REACTIVITY OF OIL SHALE ASHES IN THE BINDING OF SO$_2$

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The extensive use of fossil fuels in energy production causes serious pollution of atmosphere with SO$_2$, CO$_2$, NO$_x$, etc. In Estonia the electricity production is based mainly on the pulverized firing (PF) of low-grade local fuel – Estonian oil shale (EOS) which is characterized by a low calorific value (~9 MJ kg^{-1}) and a high content of mineral matter (65–70%) from which approximately 50% are carbonates. Since 2004, also two boilers based on circulating fluidized bed combustion (CFBC) of EOS are in exploitation.

The present study is focused on the comparative investigation of the efficiency of different ashes collected from different technological points of CFB and PF boilers as sorbents for SO$_2$. The influence of experimental temperature on the SO$_2$-binding characteristics of ashes as well as the possibilities of activation of ashes (grinding, hydration) were investigated. It was shown that the SO$_2$-binding capacity of initial ashes at 700°C and p(SO$_2$)=190 mm Hg was for CFBC ashes 24–30 mg and for PF ashes 10–23 mg SO$_2$ per 100 mg sample, the best binding capacities belonging to economizer ash (ECOA) and electrostatic precipitator ash from the 1st field (PESPA1f), respectively. However, during initial stage of binding the best results were obtained with air pre-heater ash (PHAA) and ESPA1f (both CFBC ashes). Grinding improved the SO$_2$-binding ability, being the most effective in the case of bottom ash (BA) from CFBC and cyclone ash (PCA) from PF – increase in binding capacity 2 and 2.3 times, respectively. As compared to initial CFBC ashes, the binding characteristics of PF ashes remained lower even after grinding. Hydration and previous calcination improved the binding characteristics only of PF ashes. Hereby, the SO$_2$-binding ability of CFBC ashes is better than of PF ashes and they are more promising sorbents for acidic gases, for example, for sulphur dioxide.

Keywords: circulating fluidized bed combustion, oil shale, pulverized firing, sulphur dioxide capture, waste ashes

Introduction

Using fossil fuels in energy production causes serious pollution of atmosphere with SO$_2$, CO$_2$, NO$_x$, VOC, etc. The electricity production in Estonia is concentrated into two large power plants – the Estonian and Baltic Power Plants and is based over 90% on the combustion of local solid fossil fuel – Estonian oil shale. Up to 2004 these power plants operated only on the high-temperature (1200–1400°C) combustion of pulverized EOS, but since 2004 also CFBC boilers have been in use. EOS is characterized by low calorific value (8-9 MJ kg^{-1}), moderate moisture content (10–13%) and high content of mineral part (65–70%) which consists mainly of carbonates (calcite, dolomite) and sandy-clay minerals, approximately, in equal proportion. The mechanism of the processes taking place during pulverized firing of EOS is generalized elsewhere [1, 2]. During combustion the inorganic part of OS undergoes a number of chemical transformations including decomposition of carbonates with formation of calcium and magnesium oxides. Partially, these oxides remain in the form of free oxides and, partially, take part in the formation of secondary minerals – mainly silicates with different compositions [1, 3].

Character and extent of these transformations determine the later behavior of the ashes in heterogeneous gas–solid interactions from which the SO$_2$-binding process has the highest importance. Different aspects of the use of coal fly ash as a sorbent in the binding of SO$_2$ are widely studied and discussed in the literature [4–9]. The reactivity of ashes as well as the mechanism of SO$_2$-binding process with ashes formed at PF of EOS has been studied in our earlier publications [10–13].

As compared to PF, the operating temperatures of CFBC (720–800°C) are considerably lower. Consequently, chemical and phase composition of CFBC ashes differ noticeably from these of PF ashes [14], therefore, differences in their chemical reactivity can also be expected.

Thus, the aim of the present work was the comparative investigation of the remaining efficiency of different ashes collected from different technological points of CFBC and PF boilers as sorbents for SO$_2$ capture.

Experimental

Materials

The ash samples were collected from different technological points of CFBC (BA – bottom ash, IXA – intrex ash, ECOA – economizer ash, PHAA – air

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pre-heater ash, ESPA1f and ESPA4f – electrostatic precipitator ash from the 1st and 4th field, respectively) and from PF boilers (PBA, PCA – cyclone ash and PESPA1f) at the Estonian Power Plant. As a reference sorbent, a limestone sample from Karinu deposit (Estonia) was used.

The main characteristics of the samples are presented in Tables 1 and 2, a detailed characterization has been given in earlier publications [14]. The ashes studied differed in their chemical (CaO^{free}=2.8–24.8%, MgO=8.3–15.2%, CaO=28.9–50.8%, S=1.3–7.8%, insoluble residue (I. R.) in aqua regia=8.9–42.5%), mineralogical and grain-size composition (d_{mean}= 23–197 µm) as well as in SSA (0.36–8.00 m^2 g^{-1}) (Table 1). The main mineral phases in the ashes were calcite, anhydrite, quartz, lime, periclase, and different silicates like illite-smectite, orthoclase, albite, melilite, merwinite, etc. (Table 2).

Methods

Samples were analyzed using chemical, grain-size, quantitative XRD, SEM and BET methods. XRD data was collected in powdered unoriented preparations with Dron-3M diffractometer using Ni-filtered Cu-Kα radiation. Digitally registered diffractograms were measured within the range of 2–50° 2θ, with 0.03° 2θ step sizes and 3 s counting time. The diffractograms were analyzed by code Siroquant [15], using full-profile Rietveld analysis [16]. For surface observations a scanning electron microscope Jeol JSM-8404 was used, specific surface area (SSA) data was determined by BET method with sorptometer KELVIN 1042.

Experiments in heterogeneous gas-solid system were carried out using thermogravimetric equipment (Q-derivatograph, MOM) under isothermal conditions. Temperatures of the experiments were 500, 600, 700 or 900°C, partial pressure of SO_2 190 mm Hg.

The samples (100±0.4 mg) were heated up to the test temperature in air at a heating rate of 20°C min^{-1} and the temperature was stabilized during 5 min. Then, the mixture of sulphur dioxide and dry air was led to the reaction chamber during 30 min with the flow rate of 270 mL min^{-1}. Thickness of sample layers in a multiplate Pt crucible was about 0.2–0.3 mm.

The ashes were activated by grinding (G) and grinding with subsequent hydrating (H+G). Grinding of ashes was carried out in one-ball vibration mill until the material passed through the 45 µm sieve. Hydration of previously ground ashes was carried out in porcelain pans by mixing during two minutes 5 g of sample with water, the mass of which exceeded 5 times the stoichiometric amount of water needed for slaking the free CaO in the samples. Then the samples were stored for 24 h in hermetically sealed pans, after which they were dried at 105°C for 1 h.

Three parameters were calculated to characterize the extent of gas-solid interactions: SO_2-binding capacity (BC; mg SO_2 bound by 100 mg of sample), SO_2-binding rate (W; mg SO_2 per mg sample min^{-1}), SO_2-binding efficiency, (BE, %) showing the extent of utilization of CaO and MgO contained in the sample.

Results and discussion

SO_2-binding capacity of the initial ashes at 700°C after 30 min contact between solid and gaseous phases was for CFBC ashes in the range of 24–30 mg and for PF ashes 10–23 mg SO_2 per 100 mg sample, the best binding capacities belonging to ECOA and PESPA1f, respectively. During the first two minutes of gas–solid contact, the best results among CFBC ashes were obtained with PHAA and ESPA1f which both bound 70% of the amount of SO_2 captured by the end of experiment and with PF ash PBA–58% (Fig. 1).

Table 1 Main characteristics of ashes

| Ash | Content/% | | | | | | | | d_{mean}/ µm | SSA/ m^2 g^{-1} | SSA, G/ m^2 g^{-1} |
	CaO_{total}	CaO_{free}	MgO_{total}	I.r.*	CO_2	S_{total}	$S_{sulphate}$	$S_{sulphide}$			
BA	49.39	12.48	9.25	8.85	15.14	4.53	4.32	0.10	197	2.06	4.77
IXA	47.59	18.87	13.65	13.25	1.23	7.76	7.70	0.02	95	2.61	4.16
ECOA	32.84	10.40	9.50	34.02	5.48	2.32	2.22	0	27	6.89	7.50
PHAA	35.17	12.26	10.77	29.33	4.30	3.31	3.27	0.0013	32	5.40	5.89
ESPA1f	29.52	8.45	8.33	42.45	4.60	1.71	1.71	0	25	8.00	8.63
ESPA4f	28.88	2.82	9.35	32.74	3.80	2.23	2.21	0	23	7.92	8.43
PBA	50.75	24.84	15.19	18.21	2.75	1.27	1.27	0	115	1.75	2.58
PCA	49.39	22.52	14.19	20.29	0.70	1.33	1.33	0	48	0.36	1.45
PESPA1f	36.08	13.56	11.26	26.05	1.16	2.74	2.74	0	24	0.61	0.82

*insoluble residue in aqua regia

Table 2 Mineral composition of ashes/mass%

Minerals	BA	IXA	ECOA	PHAA	ESPA1f	ESPA4f	BA, G*	IXA, G	ECOA,G	PHAA, G
Quartz, SiO$_2$	8.9	5.6	17.1	17.7	16.8	12.1	5.0	6.1	18.1	15.3
Orthoclase, KAlSi$_3$O$_8$	1.3	2.7	9.4	8.1	12.5	15.7	2.0	3.5	6.6	8.1
Albite, NaAlSi$_3$O$_8$	1.6	2.7	0	traces	0	0	0	0	0	0
Illite+Illite-Smectite Na, K$_x$(Al, Mg)2Si$_4$O$_{10}$ (OH)$_2$·H$_2$O	2.1	3.1	11.2	9.5	13.8	16.8	0	0	0	0
Belite, Ca$_2$SiO$_4$	4.6	7.3	5.8	6.2	5.3	7.5	17.7	18.9	18.5	19.4
Merwinite, Ca$_3$Mg(SiO$_4$)$_2$	4.7	5.2	3.0	3.0	3.7	4.2	6.4	5.2	14.9	11.1
Tricalcium aluminate 3CaO·Al$_2$O$_3$	1.2	1.4	2.0	2.2	2.3	3.3	3.1	1.9	6.6	3.1
Dolomite, CaMg(CO$_3$)$_2$	3.9	0	0	0	0	0	0	0	0	0
Periclase, MgO	4.2	7.0	3.8	4.4	2.7	3.3	7.1	9.6	5.8	5.1
Melilite, (Ca, Na)$_2$(Mg, Al)(Si, Al)$_3$O$_7$	1.0	3.6	1.6	1.5	1.2	2.6	4.2	5.6	7.5	9.4
Anhydrite, CaSO$_4$	19.7	29.9	11.1	14.3	9.5	11.3	22.6	31.1	10.2	19.0
Gypsum, CaSO$_4$·2H$_2$O	0	0.8	0.5	0	0	0	0	0	0	0
Lime, CaO	11.4	19.9	13.3	14.9	10.8	3.2	21.5	14.2	1.2	2.2
Calcite, CaCO$_3$	34.8	4.0	15.4	12.6	13.5	13.6	0	0	0	0
Portlandite, Ca(OH)$_2$	1.7	2.1	0.7	0.8	0	0.9	0	0	0	0
Hematite, Fe$_2$O$_3$	1.1	2.1	3.6	2.7	4.3	3.9	0.7	1.2	3.5	2.5
Pseudowollastonite CaSiO$_3$	1.4	1.8	1.9	2.1	3.6	2.2	0	1.3	6.8	3.6

Table 2 Continued

Minerals	BA, G+H**	IXA, G+H	ECOA, G+H	ESPA1f, G+H	PBA	PCA	PESPA1f	PBA,G	PCA, G+H
Quartz, SiO_2	4.3	4.5	15.9	15.8	3.1	3.3	12.0	2.2	3.2
Orthoclase, $KAlSi_3O_8$	3.0	3.3	12.4	16.9	6.6	1.7	3.8	2.2	4.1
Albite, $NaAlSi_3O_8$	0	0	0	0	0	0	0	0	0
Illite+Illite-Smectite Na, $K_x(Al, Mg)2Si_4O_{10}(OH)_2 \cdot H_2O$	0	4.2	0	traces	0	6.1	0	0	0
Belite, Ca_2SiO_4	11.5	11.5	18.7	15.5	13.5	15.9	12.3	17.0	16.5
Merwinite, $Ca_3Mg(SiO_4)_2$	3.6	4.7	6.3	5.0	9.4	13.2	6.5	8.7	13.3
Tricalcium aluminate $3CaO \cdot Al_2O_3$	traces	0	0	traces	2.3	2.2	2.8	1.7	traces
Dolomite, $CaMg(CO_3)_2$	0	0	0	0	0	0	0	0	0
Periclase, MgO	5.1	6.7	4.1	3.4	7.9	8.7	8.5	8.9	6.8
Melilite, $(Ca, Na)_2(Mg, Al)(Si, Al)_3O_7$	2.7	3.8	3.1	1.9	17.8	5.8	3.3	16.2	4.6
Anhydrite, $CaSO_4$	20.6	30.9	11.0	11.8	5.4	5.4	16.8	6.3	5.8
Gypsum, $CaSO_4 \cdot 2H_2O$	0	0	0	0	0	0	0	0	0
Lime, CaO	11.2	14.1	0.7	1.0	26.5	29.3	28.1	29.8	33.2
Calcite, $CaCO_3$	26.2	12.3	16.0	14.4	5.7	2.5	2.0	0	4.2
Portlandite, $Ca(OH)_2$	0	0	0	0	0	3.1	1.0	0	0
Hematite, Fe_2O_3	traces	1.5	3.2	4.1	0.9	1.1	1.6	0.8	1.7
Pseudowollastonite $CaSiO_3$	0.8	0.9	3.0	4.1	0.9	1.6	0.8	1.4	2.3

* ground ashes, thermally treated at 900°C 1 h
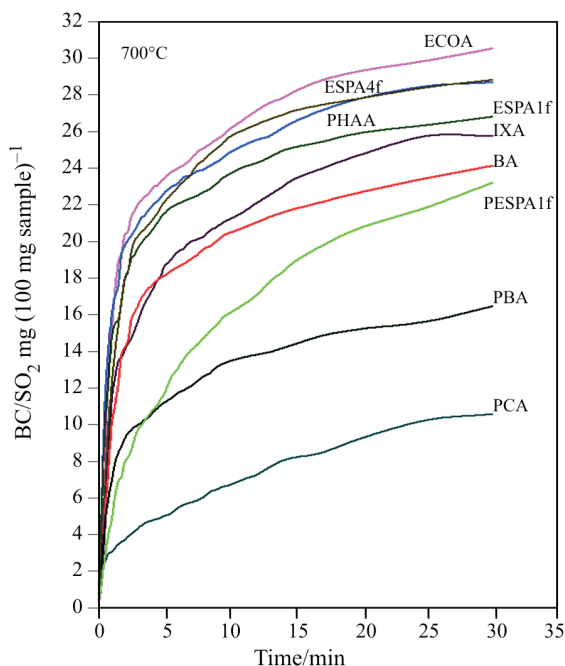** ground and subsequently hydrated ashes, thermally treated at 700°C 0.5 h

Fig. 1 SO_2-binding capacity (BC) of initial ashes at 700°C

During the initial stage of contact (the first 30 s) the most active were ESPA1f and PHAA with the average SO_2 binding rate 0.23–0.28 mg SO_2 per mg sample min^{-1}. The binding rate for ECOA was 0.18 and for BA, IXA and ESPA4f 0.11-0.13 mg SO_2 per mg sample min^{-1}. The most active among PF ashes was PBA with the average value of W 0.095 mg SO_2 per mg sample min^{-1}, for PCA and PEFA1f it was 0.045 and 0.05 mg SO_2 per mg sample min^{-1}, respectively (Fig. 2).

BE values after 30 min of contact indicated the highest utilization of CaO and MgO in the binding of SO_2 by ESPA4f – 74%. BE for ECOA and ESPA1f was 64–66%, for PHAA 57% and the lowest BE values were of BA and IXA – 37–40%. Binding efficiencies of PF ashes were like other indicators much lower than these of CFBC ashes being the highest for PESPA1f (46%). BE of PBA and PCA was 24 and 15%, respectively (Fig. 3).

The data on PF ashes correspond well to the results obtained in our earlier research [11, 12]. The noticeable differences in the SO_2-binding ability of CFBC and PF ashes can be explained by the differences in their chemical and fractional composition as well as in physical and chemical properties of the ashes. First of all, the better binding parameters of CFBC ashes can be associated with higher activity of free CaO and higher specific surface area of CFBC ashes formed at considerably lower temperatures as compared to PF ashes. Thus, the negative influence of coarse fractional composition of the samples and, respectively, the small SSA, for example, of BA and IXA, are compensated by higher level of the content of free CaO in these ashes which is the main binder of SO_2. In contrary, ESPA ashes are characterized by fine fractional composition (and high SSA), but by low content of free CaO. ECOA and PHAA are somewhere on the mean level by these parameters. PBA and PCA, both characterized by coarse fractional composition and quite high content of free CaO (~23–25%), differ noticeably in SSA which is five times higher for
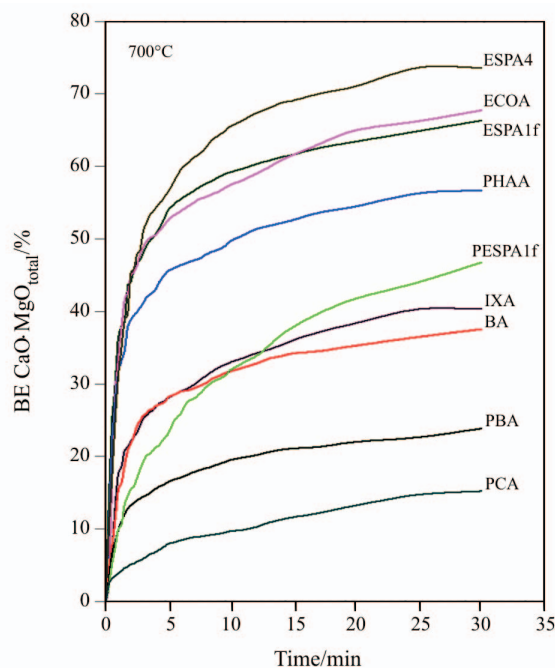

Fig. 2 SO_2-binding rate (W) of initial ashes at 700°C

Fig. 3 SO_2-binding efficiency (BE) per total CaO·MgO of initial ashes at 700°C

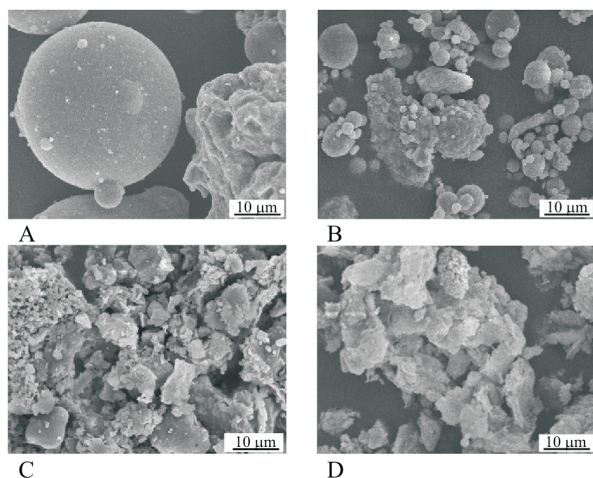**Fig. 4** SEM pictures of PF and CFBC ashes, magnification ×2000. A – PCA, B – PESPA1f, C – ECOA, D – ESPA1f

PBA – 1.75 and 0.36 $m^2 g^{-1}$, respectively. PESPA1f is characterized by fine fractional composition and low content of free CaO and by low SSA (Table 1). SEM study of ash samples (Fig. 4) confirmed the formation of glassy phases on the surface of PF ashes, especially on PCA and PESPA1f at high-temperature combustion which decreased their SSA and hindered the diffusion of SO_2 into the particles reducing at that the binding ability of these samples [13].

Preliminary grinding of ashes increased the SO_2-binding parameters for all the ashes studied, especially, for these characterized by coarse fractional composition like BA, IXA and PBA or PF ashes characterized by the presence of glassy phases on the surface of particles like PCA. Thus, at 700°C, grinding increased the BC and BE values for BA and PCA 2.2 times, for IXA and PBA 60–75%, for ECOA and PHAA 20–30%, for ESPA1f and PESPA1f about 15–20%, but for ESP4f there was no observable changes in BC (Fig. 5). Among ground CFBC ashes the highest BC values were of BA and

IXA – 42–49 mg SO_2 per 100 mg sample, the highest BE belonged to ECOA – 81.5%. Among PF ashes the highest BC value was of PBA – 33 mg SO_2 per 100 mg sample and BE of PEFA1f – 50.6%. These results correlated well with the increase in SSA of the samples during grinding – for PCA 4.4 times (from 0.36 to 1.45 $m^2 g^{-1}$, for BA, IXA and PBA 1.5–2.3 times, for the other ashes about 1.1 times, except in the case of ESPA4f and PESPA1f for which even a small decrease in SSA was observed (Table 1). Comparing the binding parameters of ashes and Karinu limestone, the BC values of the most active ash – BA were only 1.2 times lower than BC of Karinu limestone (Fig. 5). Essential increase in the average SO_2 binding rate during the initial period of contact was fixed being among CFBC ashes the highest for BA and IXA – from 0.11–0.12 to 0.20–0.21 mg SO_2 per mg sample min^{-1} (1.8 times). For PF ashes the average SO_2 binding rate increased about 1.4–2.6 times being the highest for PCA.

Surprisingly, the hydration of CFBC ashes had a more or less negative influence on the SO_2-binding ability of initial as well as of previously ground samples, but the binding ability of PF ashes was improved as described in [10]. Thus, BC of previously ground CFBC ashes decreased due to additional hydration of the samples by 16–29%, the decrease was the most remarkable for PHAA and BA – 29 and 20%, respectively (Fig. 5). For PF ashes the additional hydration of samples increased their binding ability, the highest increase was fixed for PCA – 35% or from 23 to 31 mg SO_2 per 100 mg sample (Fig. 5). A significant decrease in SSA of ground and subsequently hydrated CFBC ashes during thermal treatment at 700°C during 30 min was observed – from 9.5–12.7 to 5.5-7.7 $m^2 g^{-1}$. SSA of PCA decreased from 5.0 to 3.4 $m^2 g^{-1}$.

According to the results of XRD-analysis it could be explained with the formation of new formed
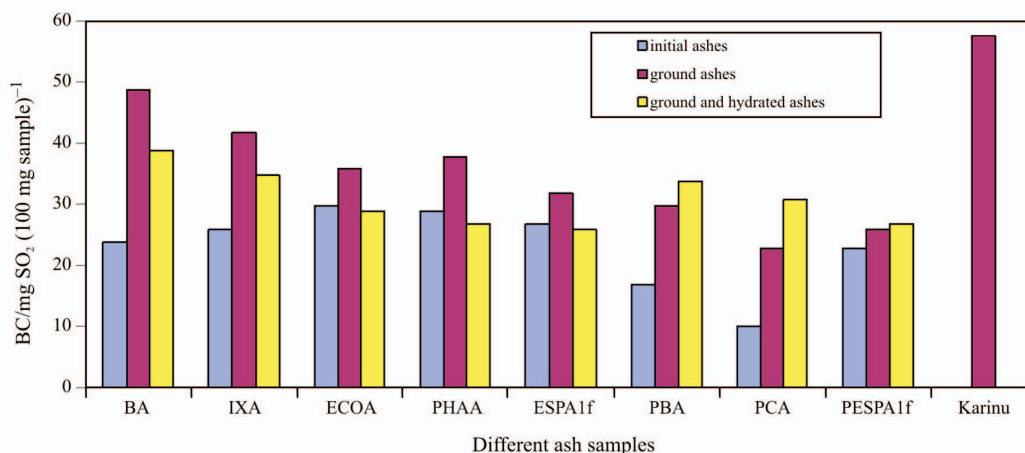

Fig. 5 SO_2-binding capacity (BC) of differently treated ashes at 700°C

Ca, Mg-oxides during heating of CFBC ashes previously hydrated up to 700°C. These new formed oxides being more active compared with the initial ones participated in solid state reactions with the other minerals like albite, illite-smectite and quartz contained in the ashes forming new secondary phases – belite, merwinite, melilite and pseudowollastonite (Table 2). In the siliceous part of PF at that only light changes were observed.

The influence of temperature on the SO$_2$-binding ability of ashes was studied using initial as well as previously ground samples. The SO$_2$-binding ability improved noticeably with increase in the temperature from 500 to 700°C (2.5–5 times) for all the samples studied. However, at 900°C the additional improvement, except for initial BA, was observed for PF ashes only. Thus, BC for initial BA increased by 29% and for PBA by

37% as compared to BC at 700°C, but for the other initial CFBC ashes the SO$_2$ binding parameters at 900°C were on the level of these at 700°C or even a slight decrease (3–5%) was noticed (Fig. 6). More significant decrease in the SO$_2$-binding ability was fixed for the ground CFBC ashes which were additionally pre-heated for calcination up to 900°C and binding carried out at 900 or 700°C (Figs 6 and 7). BC of CFBC ashes decreased depending on the origin of ash and experimental temperature by 3–20% as compared to BC at 700°C without previous calcination at 900°C (Fig. 7).

It can be presumed that during pre-heating of the ashes up to 900°C the decomposition of remaining carbonates with formation of additional amount of free Ca- and Mg-oxides takes place the amount being the higher the content of carbonates in the ashes is (like in the case of BA) (Table 1). In PF ashes these
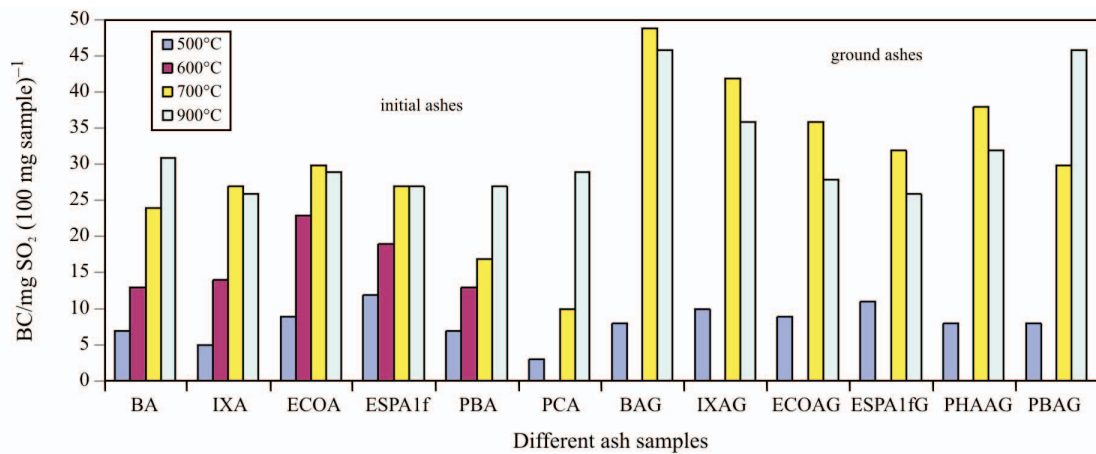

Fig. 6 SO$_2$-binding capacity (BC) of initial and ground (G) ashes at different temperatures

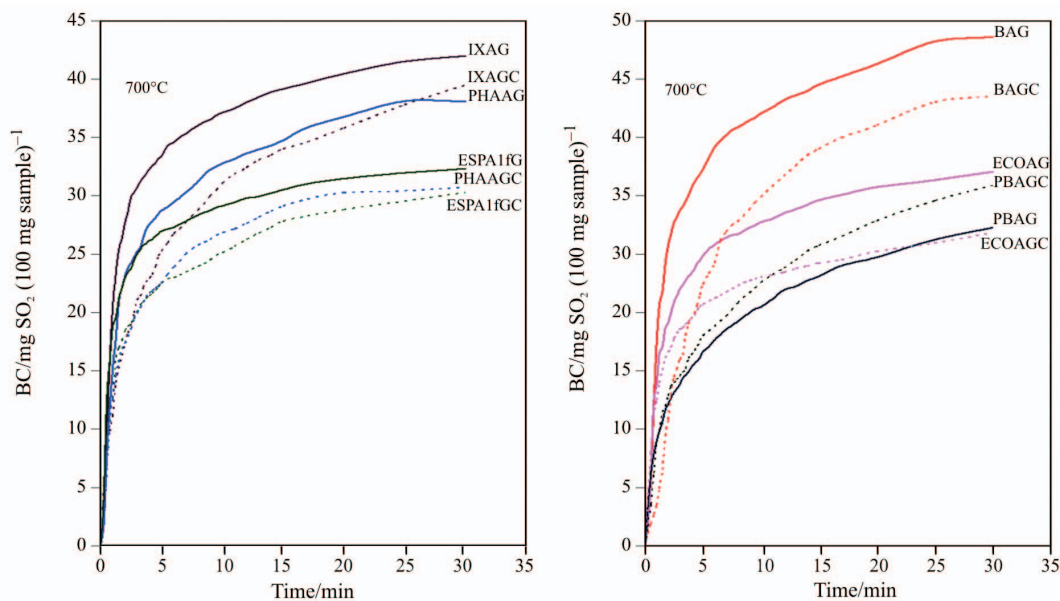**Fig. 7** SO$_2$ binding capacity (BC) of ground ashes with (C) and without previous calcination

new formed oxides are preserved in free form as the solid–solid reaction rates in PF ashes due to limited contact-surfaces are low which is caused by existing glassy phase [14]. So, the SO_2-binding ability of PF ashes remains higher. In the case of CFBC ashes that is also proved by the results of XRD analyses the free Ca- and Mg-oxides contained and/or formed during high-temperature decarbonisation, like oxides formed at thermal treatment of ashes previously hydrated, participate in solid state reactions with the other minerals. It is indicated by the decrease in the content of albite, illite-smectite and quartz contained in the ashes followed by the increase in the content of belite, merwinite, melilite and pseudowollastonite (Table 2). Apparently, the solid state reactions proceed more intensively with finer materials resulting in the decrease in SO_2-binding ability that is more severe for ground than for initial CFBC ashes (Figs 6 and 7). In the case of coarse initial BA, the high content of carbonates and formation of additional amount of free Ca- and Mg-oxides during decomposition eliminated the negative effect of solid state reactions on SO_2-binding of these oxides, but for ground BA the negative effect was observable.

In addition, a decrease in SSA, especially, of CFBC ashes during high-temperature decarbonisation of them was followed. Thus, there was observed only a small decrease in SSA of initial BA – from 2.1 to 1.9 m^2 g^{-1}, but for ground BA the decrease was more significant – from 4.8 to 3.3 m^2 g^{-1}. For the other CFBC ashes the changes in SSA were even more significant, for example, for initial ECOA from 6.9 to 2.7 m^2 g^{-1} and for ground ECOA from 7.5 to 4.8 m^2 g^{-1}.

Conclusions

SO_2-binding capacities of the initial CFBC ashes were similar, the differences were more noticeable with PF ashes. Differences in the grain-composition of CFBC ashes are compensated by differences in their chemical and mineralogical composition as well as in their physical and chemical properties.

Grinding increased noticeably (1.6–2.2 times) the SO_2-binding capacities of coarser ashes BA, IXA, PBA and PCA. Hydration improved the SO_2-binding ability only of PF ashes.

Increase in temperature from 500 to 700°C improved the SO_2-binding capacity 2.5–5 times, however, over 900°C mainly of PF ashes, because the Ca- and Mg-oxides formed at higher temperatures at PF are preserved in free form. During heat-up Ca- and Mg-oxides in CFBC ashes participate in solid state reactions with other minerals (albite, illite-smectite, quartz) forming new secondary phases – belite,

merwinite, melilite and pseudowollastonite. These solid state reactions proceed more intensively with finer materials decreasing SO_2-binding ability, especially, of ground CFBC ashes. A significant decrease in SSA of the samples at high-temperature decarbonisation was observed.

Considering the better SO_2-binding characteristics of CFBC ashes, they could be more promising sorbents for SO_2 in dry flue gas desulphurization processes, especially, after previous grinding. However, grinding with subsequent hydration increased the SO_2-binding ability of some pulverized firing ashes like PBA and PCA almost to the level CFBC ashes.

Acknowledgements

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