

# Activation and reactivity of Estonian oil shale cyclone ash towards SO<sub>2</sub> binding

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**Abstract** Electricity production in Estonia is based mainly on the pulverized firing of low-grade local fuel—Estonian oil shale—and it is concentrated mainly in two big power plants, the Balti and the Eesti power plants. Estonian oil shale is characterized by a low calorific value (8–10 MJ kg<sup>-1</sup>) and a high content of mineral matter (65–70 %, carbonates and sandy-clay minerals in about equal amounts). The sulphur content is around 1.5 %. At the Eesti Power Plant, the Alstom semi-dry DeSO<sub>x</sub> system was recently installed on four power units by 180 MW<sub>el</sub> each to guarantee deeper binding of SO<sub>x</sub> from flue gases. Commercial lime in addition to oil shale ash is used there as a binding agent. Considering that cyclone ash there contains about 20–25 % free CaO and its ability to bind acidic gases has been proved earlier, the idea to replace expensive commercial sorbent with ash was raised. Hence, activation of ash is needed. The aim of the present work was the comparative investigation of the efficiency of activated ashes and the commercial lime used in the DeSO<sub>x</sub> system. Initial ash, dry ground and semi-dry ground ashes with two different amounts of water—5 and 7 % by mass—and commercial lime as sorbents for SO<sub>2</sub> binding were studied. The experiments for testing the reactivity of sorbents towards SO<sub>2</sub> binding were carried out with the Setaram Labsys 2000 thermoanalyzer under isothermal conditions. The model gaseous mixture used contained 1 mol% sulphur dioxide in nitrogen. The temperature was

varied between 80 and 700 °C. A Pt-multiplate crucible was used with 80 ± 0.5 mg samples. The results obtained indicated that ash activation by semi-dry grinding increases noticeably the reactivity of it towards SO<sub>2</sub> binding, and as a result additional commercial lime will not be needed.

**Keywords** Flue gases · Oil shale ash · Pulverized firing · Semi-dry grinding · Sulphur dioxide capture

## Abbreviations

BC	SO <sub>2</sub> binding capacity
BE	SO <sub>2</sub> binding efficiency
CFBC	Circulating fluidized bed combustion
PF	Pulverized firing
DG	Dry ground
SDG	Semi-dry ground
OS	Oil shale

## Introduction

Electricity production in Estonia is concentrated mainly in two large power plants—Eesti and Balti Power Plants—and is based mostly on the PF of low-grade local fuel—Estonian OS. Estonian OS is characterized by a low calorific value (8–10 MJ kg<sup>-1</sup>), moderate moisture content (10–13 %) and a high content of mineral matter (65–70 %) which has a unique and complicated chemical and mineralogical composition. Mineral matter of the Estonian OS consists mainly of carbonates and sandy-clay minerals. The processes taking place during pulverized firing of Estonian OS are described by Ots [1]. At combustion, the inorganic part of OS undergoes several chemical transformations,

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from decomposition processes to formation of new secondary mineral compounds and phases at higher temperatures [1, 2]. Due to the high residual content of free Ca and Mg oxides in oil shale ashes, they should have a considerable reactivity towards acid gaseous compounds, thus being potential sorbents for deeper purification of flue gases.

Coal combustion fly ash and its mixtures with lime, hydrated lime, calcium sulphate, etc. are being widely studied as sorbents in desulphurization processes [3–12]. Mixtures of fly ash and  $\text{Ca}(\text{OH})_2$  were hydrated and tested in laboratory scale experiments for  $\text{SO}_2$  removal of flue gases in [3, 4]. The significant increase in reactivity of the sorbent for  $\text{SO}_2$  binding was established. It correlated well with the relative surface area increment [3] and the content of the calcium silicate hydrate formed in the sorbent preparation [4]. An empirical correlation between the experimental variables (temperature, pressure, fly ash/ $\text{Ca}(\text{OH})_2$  ratio, water/solid ratio and time) and the specific surface area was established also by Fernández et al. [5].

$\text{Ca}(\text{OH})_2$ /fly ash sorbents were characterized and tested for reactivity towards  $\text{SO}_2$  at conditions similar to those in the bag filters in dry and semi-dry flue gas desulphurization processes [6]. It was established that sorbents with  $\text{Ca}(\text{OH})_2$  contents larger than 33 mass% had higher masses of  $\text{SO}_2$  captured per unit of mass of sorbent than  $\text{Ca}(\text{OH})_2$  had alone, and the sorbent with 70 mass%  $\text{Ca}(\text{OH})_2$  displayed the maximum capture. The utilization of Ca for the sorbents was roughly proportional to their specific surface area or total pore or mesopore volumes.

A dry-desulphurization process using  $\text{Ca}(\text{OH})_2$ /fly ash sorbent in a circulating fluidized bed was developed [7, 8], establishing also the significant effect of  $\text{NO}_x$ ,  $\text{CO}_2$  and reaction temperature on  $\text{SO}_2$  removal.

Investigating sorbents synthesized from various types of ash (coal fly ash, coal bottom ash, oil palm ash and incinerator ash), calcium oxide and calcium sulphate for flue gas desulphurization [9] the best results was obtained using coal fly ash. In [10], it was elucidated that the activity of the sorbent based on coal fly ash, calcium oxide and calcium sulphate increased with increasing specific surface area, reaction temperature and feed concentration of NO but decreased with increasing the  $\text{SO}_2$  concentration in the gaseous phase.

As the higher desulphurization activity correlated with higher sorbent surface area, a hybrid artificial intelligence approach was used to model and optimize hydration conditions for synthesizing  $\text{SO}_2$  removal sorbents based on coal fly ash, calcium oxide and calcium sulphate [11]. Using an isoconversional method, the activation energy of the sulphation reaction ( $22.7 \text{ kJ mol}^{-1}$ ) for sorbent based on coal fly ash/ $\text{CaO}/\text{CaSO}_4$  was found to be independent of the degree of conversion [12].

For reactivation of coal combustion bottom ashes, a Szego Mill<sup>TM</sup> (trademark of General Comminution Inc., Canada, for its planetary ring-roller mills) has been used with water [13]. Activation of coal ashes from fluidized bed combustion units where limestone had been added has been studied extensively. The early work and test in a 35 MWt boiler are reported in [14]. With a given Ca/S stoichiometry ( $\text{Ca/S} = 2.5$ ), sulphur capture of the reactivated sorbent was even higher than that of the parent limestone. Subsequently, a wider range of conditions was used in another boiler. The series of test conditions and results are described in [15], and it was estimated that only moderate grinding with simultaneous moderate water supplement (up to 8 mass%) is necessary to improve greatly the  $\text{SO}_2$  binding efficiency of CFBC bed ashes. Such grinding conditions fall into the semi-dry operating range. A very important parameter characterizing  $\text{SO}_2$  binding ability of sorbents is the specific surface area (SSA), and additional grinding of potential sorbents seems to be a good method for increasing this parameter.

The reactivity of ashes as well as the mechanism of the  $\text{SO}_2$  binding process with initial as well as pre-treated ashes (including also grinding and hydration) formed with pulverized firing of Estonian OS has been studied in our earlier publications [2, 16–18], and, at that, the thermal analysis has been proved to be the most sensitive and attractive method for determination of changes in the reactivity of ashes.

The Alstom semi-dry  $\text{DeSO}_x$  system (NID—Novel Integrated Desulphurization System) was recently installed on four power units, 180 MW<sub>e1</sub> each, to guarantee deeper binding of  $\text{SO}_x$  from flue gases at the Eesti Power Plant. In addition to OS ash also commercial lime is used as a binding agent in the NID reactors. Considering that cyclone ash formed at PF of OS contains free CaO at the level of 20–25 % [19–21], and its ability to bind acidic gases has been showed earlier [2, 16, 17], the idea was raised that the expensive commercial sorbent could be replaced by cyclone ash. Hence, its activation is needed, and the Szego Mill<sup>TM</sup> [13–15] seems to be a suitable tool for that task.

Therefore, the aim of the present work was to investigate the comparative efficiency of cyclone ash, differently activated, as well as that of commercial lime for estimation the potentiality of activated CA to replace the commercial lime in the  $\text{DeSO}_x$  system at the Eesti Power Plant for  $\text{SO}_2$  binding.

## Experimental

### Materials

Initial cyclone ash, DG and SDG ash with two different amounts of water—5 and 7 % (all % are mass%), and

commercial lime and previously hydrated lime as sorbents for SO<sub>2</sub> binding were studied. The initial ash collected at the Eesti Power Plant contained CaO<sup>tot</sup>—57.2 %, CaO<sup>free</sup>—26.3 %, MgO—2.0 %, SiO<sub>2</sub>—23.8, CO<sub>2</sub>—1.7 %, S<sup>tot</sup>—1.53 % and LOI—3.4 %. The main mineral phases in the initial ash were lime, merwinite, belite, periclase, anhydride, melilite, illite–smectite, quartz, etc. A detailed characterization of ashes formed at PF as well as at circulating fluidized bed combustion of Estonian OS has been given in our earlier publication [21]. The content of free CaO in the commercial lime was 77.4 %.

## Methods

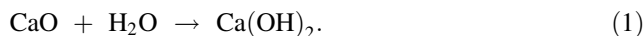
Samples were analysed using chemical, grain-size, SEM and BET methods. The surface observations were carried out with the scanning electron microscope Jeol JMS-8404A, BET SSA and porosity measurements with the Sorptometer Kelvin 1042 and the particle size distribution on the analyzer Partica LA-950V2.

The thermal analysis of samples with the Setaram Labsys Evo 1600 thermoanalyzer coupled with the Pfeiffer Omni-Star Mass Spectrometer by a heated transfer line was carried out under non-isothermal conditions by heating up to 900 °C at the rate of 5 °C min<sup>-1</sup> in an atmosphere of argon. Standard 100 µL Pt crucibles were used, the mass of samples was 50 ± 0.5 mg and the gas flow was 60 mL min<sup>-1</sup>. For reproducibility, all experiments were performed twice. Prior to experiments, the equipment was calibrated for temperature readings with calcium oxalate monohydrate.

The experiments for testing the reactivity of sorbents for SO<sub>2</sub> binding were carried out with the Setaram Labsys 2000 thermoanalyzer under isothermal conditions. The model gaseous mixture used contained 1 mol% sulphur dioxide in nitrogen. The temperatures of the experiments were 80, 300, 400, 500 and 700 °C. The 80 °C temperature was chosen because the Alstom DeSO<sub>x</sub> (NID) system operates at that temperature. The furnace was heated up to the test temperature at a heating rate of 20 °C min<sup>-1</sup> and stabilized during 20 min. Then, the SO<sub>2</sub> and N<sub>2</sub> mixture was led to the reaction chamber with the flow rate of 20 mL min<sup>-1</sup> during 45 min. A Pt-multiplate crucible was used with 80 ± 0.5 mg samples.

The ash was activated by dry or semi-dry grinding with two different amounts of water—5 and 7 %. Grinding was carried out using the Szego Mill<sup>TM</sup> SM-220 with a throughput of 400 kg h<sup>-1</sup>. SM-220 is a planetary ring-roller mill consisting of a stationary, cylindrical grinding surface, 220 mm in diameter, inside which a number of helically grooved rollers rotate. The rollers are free to move radially. The mill used has four rollers with an 8 × 8 mm ridge/groove pattern. The ash was fed by gravity into a top-feed cylinder, and water was simultaneously added using an

overhead tank with a metering valve. At semi-dry activation of ash, the hydration of CaO takes place with the formation of Ca(OH)<sub>2</sub> by the following reaction:



Considering the content of free CaO in initial ash, the stoichiometric amount of water needed for full hydration is about 9 %.

Hydration of lime was carried out in porcelain pans by mixing during 2 min 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 sample was stored for 24 h in a hermetically sealed pan, after which it was dried at 105 °C for 1 h.

All samples—initial as well as the processed ones—were stored in metal pots carefully closed hermetically. The relative moisture of air on the day of activation of samples was almost 100 % and the room temperature at +10 °C.

Two parameters were calculated to characterize the extent of gas–solid interactions:

SO<sub>2</sub>-binding capacity (mg SO<sub>2</sub> bound by 100 mg of sample):

$$BC = \frac{m_{\text{SO}_2}}{m_{\text{sorb}}} \times 100, \quad (2)$$

where  $m_{\text{SO}_2}$  is the mass of bound SO<sub>2</sub> and  $m_{\text{sorb}}$  is the mass of sorbent used and SO<sub>2</sub>-binding efficiency (%), showing the extent of utilization of free CaO contained in the sample):

$$BE = \frac{m_{\text{SO}_2} \times M_{\text{CaO}}}{m_{\text{sorb}} \times c_{\text{CaO free}} \times M_{\text{SO}_2}} \times 100, \quad (3)$$

where  $m_{\text{SO}_2}$  is the mass of bound SO<sub>2</sub>,  $M_{\text{CaO}}$  is the molar mass of CaO,  $m_{\text{sorb}}$  is the mass of sorbent,  $c_{\text{CaO free}}$  is the content of free CaO in the sorbent and  $M_{\text{SO}_2}$  is the molar mass of SO<sub>2</sub>.

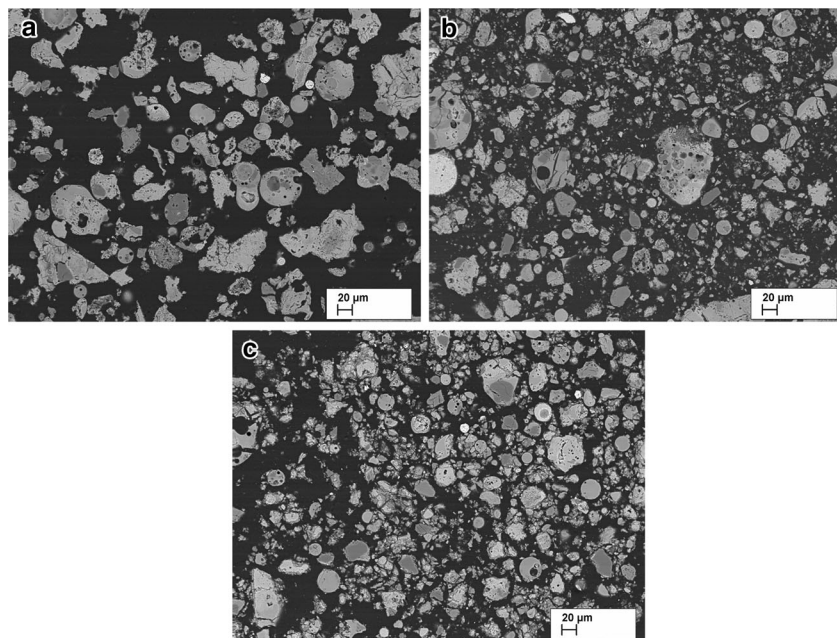
## Results and discussion

### Characterization of samples

The content of free CaO and some physico-chemical characteristics of samples studied are presented in Table 1. A slight decrease is seen in the content of free CaO—from 26.3 % for initial ash down to 25.4 % for samples activated by semi-dry grinding with 7 % water. The reason is that activated samples bind carbon dioxide from air during activation and following handling, showing how effective the activation was. The increase in the intensities of infrared absorption bands in activated samples characteristic to OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> are well seen in Fig. 8a and b, respectively. The

**Table 1** Some characteristics of samples

Content/ parameter	Sample					
	Initial	DG	SDG/(5 % H <sub>2</sub> O)	SDG/(7 % H <sub>2</sub> O)	Lime	Hydrated lime
CaO <sup>free</sup> /%	26.3	26.2	26.1	25.4	77.4	72.8
Median particle size/ $\mu\text{m}$	63.3	25.8	27.8	34.0	18.0	35.4
Mean particle size/ $\mu\text{m}$	80.0	40.3	45.8	45.3	25.8	46.6
BET SSA/ $\text{m}^2 \text{g}^{-1}$	0.67	1.50	3.77	6.10	6.17	10.72
Total pore volume/ $\text{mm}^3 \text{g}^{-1}$	3.03	9.98	20.59	38.72	8.50	22.47
Micropore volume/ $\text{mm}^3 \text{g}^{-1}$	0.0	0.0	0.0	0.0	0.09	0.0

**Fig. 1** SEM photos of initial (a) and activated CA samples: dry ground (b) and semi-dry ground with 5 % (c)

content of free CaO in lime was 77.4 % indicating to relatively poor quality of lime or its bad storage conditions.

As the formation of fly ashes at PF firing of Estonian OS takes place at temperatures higher than 1,200 °C, a molten phase plays an important role in the formation of particle shape and surface properties—many particles are characterized by a regular round shape and smooth surface (Fig. 1a). Dry grinding produced finer particles (Fig. 1b): the mean particle size for DG ash dropped twofold compared with initial samples—from 80 to 40.3  $\mu\text{m}$  (Table 1). SDG ashes are characterized by particles of irregular shape and porous surface (Fig. 1c) indicating the formation of  $\text{Ca}(\text{OH})_2$  during activation of ash. For SDG ashes, the mean particle size is little-bit bigger than for DG ash—on the level of 45  $\mu\text{m}$  for both samples (Table 1) because the molar volume of  $\text{Ca}(\text{OH})_2$  is bigger than that for CaO. The mean particle size for lime is 25.8  $\mu\text{m}$  and for hydrated lime much bigger—46.6  $\mu\text{m}$  (Table 1).

It is well seen in Fig. 2 that the particle size distribution profiles are quite similar for initial and DG ashes, and for

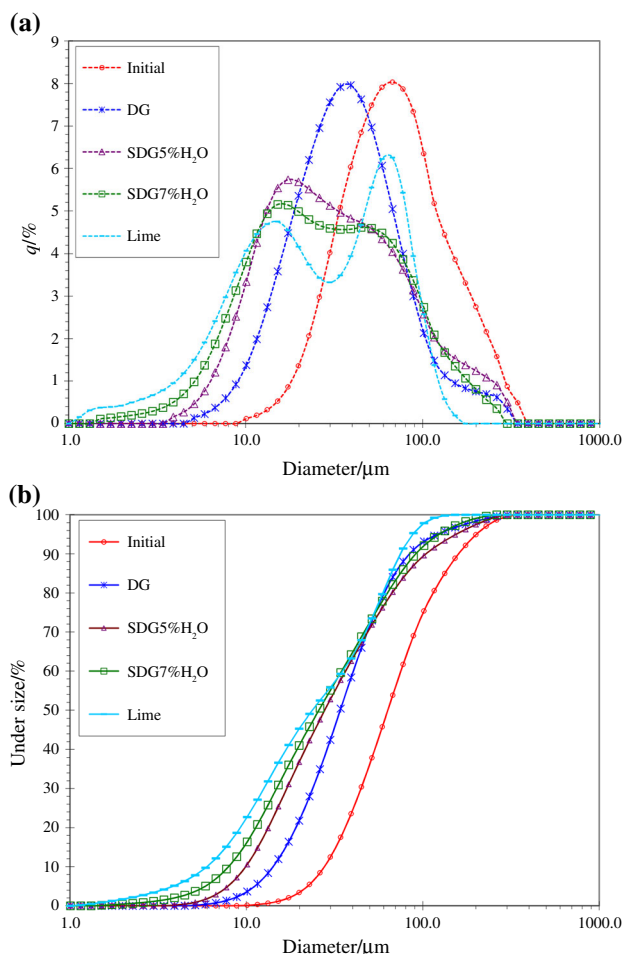
both SDG ashes (Fig. 2a), and that activation reduced the particles size significantly (Fig. 2b). For lime, the particle size distribution profile is close to the profiles of SDG samples but with two distinct peaks.

Noticeable is the increase in SSA and porosity of samples resulting from the grinding and, especially, from the simultaneous hydration of samples. Both characteristics for SDG ash with the higher ratio of water are ~10 times higher than those for initial and DG ashes. Thus, SSA increased from 0.67 to 6.10  $\text{m}^2 \text{g}^{-1}$ , and pore volume from 3.03 to 38.72  $\text{mm}^3 \text{g}^{-1}$ . For lime and hydrated lime, SSA values are 6.17 and 10.72  $\text{m}^2 \text{g}^{-1}$  and pore volumes are 8.50 and 22.47  $\text{mm}^3 \text{g}^{-1}$ , respectively (Table 1).

#### Thermal and MS analysis

Thermoanalytical curves and emission profiles of  $\text{CO}_2$  evolved at thermal treatment of initial and SDG ash with 7 % water are presented in Fig. 3 (some resulting values for the other ashes are given in the text only). Emission





**Fig. 2** Particle size distribution of samples: profile (a) and under size (b)

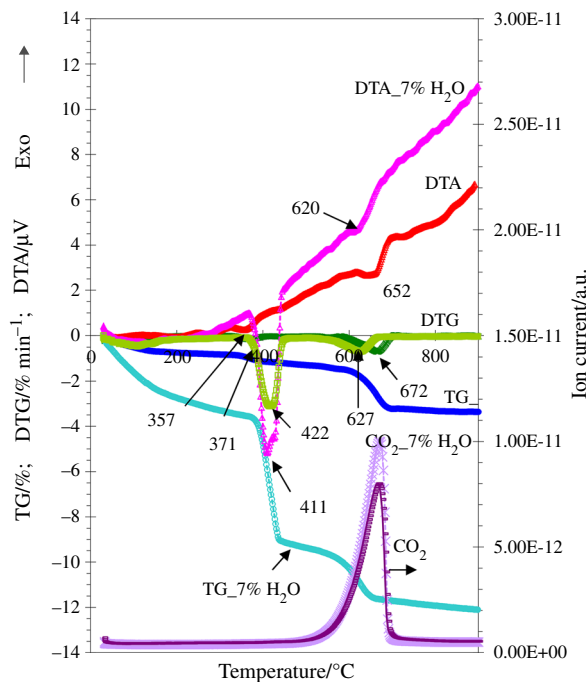
profiles of H<sub>2</sub>O for all ash samples studied are presented in Fig. 4.

The mass loss up to the temperatures of starting the decomposition of Ca(OH)<sub>2</sub> was for initial and dry ground ashes 0.85 % (Fig. 3) and 1.2 %, respectively, pointing to the modest binding of moisture from air during dry grinding of the ash. For SDG ashes with 5 and 7 % water, the mass losses were 0.61 and 3.5 % (Fig. 3), respectively, indicating some additional binding of moisture by free CaO during storing at the smaller water level, while no such addition was observed at the higher water level.

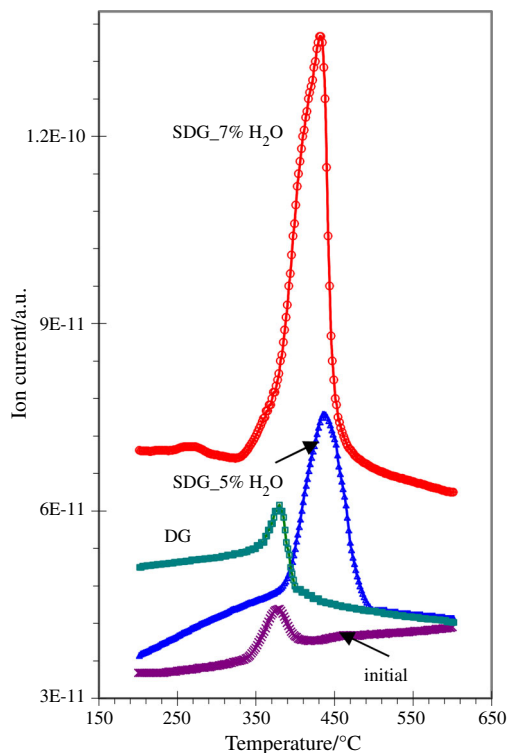
The mass losses for initial and dry ground ashes in the temperature interval 320–430 °C where the decomposition of Ca(OH)<sub>2</sub> takes place,



were 0.32 % (Fig. 3) and 0.46 %, respectively. This corresponds to 1.1 and 1.4 % of CaO, respectively, indicating that some amount of moisture from air had reacted with free CaO during dry grinding with the formation of Ca(OH)<sub>2</sub> (Fig. 8a) which was liberated now (Fig. 4).



**Fig. 3** Thermoanalytical curves and CO<sub>2</sub> emission profiles of initial and SDG with 7 % water ashes

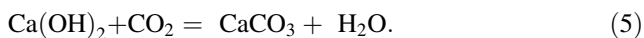


**Fig. 4** Emission profiles of H<sub>2</sub>O evolved at thermal treatment of initial and activated ashes

At semi-dry grinding of ash with 5 and 7 % water, the mass losses in the temperature interval of decomposition of calcium hydroxide were 2.9 and 5.7 % (Fig. 3), respectively, which

correspond to 9.1 and 17.3 % of CaO, respectively, bound as a constituent part of  $\text{Ca}(\text{OH})_2$  (Figs. 4 and 8a).

The additional mass loss between temperatures 430–900 °C where the decomposition of carbonates takes place was for initial ash 2.18 % (total mass loss 3.35 %) (Fig. 3), for dry and semi-dry ground ashes with 5 % water 2.28 % (total 3.97 %) and 2.39 % (total 5.89 %), respectively, pointing to the modest binding of  $\text{CO}_2$  from air during activation of samples with the formation of additional calcite:



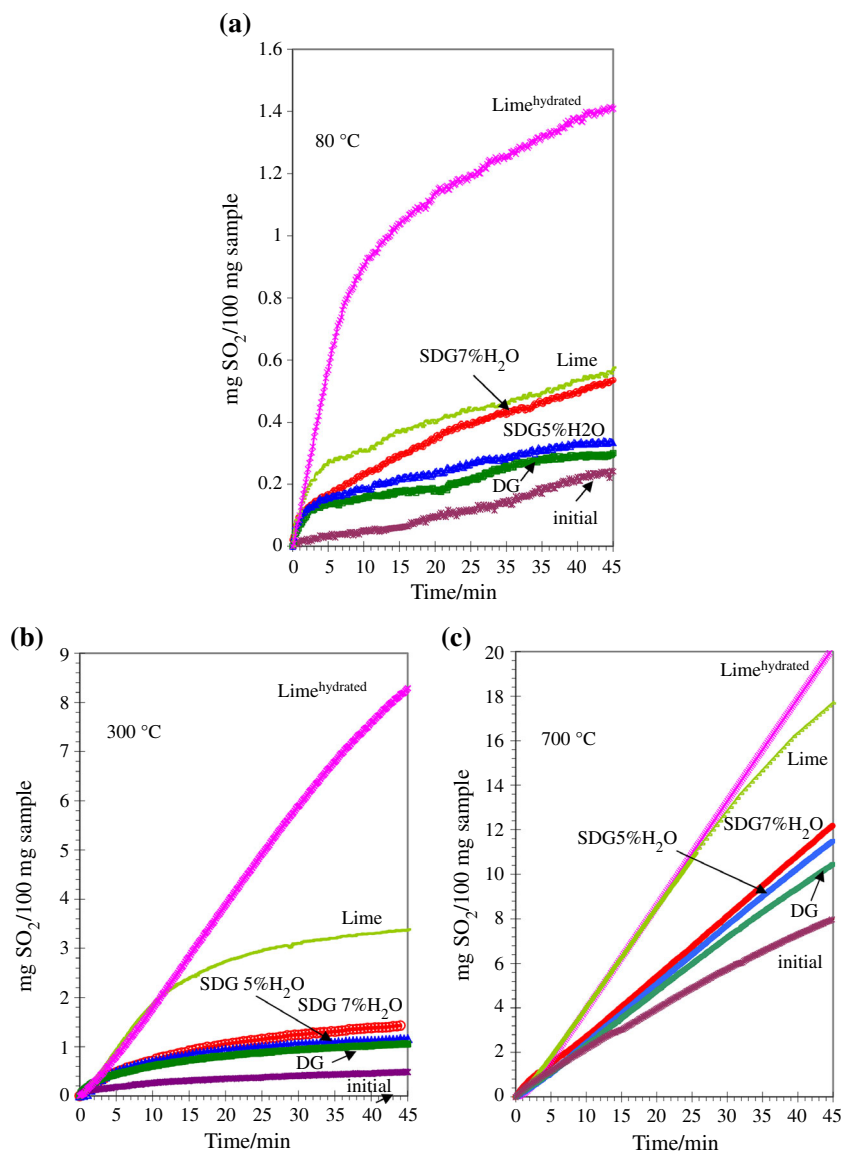
The mass loss at higher temperatures for SDG ash with 7 % of water was somewhat larger—3.08 % (total 12.12 %) (Fig. 3) pointing to the larger amount of  $\text{CO}_2$  bound from air during activation (Fig. 8b), thereby

indicating more effective activation of ash with the higher amount of water.

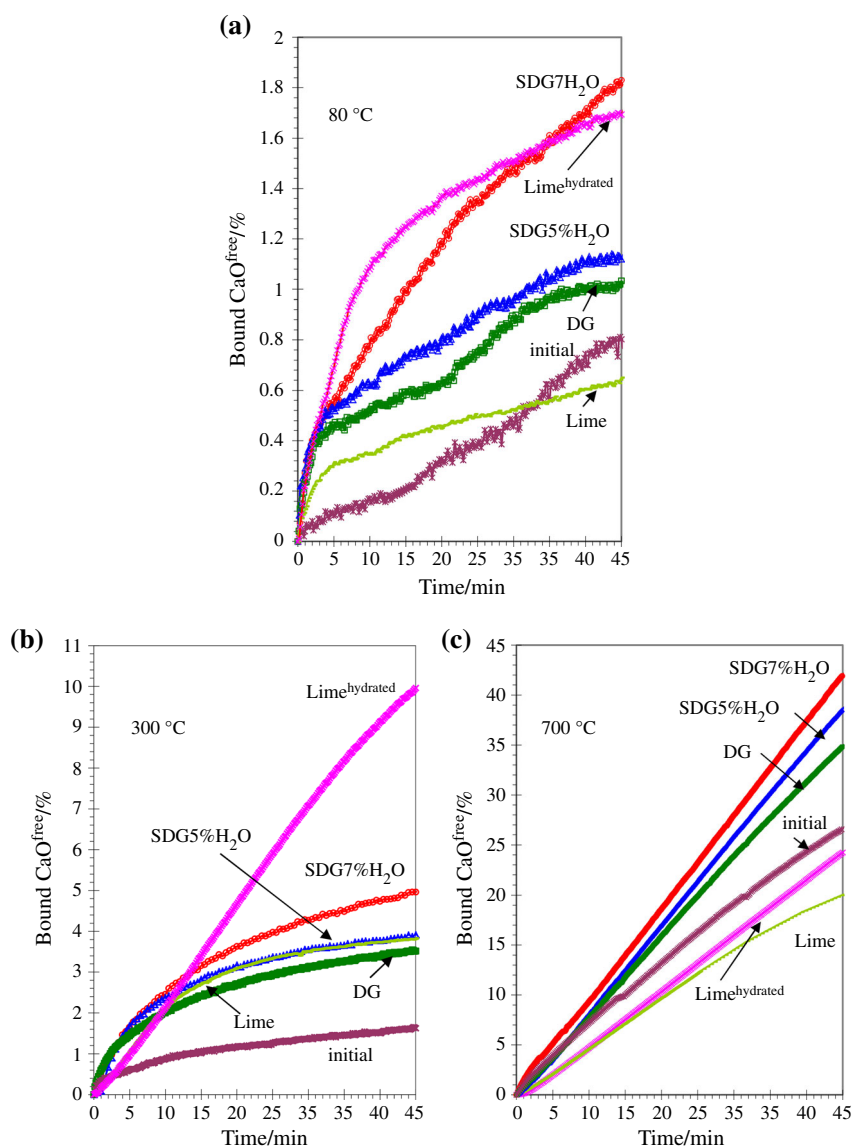
### $\text{SO}_2$ binding experiments

At 80 °C, the binding capacity of initial ash was poor: after a very slow start and 45 min contact between the solid and gaseous phases, there was bound 0.24 mg  $\text{SO}_2$  per 100 mg of sample. The other ashes exhibited a more rapid initial rate of adsorption. After 45 min, the DG and SDG with 5 and 7 % water bound 1.25, 1.7 and 2.2 times more, respectively, than the initial ash. Lime and hydrated lime bound 0.58 and 1.41 mg  $\text{SO}_2$  per 100 mg sample or 2.4 and 5.9 times more than the initial ash (Fig. 5a). At those values, 0.80 and 1.03 % of free CaO content was utilized, respectively, in the initial and DG ashes, and 1.13 and

**Fig. 5** Dependence of  $\text{SO}_2$  binding capacity (BC, mg  $\text{SO}_2$  per 100 mg of sample) of sorbents on contact time between solid and gaseous phases at 80 °C (a), 300 °C (b) and 700 °C (c)



**Fig. 6** Dependence of SO<sub>2</sub> binding efficiency (%) of sorbents calculated on the content of free CaO in samples on contact time between solid and gaseous phases at 80 °C (a), 300 °C (b) and 700 °C (c)

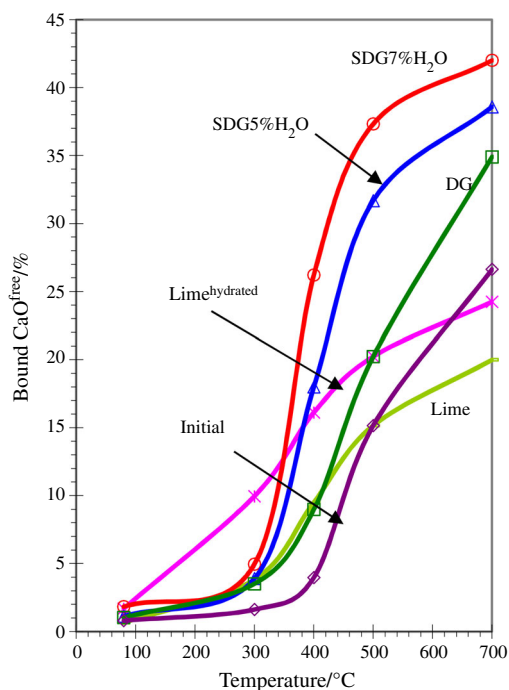


1.83 %, respectively, in SDG with 5 and 7 % water (Fig. 6a). For comparison, for lime, these data were less than for initial ash, only 0.65 %, and for hydrated lime less than for SDG ash with 7 % water, 1.69 % (Fig. 6a).

It should be emphasized here that all these and other adsorption data are valuable in a relative sense, as conditions for each sample were similar. Slow, laminar flow of gas over the crucible containing the same amount of sample does not give absolute values of adsorption capabilities of ash and lime, but does provide their relative rankings. Further, it may seem surprising that activated ashes do better than hydrated commercial lime in the utilization of the Ca(OH)<sub>2</sub>. The results may well be influenced by the way the lime was calcined. A plausible reason for difference is provided in Table 1 where the total pore volume for the hydrated lime is given as 22.5 mm<sup>3</sup> g<sup>-1</sup> and

that for the SDG ash with 7 % water as 38.7 mm<sup>3</sup> g<sup>-1</sup>. With the significantly higher accessible pore volume, it is not surprising that the SO<sub>2</sub> in the gas phase will reach adsorption sites more readily. While the lime was fully hydrated, the hydration level of the CaO in the activated ash, with the 7 % water usage, was likely in the 2/3 region. Hence, with wet grinding of the ashes, there is room for further improvement. Such testing is planned.

When the experiments are carried out at increasing temperatures, corresponding increases in SO<sub>2</sub> binding are observed (Figs. 5, 6 and 7; Table 2). For example, at 300 °C after 45 min contact, there was bound by initial and DG ashes 0.48 and 1.05 mg SO<sub>2</sub> per 100 mg of sample, respectively, by SDG ashes with 5 and 7 % water and 1.17 and 1.43 mg SO<sub>2</sub> per 100 mg of sample, respectively (Fig. 5b). The SO<sub>2</sub> binding capacities for lime and hydrated lime after 45 min



**Fig. 7** Dependence of SO<sub>2</sub> binding efficiency (%) of sorbents on experiment temperature after 45 min contact between solid and gaseous phases

contact at 300 °C were, respectively, 3.38 and 8.29 mg SO<sub>2</sub> per 100 mg of sample (Fig. 5b) or much higher than for the ashes. But at the initial stage of contact between solid and gaseous phases at 300 °C, the rate of binding by activated ashes was higher than by lime or hydrated lime (Fig. 5b). That is, more readily noticeable in Fig. 6b where the CaO utilization efficiency is shown. Prolonging the test up to 45 min, however, the hydrated lime reached 10 % utilization of free CaO (Fig. 6b) or twofold as much as SDG ash with the higher level of water, indicating the prevailing role of Ca(OH)<sub>2</sub> in the binding of SO<sub>2</sub> at this temperature.

Increasing the experimental temperature to 400 °C and higher, an especially intensive increase in the binding ability

of samples studied was observed (Table 2), and at 700 °C during 45 min, the binding of SO<sub>2</sub> into the solid proceeded almost by the linear route for all samples (Figs. 5c and 6c). It is noted in Fig. 6c that the percentage utilization of the free CaO at 700 °C was higher in all ashes than that by the lime, in contrast to the observation at 300 °C.

All data obtained after 45 min exposure are given in Table 2. In Fig. 7, all those data for free CaO utilization are also plotted over the complete temperature range. It is readily observed that the data fall in two broad categories—all ashes and lime. At 80 °C, the hydrated lime and the ash activated during grinding with 7 % water bound SO<sub>2</sub> almost on the equal level as do all the others a little lower. The amount of SO<sub>2</sub> bound by hydrated lime increased more rapidly through the 300 °C temperature range, and then levels off, binding SO<sub>2</sub> at about 350 °C on the level of hydrated ashes, and at about 500 and 600 °C, respectively, on the level of DG ash and initial ash. Lime repeats that performance at a lower efficiency level, being on the level of DG ash at about 400 °C and the initial ash at 500 °C. At 700 °C, both lime and hydrated lime end up on the lower level than all the ashes. A steep inflection region is observed for both SDG ashes in the 500 °C range, followed by the DG and initial ashes at higher temperatures.

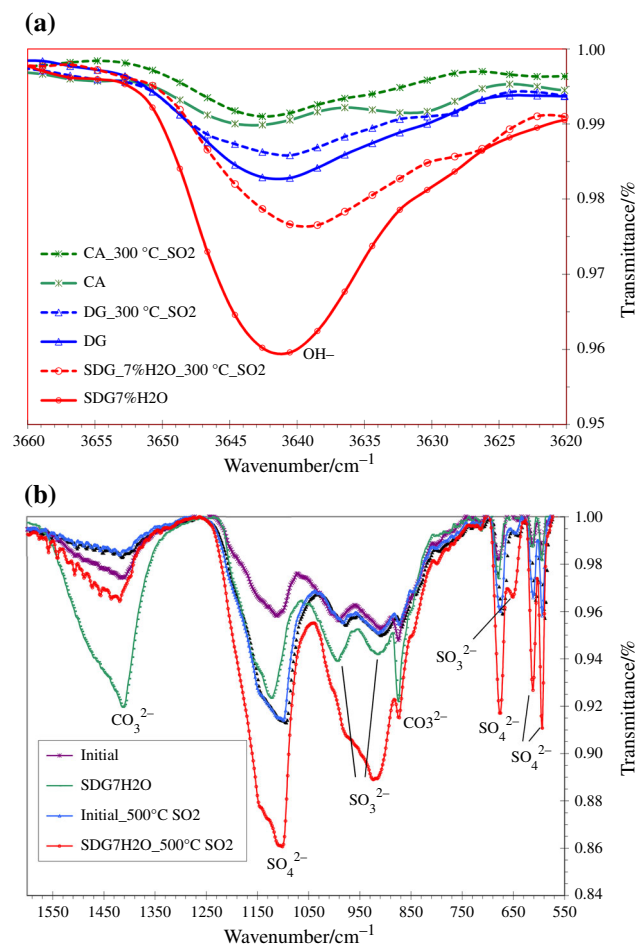
After levelling off beyond the 500 °C temperature range, the CaO utilizations for the SDG ashes at 700 °C were 38.6 and 42.0 %, respectively, of free CaO contained in these samples (Fig. 7). These were, respectively, 2 and 1.6 times higher than for lime and hydrated lime. Thus, the increase in the SO<sub>2</sub> binding ability of SDG ashes at higher temperatures indicates that activated ash can be used also for injection directly into the boiler gas tract. At that point, the injection point of activated ash into the gas tract should be chosen considering the optimum temperature for SO<sub>2</sub> binding into the solid.

The increase in SO<sub>2</sub> binding ability of ash was improved after activation by dry grinding. This was caused by breaking the sulphate shell surrounding the ash particles

**Table 2** SO<sub>2</sub> binding capacity (BC/mg SO<sub>2</sub> per 100 mg sample) and binding efficiency (BE/%) calculated on the content of free CaO in different lime-containing sorbents at different temperatures after 45 min contact between solid and gaseous phases

Sample	Temperature/°C									
	80		300		400		500		700	
	BC	BE	BC	BE	BC	BE	BC	BE	BC	BE
CA_initial	0.24	0.80	0.48	1.62	1.19	3.98	4.51	15.16	7.99	26.62
CA_DG	0.30	1.03	1.05	3.51	2.68	8.98	6.05	20.23	10.47	34.90
CA_SDG 5 % H <sub>2</sub> O	0.33	1.13	1.17	3.90	5.37	18.00	9.44	31.69	11.51	38.58
CA_SDG 7 % H <sub>2</sub> O	0.54	1.83	1.43	4.96	7.63	26.21	10.85	37.32	12.19	42.00
Lime	0.58	0.65	3.38	3.82	8.30	9.50	13.41	15.16	17.68	19.99
Hydrated lime	1.41	1.69	8.29	9.96	13.41	16.12	15.58	20.23	19.95	24.24



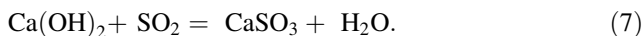


**Fig. 8** FTIR spectra of initial, activated and sulphated samples in the wavenumber regions characteristic to OH<sup>-</sup> (a) and CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> vibrational bands (b)

which blocks off the unreacted lime, thus making it accessible to SO<sub>2</sub> gas:

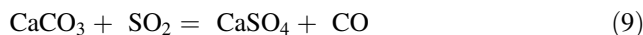
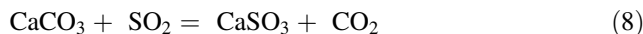


This is especially noticeable using semi-dry grinding which resulted in the formation of more active Ca(OH)<sub>2</sub> which has a larger volume than the oxide and, hence, enhances the particle break-up greatly:



The differences in the intensities of absorption bands characteristic to OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> groups in FTIR spectra before sulphation of samples indicate the differences in the binding ability of initial, DG and SDG ashes towards H<sub>2</sub>O (reaction 1) and CO<sub>2</sub> (reaction 5) during activation and handling of samples (Fig. 8a, b). The decrease in the intensities of absorption bands characteristic to these groups after sulphation of samples and the increase in the intensities of bands characteristic to SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> groups in Fig. 8b point not only to the participation of

Ca(OH)<sub>2</sub> (reaction 7) and CaO (reaction 6) but also the participation of CaCO<sub>3</sub> in the binding of SO<sub>2</sub> by reactions 8 and 9:



The differences in the intensities of these absorption bands for initial and SDG with the larger amount of water ashes (Fig. 8b) explain well the differences in the SO<sub>2</sub>-binding abilities of these ashes.

Thus, with dry grinding, the improvement of sorbent reactivity towards SO<sub>2</sub> binding is caused mostly by breaking of the sulphate shell surrounding the ash particles which hinders SO<sub>2</sub> diffusion into the particles and blocks off the unreacted lime. The semi-dry grinding, in addition, is accompanied by the formation of Ca(OH)<sub>2</sub> following reaction (1) being more active towards SO<sub>2</sub> binding compared to CaO. Noticeable was the increase in SSA and porosity of samples (Table 1) resulting from grinding and, especially, from the simultaneous hydration of samples. Both parameters, SSA and porosity, characterize well the binding ability of different sorbents. Higher values indicate improvement of the diffusion of SO<sub>2</sub> inside the ash particles and, hence, better contact between sulphur dioxide and Ca(OH)<sub>2</sub> and/or CaO.

Lime and hydrated lime bound more SO<sub>2</sub> per 100 mg of sample than ash samples which is not surprising considering the much higher content of CaO in these samples compared with ash, but the utilization efficiency of free CaO contained in ashes was, on the contrary, much higher than by lime or hydrated lime. Partially, this is caused by the scattering effect of CaO and/or Ca(OH)<sub>2</sub> along ash particles comparing with lime, especially, using the ground samples, and hence promoting better contact between sulphur dioxide and CaO or/and Ca(OH)<sub>2</sub>. Also, it can be presumed that during pre-heating of the ashes (and hydrated lime) up to 400–700 °C the decomposition of Ca(OH)<sub>2</sub> with formation of newly activated free Ca and Mg oxides takes place. The last ones are more active towards SO<sub>2</sub> binding than the initial free CaO and MgO in these samples.

## Conclusions

Experiments for testing the reactivity of initial and activated cyclone ashes formed at pulverized firing of Estonian oil shale towards SO<sub>2</sub> binding have been carried out. The ashes were activated by dry grinding with simultaneous partial hydration.

The better binding parameters of activated ashes are associated with higher activity of free CaO and formed Ca(OH)<sub>2</sub>, and higher specific surface area and porosity,

particularly resulting from grinding with simultaneous hydration when both characteristics are about tenfold higher than those for initial and dry ground ashes. Also, the newly activated free Ca and Mg oxides formed at pre-heating of previously hydrated ashes are more active towards SO<sub>2</sub> binding than free CaO and MgO in initial samples. These changes were associated with a noticeable increase in the SO<sub>2</sub> binding ability. Depending on the temperature of experiment, these data for sample activated with higher ratio of water were 1.5–6.9 times higher than this for initial ash.

Although lime and hydrated lime bound more SO<sub>2</sub> per 100 mg of sample than the activated ashes, the utilization efficiency of free CaO contained in ashes was, on the contrary, up to twice as high as that in lime or hydrated lime.

The results obtained indicate that activation of cyclone ash by semi-dry grinding increases the reactivity of ash towards SO<sub>2</sub> binding, and as a result additional commercial lime will not be needed. Besides, it can be used for injection directly into the boiler gas tract. At that point, the injection point of activated ash into the gas tract should be chosen considering the optimum temperature for SO<sub>2</sub> binding into the solid and the design of the gas tract.

Thus, semi-dry grinding of cyclone ash from pulverized firing of Estonian oil shale is a promising tool for ash activation towards SO<sub>2</sub> binding. The Szego Mill<sup>TM</sup> may be used for such grinding with simultaneous ash hydration. The thermal analysis supported by SEM, BET and other methods has been proved to be effective one for such investigation.

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## References

1. A. Ots. Oil shale fuel combustion technology. SC Estonian Energy; Tallinn 2004. p. 833.
2. Kaljuvee T, Toom M, Trikkel A, Kuusik R. Reactivity of oil shale ashes in the binding of SO<sub>2</sub>. *J Therm Anal Calorim.* 2007;88:51–8.
3. Martínez JC, Izquierdo JF, Cunill F, Tejero J, Querol J. Reactivity of fly ash and Ca(OH)<sub>2</sub> mixture for SO<sub>2</sub> removal flue gas. *Ind Eng Chem Res.* 1991;30:2143–7.
4. Ho CS, Shih SM. Ca(OH)<sub>2</sub>/fly ash sorbents for SO<sub>2</sub> removal. *Ind Eng Chem Res.* 1992;31:1130–5.
5. Fernández J, Renedo MJ, Pesquera A, Irabien JA. Preparation and characterization of fly ash/hydrated lime sorbents for SO<sub>2</sub> removal. *Powder Technol.* 1997;97:133–9.
6. Lin RB, Shih SM, Liu CF. Structural properties and reactivity of Ca(OH)<sub>2</sub>/fly ash sorbents for flue gas desulphurization. *Ind Eng Chem Res.* 2003;42:1350–6.
7. Li Y, Loh BC, Matsushima N, Nishioka M, Sadakata M. Chain reaction mechanism by NO<sub>x</sub> in SO<sub>2</sub> removal process. *Energy Fuels.* 2002;16:155–60.
8. Matsushima N, Li Y, Nishioka M, Sadakata M. Novel dry-desulphurization process using Ca(OH)<sub>2</sub>/fly ash sorbent in a circulating fluidized bed. *Environ Sci Technol.* 2004;38:6867–74.
9. Lee KT, Bhatia S, Mohamed AR. Preparation and characterization of sorbents prepared from ash (waste material) for sulfur dioxide (SO<sub>2</sub>) removal. *J Mater Cycles Waste Manag.* 2005;7:16–23.
10. Lee KT, Mohamed AR, Bhatia S, Chu KH. Removal of sulfur dioxide by fly ash/CaO/CaSO<sub>4</sub> sorbents. *Chem Eng J.* 2005;114:171–7.
11. Lee KT, Bathia S, Mohamed AR, Chu KH. Optimizing the specific surface area of fly ash sorbents for flue gas desulphurization. *Chemosphere.* 2006;62:89–96.
12. Lee KT, Bhatia S, Mohamed AR. Kinetic model for the reaction between SO<sub>2</sub> and coal fly ash/CaO/CaSO<sub>4</sub> sorbent. *J Therm Anal Calorim.* 2005;79:691–5.
13. Trass O, Papachristodoulou GL, Gandolfi EAJ. Wet grinding of coal in the Szego Mill: Limiting predictions and experimental results. *Coal Prep.* 1995;16:179–201.
14. Anthony EJ, MacKenzie A, Trass O, Iribarne AP, Iribarne JV, Burwell SM. Advanced fluidized bed combustion sorbent reactivation technology. *Ind Eng Chem Res.* 2003;42:1162–73.
15. Trass O, Delibas C, J. Anthony E. Efficient reactivation of fluidized bed combustor ashes; test results from a 35 MWt utility boiler, proceedings 9th international conference on circulating fluidized beds, CFB-9, Hamburg, May 2008, 869–74.
16. Kaljuvee T, Trikkel A, Kuusik R. Reactivity of oil shale ashes towards sulfur dioxide. 1. Activation of high-temperature ashes. *Oil Shale.* 1997;14:393–408.
17. Kaljuvee T, Trikkel A, Kuusik R. Decarbonization of natural lime-containing materials and reactivity of calcined products towards SO<sub>2</sub> and CO<sub>2</sub>. *J Therm Anal Cal.* 2001;64:1229–40.
18. Kaljuvee T, Kuusik R, Trikkel A, Bender V. The role of MgO in the binding of SO<sub>2</sub> by lime-containing materials. *J Therm Anal Cal.* 2005;80:591–7.
19. Konist A, Pihu T, Neshumayev D, Siirde A. Oil shale pulverized firing: boiler efficiency, ash balance and flue gas composition. *Oil Shale.* 2013;30:6–18.
20. Pihu T, Arro H, Prikk A, Rootamm R, Konist A, Kirsimäe K, Liira M, Mõtsep R. Oil shale CFBC ash cementation properties in ash fields. *Fuel.* 2012;93:172–80.
21. Kuusik R, Uibu M, Kirsimäe K. Characterization of oil shale ashes formed at industrial-scale CFBC boiler. *Oil Shale.* 2005;22:407–20.