CO$_2$ and SO$_2$ uptake by oil shale ashes

Effect of pre-treatment on kinetics

Andres Trikkel · Merli Keelmann · Tiit Kaljuvee · Rein Kuusik

Abstract In the present research, CO$_2$ and SO$_2$ binding ability of different oil shale ashes and the effect of pre-treatment (grinding, preceding calcination) of these ashes on their binding properties and kinetics was studied using thermogravimetric, SEM, X-ray, and energy dispersive X-ray analysis methods. It was shown that at 700 °C, 0.03–0.28 mmol of CO$_2$ or 0.16–0.47 mmol of SO$_2$ was bound by 100 mg of ash in 30 min. Pre-treatment conditions influenced remarkably binding parameters. Grinding decreased CO$_2$ binding capacities, but enhanced SO$_2$ binding in the case of fluidized bed ashes. Grinding of pulverized firing ashes increased binding parameters with both gases. Calcination at higher temperatures decreased binding parameters of both types of ashes with both gases studied. Clarification of this phenomenon was given. Kinetic analysis of the binding process was carried out, mechanism of the reactions and respective kinetic constants were determined. It was shown that the binding process with both gases was controlled by diffusion. Activation energies in the temperature interval of 500–700 °C for CO$_2$ binding with circulating fluidized bed combustion ashes were in the range of 48–82 kJ mol^{-1}, for SO$_2$ binding 43–107 kJ mol^{-1}. The effect of pre-treatment on the kinetic parameters was estimated.

Keywords CFBC ashes · CO$_2$ capture · Kinetics · Oil shale · SO$_2$ capture

A. Trikkel (✉) · M. Keelmann · T. Kaljuvee · R. Kuusik
Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate 5, 19086 Tallinn, Estonia
e-mail: andres.trikkel@ttu.ee
URL: http://www.kl.ttu.ee/eng/

Introduction

Circulating fluidized bed combustion (CFBC) is becoming a common technology for power production in Estonia, whose energy sector is predominantly based on combustion of a local low-grade fossil fuel—Estonian oil shale. Due to the high content of mineral matter in oil shale and its carbonaceous origin, combustion is related to the formation of alkaline ashes (about 6 million tons annually, content of free CaO 8–30% and MgO 8–15%), which could be utilized as sorbents for abatement of CO$_2$ and/or SO$_2$ emissions.

The processes taking place during pulverized firing (PF) of oil shale have been analyzed in detail by Ots [1]. During combustion, the inorganic part of oil shale undergoes a number of chemical transformations including decomposition of carbonates with the 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. As compared to PF, the operating temperatures of CFBC are considerably lower (720–800 °C). Consequently, chemical and phase composition of CFBC and PF ashes differ noticeably [2], therefore, also their binding abilities in the reactions with acidic gases vary to a great extent [3, 4].

Data about CO$_2$ uptake by CFBC ashes, especially, oil shale ashes are quite limited [3, 5–8], more information can be found about limestone decarbonization and recarbonization [9–13]. At lower temperatures, CO$_2$ is bound by calcium oxide with the formation of calcium carbonate. However, this reaction is far from reversibility as described by Abanades [9]. The process is initially controlled by chemical kinetics, but the end of this fast stage is determined already by the formation of 0.1 μm of product layer [9, 12]. The rates of carbonation are rapid at low conversion levels, with the initial rates depending notably on

temperature in the range of 550–725 °C. At higher temperatures almost up to the ultimate conversion levels, carbonation is controlled by the chemical reaction in combination with less effect of diffusion limitation. Conversion levels at which diffusion becomes rate limiting are lowered as temperature decreases [10]. Additives in limestone—belite, aluminum silicates, and aluminum ferrates can react with CaO and up to 50% of the capture capacity might be lost in the fluidized bed boilers [14]. The reaction between CO_2 and bottom ash from coal-fired CFB boiler starts at 640–645 °C and achieves its maximum rate at 725 °C [6]. CaO conversion level remains in between 9 and 23%. It has been shown that grinding enhances CO_2 uptake by oil shale PF ash up to 40% [8].

SO_2 uptake by different types of waste ashes has been widely studied and discussed in the literature [4, 15–18], however, more attention has been paid to limestone and dolomite as sorbents for SO_2 [19–22]. The product of the reaction of SO_2 and CaO above 800 °C is mainly $CaSO_4$, at lower temperatures also CaS and $CaSO_3$ can be present in small quantities. Diffusion of SO_2 through the formed $CaSO_4$ layer has been reported to be the rate limiting stage of this process [20, 23]. At CFBC temperatures, MgO does not take part in CO_2 uptake, although it has a certain role in SO_2 capture forming $CaMg_3(SO_4)_4$ and β-$MgSO_4$ as clarified in [24].

Although CO_2 and SO_2 binding processes proceed according to thermodynamic calculations [5] in different temperature regions, their comparative study and estimation of the effect of temperature can give information for process design, for example, for determining decarbonization–recarbonization conditions. Grinding is a method often used for enhancing heterogeneous sorption processes.

The aim of the present research was to study comparatively CO_2 and SO_2 uptake by different oil shale ashes formed at CFBC in comparison with some PF ashes and to clarify the effect of pre-treatment (grinding, calcination temperature) on the process and binding kinetics.

Experimental

The ash samples used were collected from different points of the ash separation systems of CFBC and PF boilers at Estonian Thermal Power Plant. The CFBC ashes studied were bottom ash (BA), intrex ash (IXA), economizer ash (ECOA), air pre-heater ash (APHA), and electrostatic precipitator ash from fields 1 and 4 (EPA1 and EPA4). The PF ashes used were bottom ash (PBA), cyclone ash (PCA), and electrostatic precipitator ash from field 1 (PEPA1). The chemical composition and physical properties of these ashes are presented in Table 1 and discussed in more detail in article of Kuusik et al. [2].

The experiments for testing the reactivity of ashes with CO_2 and SO_2 in heterogeneous system gas–solid were performed with thermogravimetric equipment (MOM and Setaram Labsys) under isothermal conditions in the flow of air–gas mixture 270 mL min^{-1} with the partial pressure of CO_2 0.15 or SO_2 0.25 atm. Multiplate Pt crucibles were used to diminish diffusion in sample-bed, thickness of the sample layer being about 0.2 mm. Mass of the samples was 100 ± 2 mg. Relatively high flow rate was selected to guarantee sufficient amount of reactive gas and minimize the effect of external diffusion at the beginning of the experiment. In the experiments with CO_2, the samples were heated up to the experiment temperature in air with the heating rate of 10 K min^{-1} and kept until most part of the carbonates present in the sample was decomposed (decarbonization duration about 10 min). After that the gas mixture was led into the furnace, duration of the experiments was 30 min. At this partial pressure of CO_2 $CaCO_3$ is not stable above 740–750 °C, so the isothermal binding

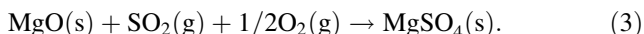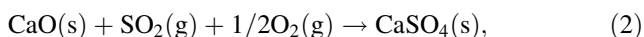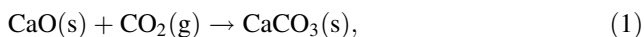**Table 1** Characterization of the ash samples and their SO_2 and CO_2 binding properties (BC, X)

Sample	Content/%							SSA/m^2 g^{-1}		d_{mean}/μm	SO$_2$ binding	CO$_2$ binding
	CaO^t	CaO^f	CaO^{fc}	MgO	CO$_2$	I.r.	S^{sulfate}	Initial	Ground		BC/X	BC/X
BA	49.4	12.5	31.7	9.3	15.1	8.9	4.3	2.1	4.8	197.0	25.9/50.4	12.1/74.2
IXA	47.6	18.9	20.4	13.7	1.2	13.3	7.7	2.6	4.2	95.0	26.1/57.7	9.5/42.4
ECOA	32.8	10.4	17.4	9.5	5.5	34.0	2.2	6.9	7.5	27.0	30.3/86.4	6.0/43.3
APHA	35.2	12.3	17.7	10.8	4.3	29.3	3.3	5.4	5.9	32.0	25.2/97.0	7.5/33.8
EPA1	29.5	8.5	14.3	8.3	4.6	42.5	1.7	8.0	8.6	25.0	27.1/91.3	5.0/32.8
EPA4	28.9	2.8	7.7	9.4	3.8	32.7	2.2	7.9	8.4	23.0	28.5/120	1.3/19.2
PBA	50.8	24.8	28.3	15.2	2.8	18.2	1.3	1.8	2.6	114.0	16.1/28.4	12.5/51.8
PCA	49.4	22.5	23.4	14.2	0.7	20.3	1.3	0.4	1.5	48.0	10.4/21.0	4.7/22.1
PEPA1	36.1	13.6	15.0	11.4	1.2	26.1	2.7	0.6	1.6	24.0	25.0/70.4	1.5/8.7

CaO^t—total CaO, CaO^f—free CaO, CaO^{fc}—free CaO and CaO from CaCO$_3$, I.r.—insoluble in *aqua regia* residue, d_{mean}—mean particle diameter

experiments were performed in the temperature interval of 500–700 °C, mainly, at 700 °C. In the experiments with SO$_2$, the samples were heated up to experiment temperature (500–900 °C) in air and after stabilizing the temperature, the air–gas mixture was led into the furnace.

To study the effect of grinding, the initial samples were ground in a one-ball vibrational mill until most of the sample (at least 95%) passed the 45 μm sieve. In some experiments with CO$_2$, the samples were decarbonized prior to binding at higher temperature (900 °C, marked as *dc* 900 °C) to achieve complete decomposition of carbonates and to estimate the effect of decarbonization temperature on the binding properties. After that the samples were cooled quickly to 700 °C (or any other experiment temperature) to perform isothermal binding.

The main parameters used to characterize the gas–solid interaction were the CO$_2$ or SO$_2$ binding capacity BC (mass of CO$_2$ or SO$_2$ bound by 100 mg of sample, mg (100 mg)$^{-1}$) and CaO conversion level X per free and formed during decarbonization stage calcium oxide—X(CaO^{fc}). In the case of SO$_2$, the conversion level X was calculated per both oxides—MgO and CaO^{fc}. The calculations of X were made on the basis of the following summary binding reactions:

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

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

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

Results and discussion

The main binder of CO$_2$ in the ashes is free CaO, in the case of SO$_2$ also MgO can take part in binding [24]. Pulverized firing ashes PBA and PCA are characterized by a quite high content of free CaO (23–25%), but they differ noticeably in their specific surface area SSA (Table 1), besides, their SSA is lower (0.4–1.8 m^2 g^{-1}) as compared to CFBC ashes (2.1–8.0 m^2 g^{-1}). Generally, PF ashes have higher free CaO content as compared to CFBC ashes due to higher combustion temperature and almost full decomposition of carbonates. The negative influence of coarser fractional composition of BA and IXA among CFBC ashes and, respectively, the lower level of SSA, should be compensated by higher content of CaO^{fc} (20.4–31.7%).

The CO$_2$ capture capacity BC of the ashes at 700 °C was considerably lower as compared to SO$_2$ binding capacity, respectively, 1.3–12.5 mg (0.03–0.28 mmol) of CO$_2$ and 10–30 mg (0.16–0.47 mmol) of SO$_2$ per 100 mg of ash in 30 min (Table 1). It was found that CO$_2$ binding capacities were determined mainly by CaO^{fc} content in the ashes. CFBC ashes showed higher CaO conversion levels (19–74% with CO$_2$) as compared to PF ones (9–52%) and in the

case of SO$_2$ 50–91% for CFBC ashes and 21–28% for PF ashes. The highest BC values with CO$_2$ were calculated for the bottom ashes BA and PBA, but also IXA, all having high CaO^{fc} content. BA differs from the other ashes in a quite high CO$_2$ content (residual carbonates), though its CaO^{fc} content is similar to PBA. PBA has also higher CO$_2$ content as compared to other PF ashes. During decarbonization stage, these carbonates decompose and create additional porosity that can reduce the negative effect of their coarser fractional composition. With SO$_2$, the BC values were close in the case of CFBC ashes. The best results were obtained with the ashes having higher SSA values. PF ashes having low values of SSA bound less SO$_2$. With CO$_2$, there was no evident effect of SSA on BC—even a slight decrease in BC could be followed with the increase in SSA, especially, in the case of CFBC ashes.

Effect of pre-treatment on binding capacity

To study the effect of grinding on CO$_2$ and SO$_2$ uptake, some of the samples were ground to particle size <45 μm. Grinding increased SSA noticeably for BA, IXA, PCA, and PBA (1.6–4 times). For the other ashes, the increase was about 10%.

The experiments showed that grinding decreased CO$_2$ binding capacity of all the CFBC ashes studied (Fig. 1). Differently, capture capacity of PF ashes PBA and PCA increased in the result of grinding—1.3 and 2.4 times, respectively, which is in correlation with the increase in their SSA (Table 1).
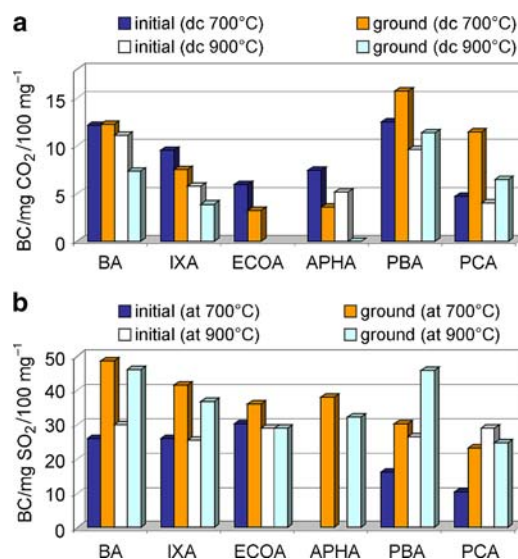
Fig. 1 Effect of grinding and decarbonization or experiment temperature on the CO$_2$ (**a**) and SO$_2$ (**b**) binding capacities of different ashes

With SO_2, grinding increased BC of both types of ashes. The increase was more visible in the case of the samples having coarser fractional composition (BA, IXA) and PF ashes.

The experiments also showed that decarbonization temperature had a noticeable effect on CO_2 uptake (Fig. 1a). It was found that decarbonization at 900 °C decreased BC of the CFBC ashes 1.3–1.4 times. When the ground samples were used in these experiments, the decrease was even more severe—2.1 to 5.5 times. At that, APHA lost its CO_2 binding ability at all.

In the case of SO_2, some binding experiments were carried out at 900 °C. Also here it can be seen (Fig. 1b) that, especially, the ground CFBC ash samples bound less SO_2 at 900 °C than at 700 °C. When PF ash samples were used the BC values were higher at 900 °C.

So, increasing the temperature can reduce binding capacities of the ashes, the effect is more visible in the case of ground CFBC ashes and, especially, in the reaction with CO_2.

Kinetics of binding reactions

Kinetic curves of CO_2 and SO_2 binding of BA are presented on Fig. 2. Both processes start with higher rates after which there is a noticeable slow-down. Pre-treatment affects processes differently. In the case of CO_2 binding, the ground sample had an initial rate comparable to the untreated sample, but the slow-down took place at a lower BC value. The samples treated at 900 °C had much lower initial binding rates. In contrary, in the case of SO_2, the untreated BA sample had the lowest initial binding rate, but the ground sample a noticeably higher rate. In 2 min, 50–60% of the final BC value was gained. In the case of CO_2, this percentage decreased when the ground samples were used, in the case of SO_2 it increased.

In the present research, reaction mechanisms were analyzed on the basis of different well-known reaction mechanisms presented, e.g., in the article of Reich and Stivala [25], which can be used to analyze both isothermal and non-isothermal processes as described, for example, in [26]. However, analyzing isothermal data can give better results in determining reaction mechanism. It was found that the overall process is controlled by CO_2 or SO_2 intra-particle diffusion (mechanism D3).

D3: Three-dimensional diffusion, spherical symmetry

$$\left[1 - (1 - X)^{1/3}\right]^2 = k\tau, \tag{4}$$

where k is the rate constant (min^{-1}) and τ the time (min).

In the case of decarbonized at 700 °C ash samples and with CO_2, a short kinetically controlled initial stage could be differentiated (mechanism F1).
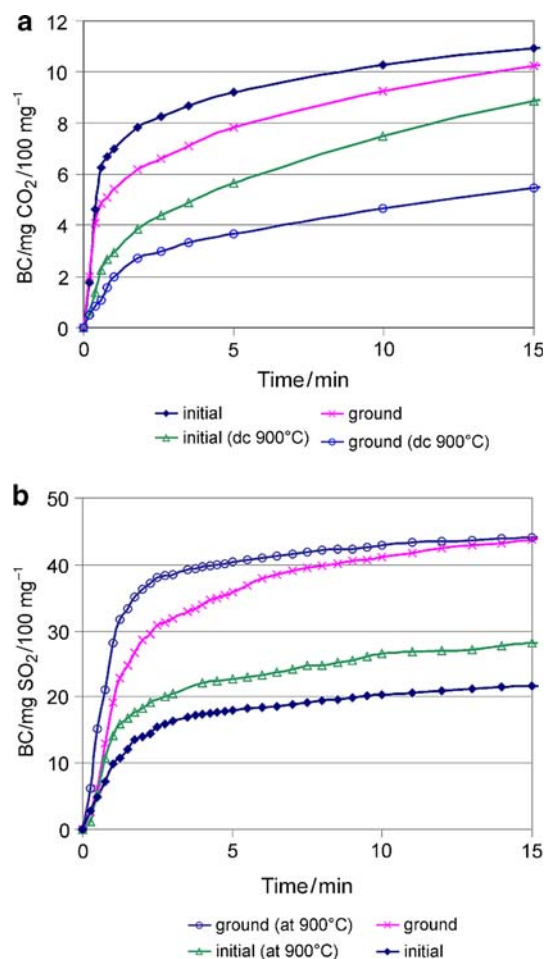
Fig. 2 Kinetic curves of CO_2 (**a**) and SO_2 (**b**) binding with BA

F1: First order kinetics, random nucleation

$$-\ln(1 - X) = k\tau \tag{5}$$

having somewhat lower activation energy (E_A) in the case of CFBC ashes. This stage could not be distinguished for the samples decarbonized at 900 °C and not in the case of SO_2 binding. However, also in the case of SO_2, a faster initial stage could be differentiated on the kinetic curves (Fig. 2b) lasting 1.5–2.5 min that indicates to the certain role of chemical kinetics during this stage.

The kinetic parameters found are presented in Table 2. Activation energies of CFBC ashes in the temperature interval of 500–700 °C were for CO_2 binding 48–82 kJ mol^{-1} and for SO_2 binding 72–107 kJ mol^{-1}. Activation energies for CO_2 binding by coal fly ash that have been reported in literature [6] were in the range of 87–165 kJ mol^{-1} and for decarbonized limestone 30 kJ mol^{-1} [14], so, oil shale CFBC ashes can be recarbonized a bit more easily as compared to coal fly ash. Activation energies for SO_2 binding by CFBC ashes were slightly higher as compared to literature data on different CaO based sorbents and

Table 2 Rate constants and activation energies of binding reactions

Sample	D3, overall process		F1, initial stage
	k at 700 °C/min^{-1}	E_A/ kJ mol^{-1} 500–700 °C	E_A/kJ mol^{-1} 500–700 °C
CO$_2$ binding			
BA initial	$9 \cdot 10^{-4}$	47.7	33.8
BA ground	$8 \cdot 10^{-4}$	101	44.0
BA ground (dc 900 °C)	$4 \cdot 10^{-4}$	50.4	–
APHA initial	$1 \cdot 10^{-3}$	82.3	48.1
APHA ground	$3 \cdot 10^{-4}$	112	49.0
PBA initial	$1 \cdot 10^{-3}$	23.2	43.6
PBA ground	$3 \cdot 10^{-3}$	50.2	47.8
PBA ground (dc 900 °C)	$1 \cdot 10^{-3}$	60.4	–

Sample	D3, overall process		
	k at 700 °C/min^{-1}	k at 900 °C/min^{-1}	E_A/kJ mol^{-1} 500–700 °C
SO$_2$ binding			
BA initial	$2 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	71.9
BA ground	$1 \cdot 10^{-3}$	$7 \cdot 10^{-4}$	110
IXA initial	$3 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	107
IXA ground	$9 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	97.1
ECOA initial	$3 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	73.5
ECOA ground	$5 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	87.1
APHA ground	$6 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	106
EPA1 initial	$2 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	43.2
EPA1 ground	$4 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	72.8
PBA initial	$8 \cdot 10^{-5}$	$3 \cdot 10^{-4}$	82.1
PBA ground	$5 \cdot 10^{-4}$	$9 \cdot 10^{-4}$	124

pure CaO or Ca(OH)$_2$ [15, 20, 27, 28]. Initial stage of the binding processes having lower activation energy has been reported also by other authors [6, 27, 28].

Grinding of the samples generally increased E_A values. Increase in decarbonization (CO$_2$ binding) or experiment (SO$_2$ binding) temperature decreased rate constants of the binding reaction, the effect was more severe in the case of CO$_2$. With SO$_2$, grinding increased the values of rate constants. In the case of CO$_2$ grinding decreased the values of rate constants for CFBC ashes, especially, when the ground samples had been decarbonized at 900 °C.

Effect of pre-treatment on ash structure and phase composition

To explain the effect of pre-treatment, some ash samples were heated in an electric tube furnace at different

Table 3 Effect of decarbonization temperature on SSA (m^2 g^{-1})

| Sample	Initial	dc 700 °C	dc 900 °C	dc 1,100 °C
BA	4.7	5.1	2.4	0.7
IXA	4.3	4.7	2.3	0.5
APHA	5.8	5.5	2.4	0.6
PBA	2.9	4.1	3.2	0.6
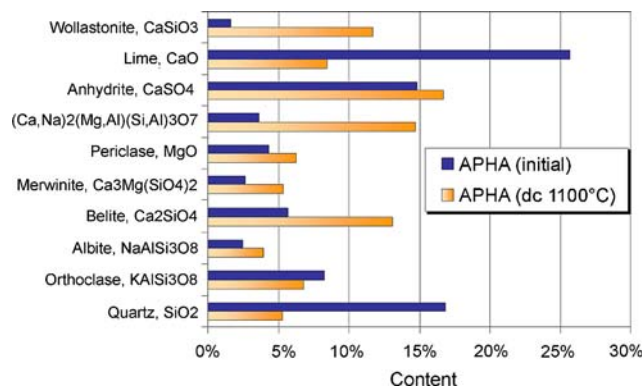
Fig. 3 Changes in phase composition of APHA at heating to 1,100 °C

temperatures up to 1,100 °C during 30 min. The changes in their SSA were determined (Table 3). It can be seen that heating up to 700 °C increased SSA of all the samples except of APHA. Increase in SSA can be explained by decomposition of carbonates and calcium hydroxide, present in small quantities due to quick hydration of the samples when exposed to air.

Heating at 900 °C decreased SSA of all the samples noticeably and at 1,100 °C even up to 10 times. This kind of decrease indicates to possible formation of liquid phases inside and on the surface of the ash particles and to the partial loss of porosity.

The products obtained were analyzed using quantitative X-ray diffraction analysis method. It was found that the content of quartz (SiO$_2$) in the samples decreased significantly during heating at 1,100 °C (Fig. 3). In parallel, also the content of CaO, the main binder of CO$_2$ and SO$_2$ decreased—for BA from 37.2 to 32.6%, for PBA from 36.4 to 29.3%, and for APHA from 25.6 to 8.5% (calculated on the basis of CO$_2$ and H$_2$O free composition). X-ray analysis also showed the increase in the content of wollastonite, belite, and melilite in the heating products. It can be assumed that SiO$_2$ partly reacts with the free and formed from CaCO$_3$ and Ca(OH)$_2$ calcium oxide and other ash constituents in secondary solid-state processes according to the following simplified reactions giving different silicates:

$$CaO + SiO_2 \rightarrow CaSiO_3, \tag{6}$$

$$2CaO + SiO_2 \rightarrow Ca_2SiO_4. \tag{7}$$
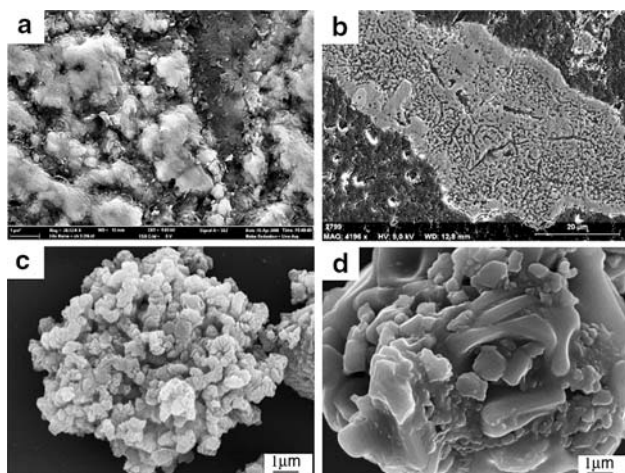
Fig. 4 SEM photos of APHA decarbonized at 900 °C: surface (**a**) and cross-section (**b**). APHA particle: initial (**c**) and heated up to 1,100 °C (**d**)

SEM analysis of the initial and treated samples showed that after heating at 900 °C no essential changes were seen on the surface of the BA particles, but signs of melting were present on the surface of APHA particles (Fig. 4a). Generally, during heating porosity slightly increased inside the particles, but outer surface became more dense and monolithic (Fig. 4b). Significant melting can take place during heating up to 1,100 °C as can be seen on the SEM picture of APHA sample (Fig. 4d).

Energy dispersive X-ray (EDX) analysis of the cross-sections of the heated up to 900 °C particles showed that Ca, Al, and Si usually coexist, indicating to the presence of different Ca-, Al-silicates. These silicates tend to concentrate on the surface of the particles in the areas where also melts and shell formation can be seen. So, it can be assumed that at higher decarbonization temperatures, a dense core forms on the surface of ash particles through different silicate formation reactions. These silicates can form eutectics with lower melting temperatures. Accompanying melting phenomenon reduces porosity and SSA, hindering diffusion of gases through this shell. Besides, the content of free CaO decreases in these solid-state processes, which are accelerated in the case of ground samples and at higher temperatures reducing CO_2 and SO_2 uptake potential of the ash. The effect is less expressed in the case of SO_2 binding, because SO_2 can partly react with the silicates formed and MgO present in the ash. High conversion levels with SO_2 (even over 100% in the case of EPA4) are a proof of this assumption.

In the particles of PF ashes, these kinds of processes have partially taken place already in the boiler during combustion and grinding of these particles can favor CO_2 and SO_2 uptake, because the nonporous shell on the

particles, which are quite often melted to spheres is crushed and more reactive CaO surface is freed.

So, high temperatures should be avoided, especially, in the case of CFBC ashes, which are obtained at lower temperature combustion regimes as compared to PF ashes. Grinding enhances SO_2 uptake but misfits in the case of CO_2.

Conclusions

Using thermogravimetric methods, CO_2 and SO_2 uptake by circulating fluidized bed oil shale ashes from different technological devices (furnace, cyclones etc.) of an operating power plant was studied in comparison with some pulverized firing ashes.

It was found that CO_2 binding capacities depend mainly on the free CaO content in the ashes, thereby, fluidized bed ashes showed higher levels of CaO conversion as compared to pulverized firing ones. Increase in specific surface area enhanced SO_2 binding.

It was shown that grinding and calcination temperature influence noticeably CO_2 and SO_2 uptake. Grinding decreased CO_2 binding capacities, but enhanced SO_2 binding in the case of fluidized bed ashes. Grinding of pulverized firing ashes increased binding parameters with both gases. Calcination at higher temperatures decreased binding parameters of both types of ashes with both gases studied. Clarification of this phenomenon was given.

Kinetic analysis of the binding process was carried out, mechanism of the reactions and respective kinetic constants were determined. Pre-treatment of ash influence remarkably kinetics of binding due to different solid-state processes taking place during heating.

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