 to 7.7 m^2/g, but heating of this ground sample to 900 °C decreased its SSA to 3.1 m^2/g. Also content of free CaO decreased remarkably during heating – from 12.2 to 2.4%. In the samples heated only to 700 °C content of free CaO was 4.8% and SSA of the samples was 10.3 m^2/g.

The effect of grinding and decarbonization temperature on *BC* and *BE* needs a more detailed research. Presumably, the decomposition of carbonates and resulting formation of CaO are accompanied by the formation of secondary compounds with free CaO, as noticed earlier [15]. These solid-state reactions taking place during heating of the ash samples of low-temperature CFBC and reducing CaO reactivity could be accelerated in the case of ground samples. Besides, the formation of liquid phases at higher temperatures due to higher content of sulphates, which forms different eutectic mixtures, is possible. It can result in decreasing porosity and increasing diffusion resistance of particles. PF ash samples exposed in boiler to high temperatures and characterized by lower SO$_4^{2-}$ content seem to be more resistant to decarbonization temperature.

Increase in CO$_2$ concentration from 15 to 100% does not influence *BC* much (see Fig. 4) – the increase in *BC* for the ground sample is about 30%, however, binding rate *W* at the beginning of the process is higher.

Thus, as compared to PF ashes, CO$_2$ binding capacities of CFBC ashes are 2-3 times higher. The best results were obtained in both cases with

bottom ashes. The method of grinding used improved noticeably binding parameters of PF ashes and reduced those of CFBC ashes. According to the results obtained, it can also be concluded that intensive contamination of heating surfaces in CFB boilers with secondary carbonaceous deposits should not be a serious problem.

CO_2–Ash–Water System

To characterize CO_2-binding in ash–water suspensions the following parameters were used. Carbonization extent was described by index N indicating the excess of the CO_2 amount entrained into suspensions over the stoichiometric ratio calculated according to Equation (1). Effectiveness of the carbonization process was described by the CO_2-binding degree (BD_{CO2}). BD_{CO2} shows which part of the theoretical ash-binding capacity is utilized. It was calculated basing on the changes in CO_2 content:

$$BD_{CO2} = \frac{CO_2}{CO_{2\,max}} \cdot 100 \ (\%) \tag{4}$$

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

$CO_{2\,max}$ is the maximal possible CO_2 content of the sample (%), calculated on the basis of content of free or total CaO in the initial sample as follows:

$$CO_{2\,max} = \frac{CaO^i \cdot M_{CO_2} / M_{CaO} + CO_2^i}{100 + CaO^i \cdot M_{CO_2} / M_{CaO}} \cdot 100 \tag{5}$$

where CaO^i and CO_2^i denote the content (%) of free or total CaO and CO_2 in the initial sample, respectively.

The results obtained are presented in Table 3 and Figures 5–6. Chemical analysis of the liquid phase indicated that after carbonization the suspensions of both kinds of ashes contain small amounts of alkaline components. In the suspensions of CFBC ashes, content of Ca^{2+} ion is near saturation point or even higher (in the case of intrex ash 1110 mg/l). In the suspensions of PF ashes, the concentrations of Ca^{2+} ions stay on a noticeably lower level (240–590 mg/l). The TDS values were proportional to the content of Ca^{2+} ion.
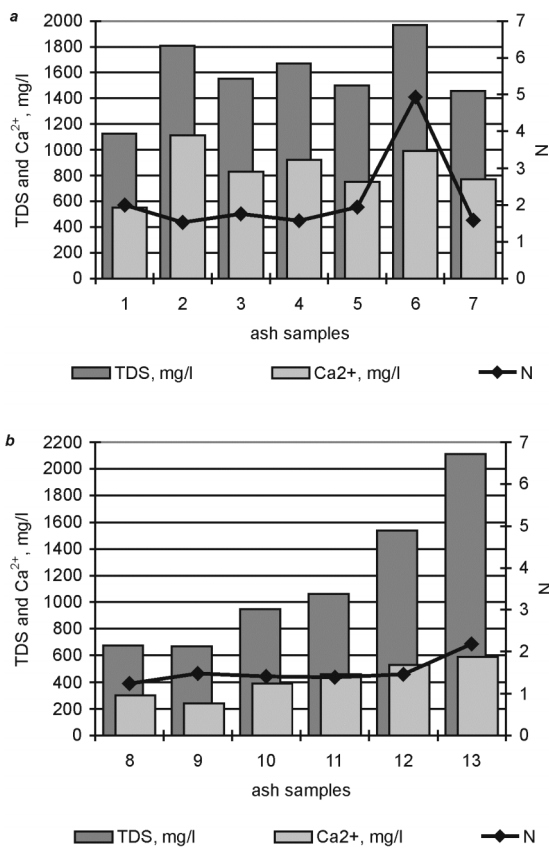
Compared to PF ashes, CFBC ashes can be carbonized more deeply accompanied by lowering of pH of the solid residue in most cases below 9 (with the exception of CFBC/BA, full carbonization of which is inhibited due to coarse fractional composition, see Table 1). Higher pH value (10.9–11.9) is elicited by higher content of free CaO (0.57–3.47%) in solid residues of carbonized PF ashes. Apparently, in the case of PF ashes as nonporous materials some part of free CaO present is not accessible and therefore cannot take part in reaction under these conditions. The content of CO_2 is proportional to that of free CaO and CO_2 in the initial samples (see Table 1).

Table 3. **Characterization of Carbonized Ashes**

Ash type	CO_2, %	CaO_f, %	BD_{CO}, %	BD_{CO_2}[*1], %	pH[*2]	N	$\dfrac{m^3 CO_2}{t\_ash}$
CFBC/BA	23.29	0.88	104.1	59.93	11.55	2.00	944.44
CFBC/INT	15.51	0.43	110.92	55.17	9.6	1.53	1152.77
CFBC/ECO	14.17	0.21	112.28	56.98	8.85	1.76	731.53
CFBC/PHA	14.30	0.22	112.97	57.15	9.33	1.57	759.31
CFBC/ESPA1	12.68	0.18	120.31	56.20	7.24	1.94	652.78
CFBC/ESPA4	11.26	0.12	191.32	52.15	7.43	4.94	555.55
CFBC/Mix	16.09	0.20	119.75	62.34	8.93	1.58	652.78
PF/BA	19.46	1.41	104.45	64.01	11.55	1.24	1229.17
PF/SHA	18.99	1.79	117.49	61.79	11.88	1.48	1361.11
PF/ECO	13.4	3.47	99.92	45.89	11.88	1.41	902.78
PF/CA	17.18	0.61	109.92	60.36	10.88	1.39	1250.83
PF/ESPA1	12.96	0.75	121.39	56.37	10.98	1.46	791.67
PF/ESPA3	7.62	0.57	145.09	42.14	10.95	2.19	523.19

[*1] - CO_2-binding degree calculated on the basis of total CaO in initial sample.

[*2] - pH of aqueous suspension of solid residue.

Fig. 5. Ca^{2+} and TDS contents in suspensions of CFBC (*a*) and PF (*b*) ashes:
1 – CFBC/BA,
2 – CFBC/INT,
3 – CFBC/ECO,
4 – CFBC/PHA,
5 – CFBC/ESPA1,
6 – CFBC/ESPA4,
7 – CFBC/Mix,
8 – PF/BA,
9 – PF/SHA,
10 – PF/ECO,
11 – PF/CA,
12 – PF/ESPA1,
13 – PF/ESPA3

Binding degrees that were calculated basing on content of free CaO in the initial samples were in CFBC and PF ashes predominantly over 100% (104.1–191.32% and 99.92–145.09%, respectively) because there can be other CO_2-binding compounds (MgO, Ca-silicates) present in oil shale ash of heterogeneous composition. In general, for total utilization of free CaO the CFBC ashes need less CO_2 per tonne of ash as they contain less free CaO in the initial ash.
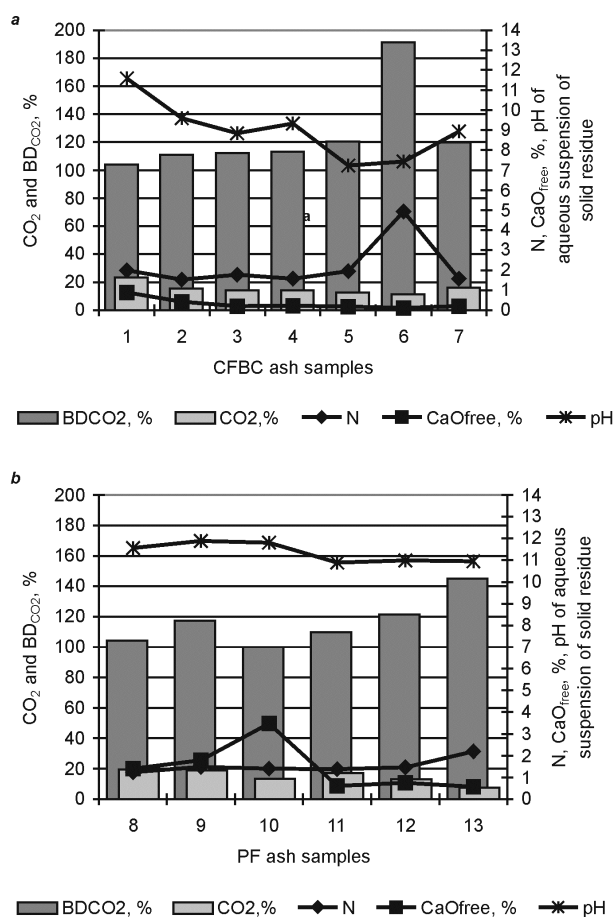

Fig. 6. Characteristics of carbonization process and its final product for CFBC (*a*) and PF (*b*) ashes.
1 – CFBC/BA,
2 – CFBC/INT,
3 – CFBC/ECO,
4 – CFBC/PHA,
5 – CFBC/ESPA1,
6 – CFBC/ESPA4,
7 – CFBC/Mix,
8 – PF/BA,
9 – PF/SHA,
10 – PF/ECO,
11 – PF/CA,
12 – PF/ESPA1,
13 – PF/ESPA3

Conclusions

1. Oil shale ashes formed in boilers operating at different combustion technologies differ by their chemical reactivity towards acidic gases.

2. Sulphation of ashes in model conditions shows that SO_2-binding capacity of CFBC ashes at enhanced temperature (700 °C) remained within a narrow range of 26–30 mg (0.41–0.47 mmoles) of SO_2 per 100 mg sample, and in the case of PF ashes between 10 and 27 mg SO_2 per

100 mg sample, being the highest for PF/BA. Grinding of coarser ashes increased their *BC* values noticeably (60–120%). For the other kinds of ashes the increase remained on the level of 15–30%. Consequently, SO_2-binding capacity of CFBC as well as of PF ashes is not completely utilized. Being characterized by a higher binding rate during the initial stage of gas–solid contact, CFBC ashes could be more promising as potential SO_2 sorbents for desulphurization processes of flue gases.

3. Transformations in the gas–solid system CO_2–ash which are important also in evaluating the possibilities for formation of calcareous precipitations on heat transfer surfaces in boilers, especially the recarbonization process of ashes, were investigated. CO_2-binding ability of the ashes at 700 °C was relatively low – in the range of 0.02–0.30 mmoles of CO_2 per 100 mg sample being 2-3 times higher for CFBC ashes. Within 30 minutes   8–52% of free CaO present in the sample was utilized. According to these data intensive formation of secondary carbonaceous precipitations on the heat transfer surfaces of the CFB boiler is not foreseen.

4. The results of the experiments on binding gaseous CO_2 by ash–water suspension indicated that in the same conditions, CFBC ashes can be carbonized more intensively and deeply than PF ashes. Besides lime as a compound of the highest reactivity towards CO_2 also other components like MgO and Ca-silicates present in ash take part in CO_2-binding reactions. Owing to improved CO_2-binding rate, more intensive natural CO_2-mineralization of CFBC ashes as compared to PF ashes in open-air deposits as well as intensive binding of CO_2 from flue gases by aqueous suspension of ash are expected.

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