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## REACTIVITY OF OIL SHALE ASHES TOWARDS SULFUR DIOXIDE 1. ACTIVATION OF HIGH-TEMPERATURE ASHES

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*Initial and activated by different methods ashes formed at the Baltic Thermal Power Plant (TPP) during high-temperature combustion (1100-1200 °C) of powdered Estonian oil shale, and some samples of mud from sediment ponds of the hydraulic ash separation system at the Baltic TPP as sorbents for SO<sub>2</sub> were studied in the temperature range of 700-950 °C by means of SO<sub>2</sub>-air mixture (p<sub>SO<sub>2</sub></sub>=190 mm Hg) and a thermogravimetric equipment. It was determined that the SO<sub>2</sub>-binding capacity for the initial samples of high temperature ashes at a two-minute contact was in the range of 7.3-13.1 mg SO<sub>2</sub> per 100 mg sample. Dry grinding increased the SO<sub>2</sub>-binding capacity of the initial ashes 1.15-1.25 times, wet grinding 1.3-1.6, hydration 1.3-1.7, the combination of grinding and hydration 1.9-2.1 times. Using preliminary activation of the oil shale ashes it was possible to diminish the difference in their SO<sub>2</sub> capturing ability, compared to samples of natural Estonian limestones and dolomites, from 3-4 times to 1.6-2 times. The SO<sub>2</sub>-binding capacity of the samples of mud from the sediment ponds was on the same level as that of natural limestone and dolomites.*

### Introduction

Combustion of sulfur containing fossil fuels at thermal power plants (TPP) induces the acidic pollution of the atmosphere with sulfur dioxide. There are two large TPPs in Estonia - the Estonian and the Baltic TPP, which burn Estonian oil shale containing 60-70 % of mineral components and 1.5 % of sulfur and which are the major air polluters with SO<sub>2</sub> in the Baltic Sea region.

Beside different industrial sorbents and wastes for SO<sub>2</sub> removal from flue gases, like sodium carbonate [1], silicalite [2], red mud from alumina

process [3, 4] etc., the ashes formed during the combustion of fossil fuels, and particularly in the processes with simultaneous injection of limestone or dolomite into the boiler or gas tract [5-9] have been investigated and recommended. Before recycling, usually grinding or hydrating of the ashes is carried out for their activation. During grinding, mechanical activation of the sorbents takes place - the crust surrounding the particles (consists partially of sintered areas and partially of the product of sulfatization -  $\text{CaSO}_4$ ) is broken. Hydration increases the specific surface area (SSA) of the samples and a new very active towards  $\text{SO}_2$  phase -  $\text{Ca}(\text{OH})_2$  is formed.

Due to the rather high content of free  $\text{CaO}$  (up to 20 %) and other alkali compounds, oil shale ashes are potential sorbents for the additional removal of  $\text{SO}_2$  from flue gases. The ash formed during the combustion of oil shale in boilers is removed in different technological points - furnace (10-15 % of total amount of formed ashes), superheater (15-25 %), cyclone (35-50 %) and electrostatic precipitator (15-20 %) [10, 11]. Furnace and superheater ashes are removed by means of hydroseparation method, cyclone and electrostatic precipitator (ESP) ashes by dry method. The ashes removed in different points differ from each other in chemical composition and in physical and chemical properties [10, 11]. As the ash from ESP has the smallest content of free  $\text{CaO}$  and the highest content of alite and belite, compared to the other ashes, it has found a large-scale use in cement industry. And this is why in the present work the first three types of oil shale ashes were investigated.

The possibility of using the ashes formed at the Estonian and Baltic TPPs as sorbents for binding  $\text{SO}_2$  from the flue gases by dry method has been shown by us earlier [12, 13]. The goal of these investigations was a comparative determination of the  $\text{SO}_2$ -binding efficiency of different ashes formed at the TPPs and to study the possibilities of activating them. Besides, the reactivity of mud from the sediment ponds of the ash separation system at the Baltic TPP towards  $\text{SO}_2$  was studied. Two parameters were used for the characterization of the extent of  $\text{SO}_2$ -binding: the  $\text{SO}_2$ -binding rate ( $\text{mg SO}_2/\text{mg sample per min}$ ) and the  $\text{SO}_2$ -binding capacity ( $\text{mg SO}_2$  per 100 mg sample or  $\text{mg SO}_2$  per 100 mg free  $\text{CaO}$ ).

## Experimental

Three different high-temperature oil shale ashes from the Baltic TPP (HTA): furnace ash-(FA), cyclone ash-(CA), superheater ash-(SHA) formed at 1100-1200 °C, have been studied. The ashes were activated in laboratory conditions by dry grinding (G), hydrating (H), grinding and



subsequent hydrating (G + H) and wet grinding (WG). Dry grinding of the ashes was carried out in one ball vibromill (weight of samples 5 g, grinding time 30 min). Hydration of the initial and previously ground samples was carried out in porcelain pans by mixing during two minutes 5 g of the sample with water, the weight of which exceeded 5 times the stoichiometric amount of water requested for slaking the free CaO in the ashes. Two different contact times were used - 0.5 (H.5) and 24 hours (H24), during which the pans were kept hermetically sealed. After that the hydrated samples were dried at 105 °C for 1 hour. In wet grinding of the ashes, the amount of the added water exceeded two (WG2) or five times (WG5) the amount needed for slaking of the free CaO in the samples.

Table 1. Characterization of the Samples

Parameters	Samples						
	FA	SHA	CA	Mud-I	Mud-II	Karinu	Adavere
Content (wt. %) of:							
CaO <sub>total</sub>	58.6	52.5	49.1	52.6	49.8	57.4	37.1
CaO <sub>free</sub>	20.5	14.8	13.1	1.1	1.97	—	—
MgO	5.8	5.4	5.1	0.3	0.5	1.5	17.7
SO <sub>4</sub>	1.5	7.1	6.9	3.9	5.4	0	0
Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub>	11.4	11.2	12.6	1.3	2.3	0.3	3.5
SiO <sub>2</sub>	21.7	22.3	23.5	1.2	8.7	1.1	1.7
BET surface area (m <sup>2</sup> /g) for the:							
initial samples	0.87	0.83	0.62	8.64	20.1	2.98	4.54
ground samples (G)	1.45	1.88	1.01	—	—	—	—
hydrated samples (H24)	1.87	3.22	1.41	—	—	—	—
ground and hydrated samples (G + H24)	—	4.02	3.33	—	—	—	—
Content (wt. %) of the fractional class of <math>-100\ \mu\text{m}</math> for the:							
initial samples	23.7	42.1	58.5	99.1	99.2	99.5	99.5
ground samples	88.5	90.8	89.8	—	—	—	—

The duration of hydrating the samples was chosen according to special calorimetric experiments. The previously warmed up to the experiment temperature (20, 50 or 80 °C) ash (10 g) was added to the thermostated water (20 g) and at continuous stirring the temperature increase was fixed. The mole ratio of H<sub>2</sub>O/free CaO in the mixture was in the range of 30-40.

For comparison, a limestone sample from Karinu and a dolomite sample from Adavere deposit were studied. Different methods of analysis to characterize the samples (chemical, BET nitrogen dynamic desorption, SEM, etc.) were used. The results for the initial samples are presented in Table 1.

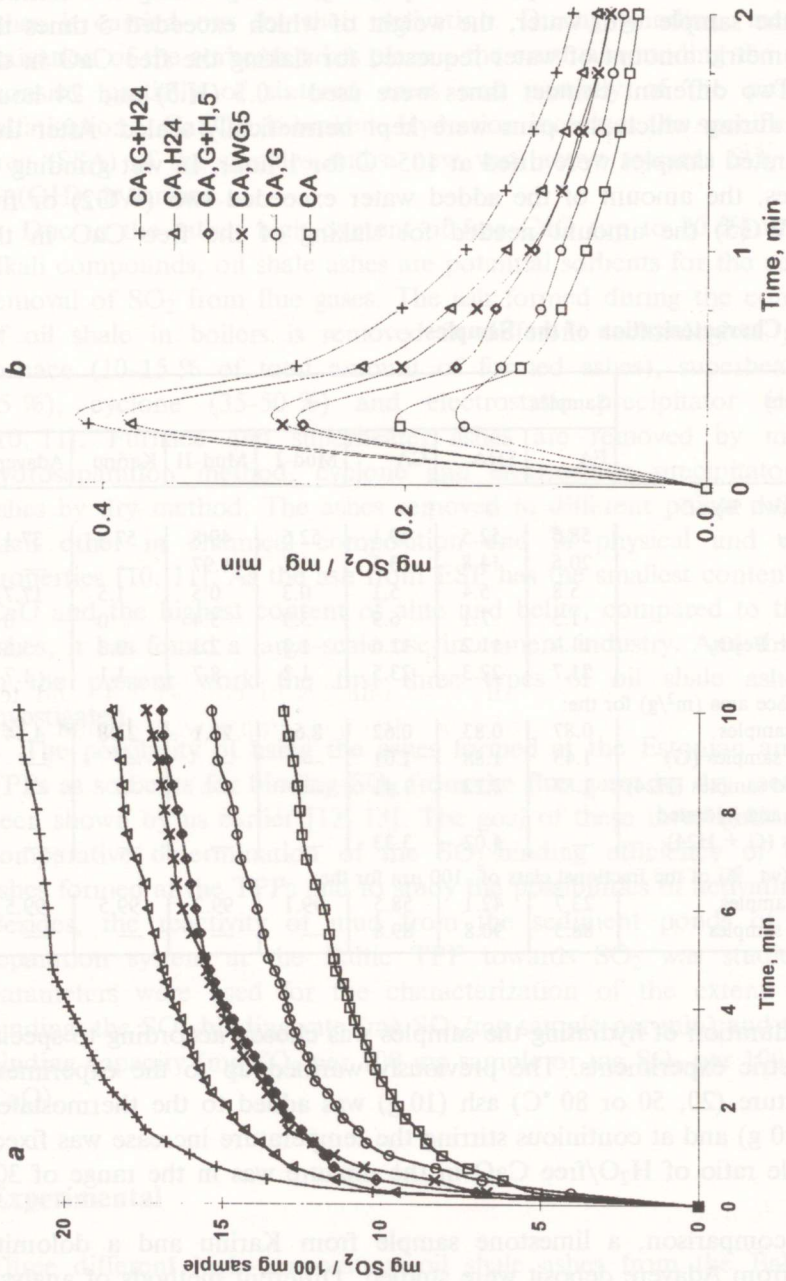


Fig. 1. SO<sub>2</sub> binding capacity (a) and binding rate (b) of the initial and activated samples of cyclone ash (CA) at 700 °C



The experiments for studying the  $\text{SO}_2$ -binding efficiency were carried out in Q-derivatograph (MOM, Hungary) in isothermal conditions in air- $\text{SO}_2$  mixture at temperatures 700-950 °C during 30 minutes. A plate type platinum crucible was used, the weight of the samples was 100 mg, the thickness of the sample layer 0.2-0.3 mm, the rate of the gas flow 270 ml per min and the  $\text{SO}_2$  partial pressure in the air- $\text{SO}_2$  mixture 190 mm Hg.

## Results and Discussion

The results of the experiments on hydration confirmed that the most active samples were those of FA, which had the greatest increase in temperature at hydration ( $\Delta T$ ). For fresh samples of FA the value of  $\Delta T$  at 20 °C was 14-21 °C, for CA and SHA 6-8 °C and it was achieved in 1-8 minutes, depending on the sample. For the samples stored for a longer period (> 3 months) the value of  $\Delta T$  was 3-5 °C and it was achieved in 1.5-2 hours. Previous grinding accelerated the slaking of the samples - the time for achieving the respective value of  $\Delta T$  decreased 1.2-1.5 times. The increase in the experiment temperature influenced the slaking of the samples differently: for FA the slaking rate increased 5-8 times, for CA and SHA it decreased. Obviously it was caused by the higher content of clinker minerals in CA and SHA.

For the initial sample of CA the  $\text{SO}_2$ -binding rate at the first seconds of contact between the solid and gaseous phases at 700 °C was 0.20 mg  $\text{SO}_2$ /mg sample per min. During two minutes of contact 9.4, and ten minutes of contact 13.1 mg  $\text{SO}_2$  per 100 mg sample were bound. This means that within 2 minutes already 72 % of the total amount of  $\text{SO}_2$  removed during 10-minute contact was bound (Fig. 1). Grinding increased the  $\text{SO}_2$ -binding capacity at two- and ten-minute contact to 11.4 and 16.8 mg  $\text{SO}_2$  per 100 mg sample, respectively, or 21 % and 15.3 % more than for the initial CA.

More effective than grinding was the previous hydrating of the samples. The effect of water treatment on the sample depends on the contact time between the solid and liquid phases. When the time was limited for 0.5 hour, the efficiency was practically at the same level as when CA,G was used. Extending the contact time to 24 hours increased the  $\text{SO}_2$ -binding rate to 0.38 mg  $\text{SO}_2$ /mg sample per min and the  $\text{SO}_2$ -binding capacity to 14.9 at two-minute contact. In this case the capacity of the bound at two-minute contact  $\text{SO}_2$  was 58 % higher than for the initial CA and 30 % higher than for CA,G. The best results were obtained using CA,G + H24 - the  $\text{SO}_2$ -binding rate increased to 0.41 mg  $\text{SO}_2$ /mg sample per min and the  $\text{SO}_2$ -binding capacity at 2- and 10-minute contact to 18.1 mg and 21.4 mg  $\text{SO}_2$  per 100 mg sample, respectively, or 93 % more than for CA and 59 % more than for CA,G.

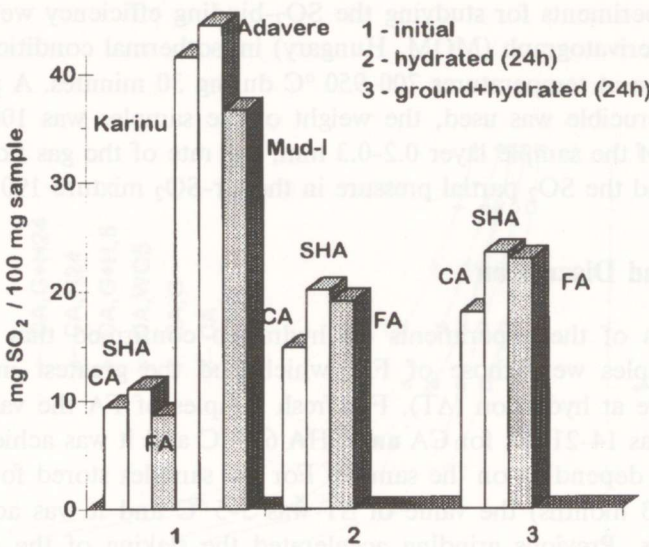


Fig. 2. The amount of SO<sub>2</sub> bound by different lime-containing materials at 700 °C at 2-minute contact

Wet grinding (WG5) of CA enhanced the SO<sub>2</sub>-binding rate to 0.28 mg/mg sample per min and increased the SO<sub>2</sub>-binding capacity at two-minute contact up to 13.1 mg SO<sub>2</sub>/100 mg sample, which exceeded the capacity of the initial sample by 40 %. These data were close to those achieved for CA,G +H0.5 sample - the SO<sub>2</sub>-binding rate was 0.27 mg SO<sub>2</sub>/mg sample per min and the SO<sub>2</sub>-binding capacity - 12.3 mg SO<sub>2</sub> per 100 mg sample. For CA activated by WG2 the SO<sub>2</sub>-binding rate and binding capacity obtained were approximately on the same level as in the case of CA,G or CA,H.5 samples.

Similar tendencies were observed by activation of the samples of SHA and FA (Fig. 2; Table 2). For the initial sample of SHA the SO<sub>2</sub>-binding rate was 0.27 mg SO<sub>2</sub>/mg sample per min and the SO<sub>2</sub>-binding capacity at two-minute contact - 11.1 mg SO<sub>2</sub> per 100 mg sample or 18 % more than for CA. Comparing the activated by a similar way samples of CA and SHA, the latter have an advantage of 22-36 %. For example, grinding of the samples increased the SO<sub>2</sub>-binding rate for SHA to 0.31 mg SO<sub>2</sub>/mg sample per min and the SO<sub>2</sub>-binding capacity at two-minute contact to 14.0 mg SO<sub>2</sub> per 100 mg sample or 26 % more compared to the initial SHA and 23 % more compared to the ground sample of CA. The best results were achieved, like for CA, by long-term (24h) hydration of SHA. The SO<sub>2</sub>-binding capacity increased in the case of SHA,H24 and SHA,G + H24 up to 20.1 and 23.5 mg SO<sub>2</sub> per 100 mg sample at two-minute contact or 80 and 110 % more than for the initial SHA. The advantage of these samples, compared to CA, was 35 and 30 %, respectively.



Table 2. SO<sub>2</sub>-binding Capacity (*A*, mg SO<sub>2</sub>/100 mg sample) and Binding Rate (*B*, mg SO<sub>2</sub>/mg sample min) of the Samples

Sample	<i>A</i>						<i>B</i>
	Time, min						
	0.5	1	2	5	10	30	0.25
700 °C							
CA	6.2	8.1	9.4	11.5	13.1	16.8	0.20
CA,G	6.8	9.7	11.4	13.5	15.3	19.3	0.16
CA,WG 2	6.4	9.8	10.5	12.7	13.8	18.6	0.15
CA,WG 5	10.1	11.8	13.1	15.5	16.9	19.5	0.28
CA,H 0.5	8.2	9.5	10.9	13.1	14.6	18.7	0.25
CA,H 24	11.4	13.4	14.9	17.0	18.5	21.6	0.38
CA,G+H 0.5	8.3	11.5	12.2	15.6	16.0	21.5	0.27
CA,G+H 24	13.6	16.0	18.1	20.4	21.4	24.2	0.41
SHA	8.7	9.9	11.1	13.3	14.5	18.6	0.27
SHA,G	9.9	11.9	14.0	16.2	18.6	23.0	0.31
SHA,WG 2	11.6	13.8	13.9	16.5	16.6	21.1	0.34
SHA,WG 5	11.3	15.2	17.3	20.8	23.0	27.0	0.33
SHA,H 0.5	8.9	11.4	13.2	16.1	16.5	20.4	0.30
SHA,H 24	15.3	18.0	20.1	22.2	24.1	27.0	0.40
SHA,G+H 0.5	13.4	16.6	16.7	19.6	20.5	26.8	0.33
SHA,G+H 24	17.4	21.1	23.5	25.5	27.4	29.9	0.47
FA	5.7	7.4	8.7	10.6	12.0	15.4	0.19
FA,H 24	14.4	17.2	19.1	21.5	23.5	26.3	0.41
FA,G+H 24	17.4	20.0	22.9	26.4	28.1	30.3	0.45
Karinu	23.0	34.6	41.5	47.2	52.2	57.4	0.45
Adavere	31.9	39.9	44.4	48.6	51.7	56.4	0.67
Mud-I	26.7	31.6	36.6	42.0	45.7	52.4	0.74
Mud-III	29.0	33.4	36.2	38.1	39.9	44.0	0.75
950 °C							
CA	3.3	5.2	7.3	10.6	13.7	19.5	0.08
CA,G	6.2	8.7	10.9	15.1	18.3	23.8	0.16
CA,WG 5	14.1	15.7	16.7	20.3	25.0	30.8	0.48
CA,H 24	13.2	15.8	18.2	21.3	24.1	30.5	0.44
CA,G+H 24	15.9	18.5	21.0	24.4	27.4	32.0	0.46
SHA	8.0	10.4	13.1	17.3	21.2	27.9	0.18
SHA,G	7.4	11.7	15.1	19.9	23.6	30.2	0.12
SHA,WG 5	14.3	17.1	19.8	22.9	26.4	32.5	0.44
SHA,H 24	15.6	18.7	20.9	23.9	26.4	31.4	0.44
SHA,G+H 24	23.7	28.0	31.0	34.5	37.6	42.0	0.65
Mud-I	23.2	42.1	47.3	51.4	55.4	64.0	0.29

that the temperature in the oil shale ash reaction point into the burning chamber or gas tract higher than 900-950 °C could not be recommended, as the SO<sub>2</sub>-binding efficiency of ashes would considerably decrease, especially during a short-time contact.

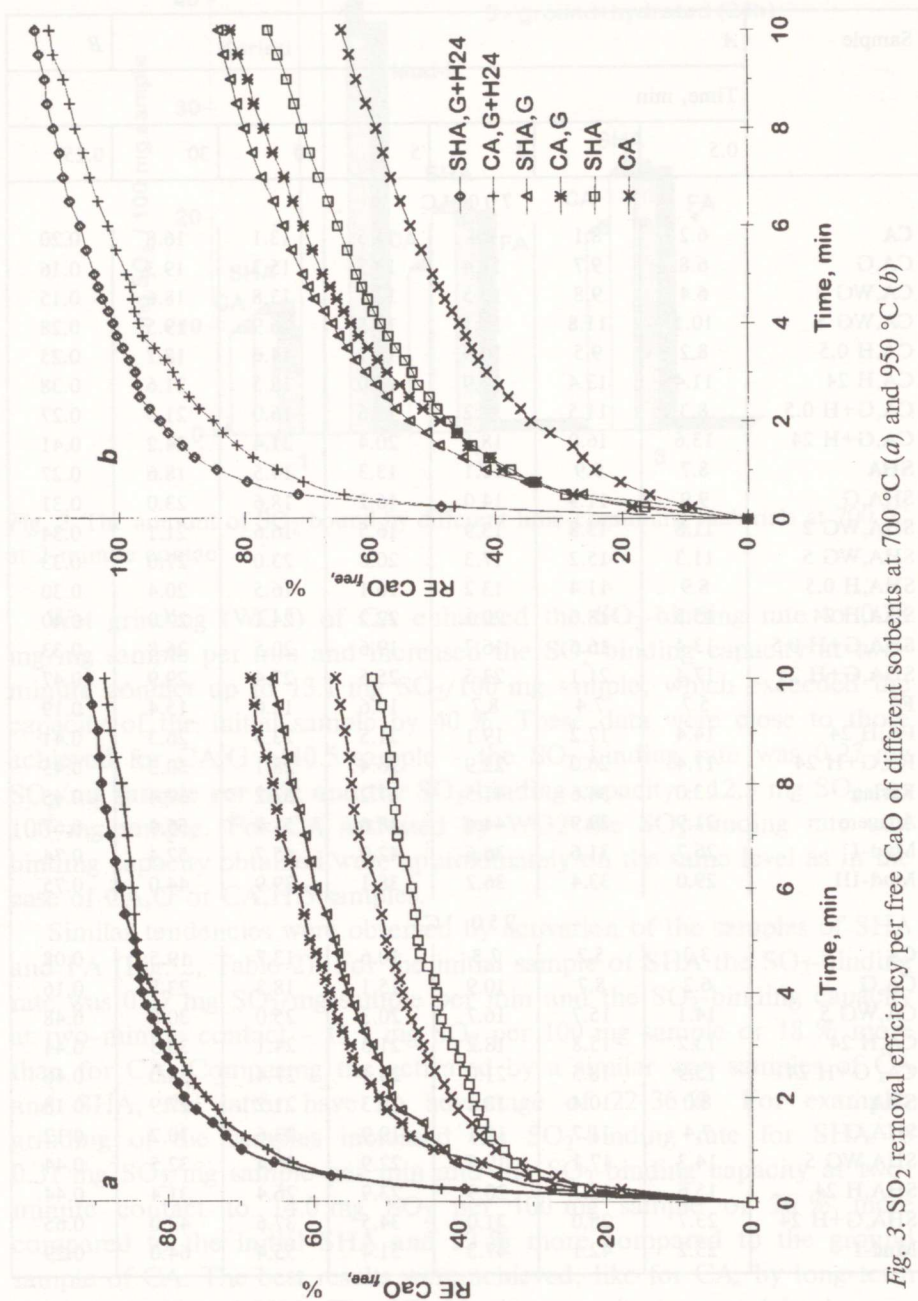


Fig. 3. SO<sub>2</sub> removal efficiency per free CaO of different sorbents at 700 °C (a) and 950 °C (b)



Due to the more coarse granulometrical composition of the initial sample of FA, 7.4 % less  $\text{SO}_2$  was bound than by CA - 8.7 mg  $\text{SO}_2/100$  mg sample. The hydration (24h) of FA increased the  $\text{SO}_2$ -binding capacity of the sample approximately 2 times - up to 19.1 mg per 100 mg sample, and previous grinding 2.5 times - up to 22.9 mg  $\text{SO}_2$  per 100 mg sample at two-minute contact. These data have an advantage of 27-31 %, compared to the results obtained for the corresponding samples of CA, and the  $\text{SO}_2$ -binding rate and capacity are at the same level as for the samples of SHA (Fig. 2; Table 2).

The behaviour of free CaO during heterogeneous interaction  $\text{SO}_2$ -ash is shown in Fig. 3. Considering the content of free CaO (as CaO and/or  $\text{Ca}(\text{OH})_2$ ) in different samples, the  $\text{SO}_2$ -binding capacity of free CaO at 10-minute contact between the solid and gaseous phases at  $700^\circ\text{C}$  was from 52-57 % in the initial to 90 % of the stoichiometric amount in the ground and hydrated samples (Fig. 3A) and at 30-minute contact from 65-73 % to 100 %, respectively. At  $950^\circ\text{C}$  these data were at 10-minute contact from 65-73 % in the initial samples to 110 % in the ground and hydrated samples (Fig. 3B) and at 30-minute contact from 90-100 % to 127-129 %, respectively. These data confirmed the results obtained previously [11, 12] that, beside free CaO, also the other alkali compounds present in ashes take part in the  $\text{SO}_2$ -binding process.

It was noticed that at  $950^\circ\text{C}$  during the first minutes of contact the ashes without previous hydration (initial samples and ground samples) bound less  $\text{SO}_2$  than at  $700^\circ\text{C}$ , which was caused by the decrease of SSA of the samples at the temperatures over  $900^\circ\text{C}$ . Prolongation of the contact time at  $950^\circ\text{C}$  to 2-3 minutes and more led the initial and ground samples of the ashes as well as the hydrated ones to bind more  $\text{SO}_2$  than at  $700^\circ\text{C}$ . Depending on the concrete ash and the treatment conditions of activation the advantage varied up to 1.45 times. For example, the  $\text{SO}_2$ -binding capacity of the initial SHA at 10-minute contact increased from 14.5 mg  $\text{SO}_2/100$  mg sample at  $700^\circ\text{C}$  to 21.2 mg  $\text{SO}_2/100$  mg sample at  $950^\circ\text{C}$  or 46 % more  $\text{SO}_2$  was bound than at  $700^\circ\text{C}$ . For the ground and hydrated SHA these data were 27.4 and 37.6 mg  $\text{SO}_2$  per 100 mg sample, respectively, or 37.2 % more  $\text{SO}_2$  than at  $700^\circ\text{C}$ . For the initial sample of SHA the  $\text{SO}_2$ -binding rate at  $950^\circ\text{C}$  at the first seconds of contact was 0.18 mg  $\text{SO}_2/\text{mg}$  sample per min compared to 0.27 mg  $\text{SO}_2/\text{mg}$  sample per min at  $700^\circ\text{C}$  and for the ground and hydrated sample of SHA 0.65 and 0.47 mg  $\text{SO}_2/\text{mg}$  sample per min, respectively (Fig. 4; Table 2).

Thus, the results of the experiments obtained at  $950^\circ\text{C}$  demonstrated that the temperature in the oil shale ash injection point into the burning chamber or gas tract higher than  $900\text{-}950^\circ\text{C}$  could not be recommended, as the  $\text{SO}_2$ -binding efficiency of ashes would considerably decrease, especially during a short-time contact.

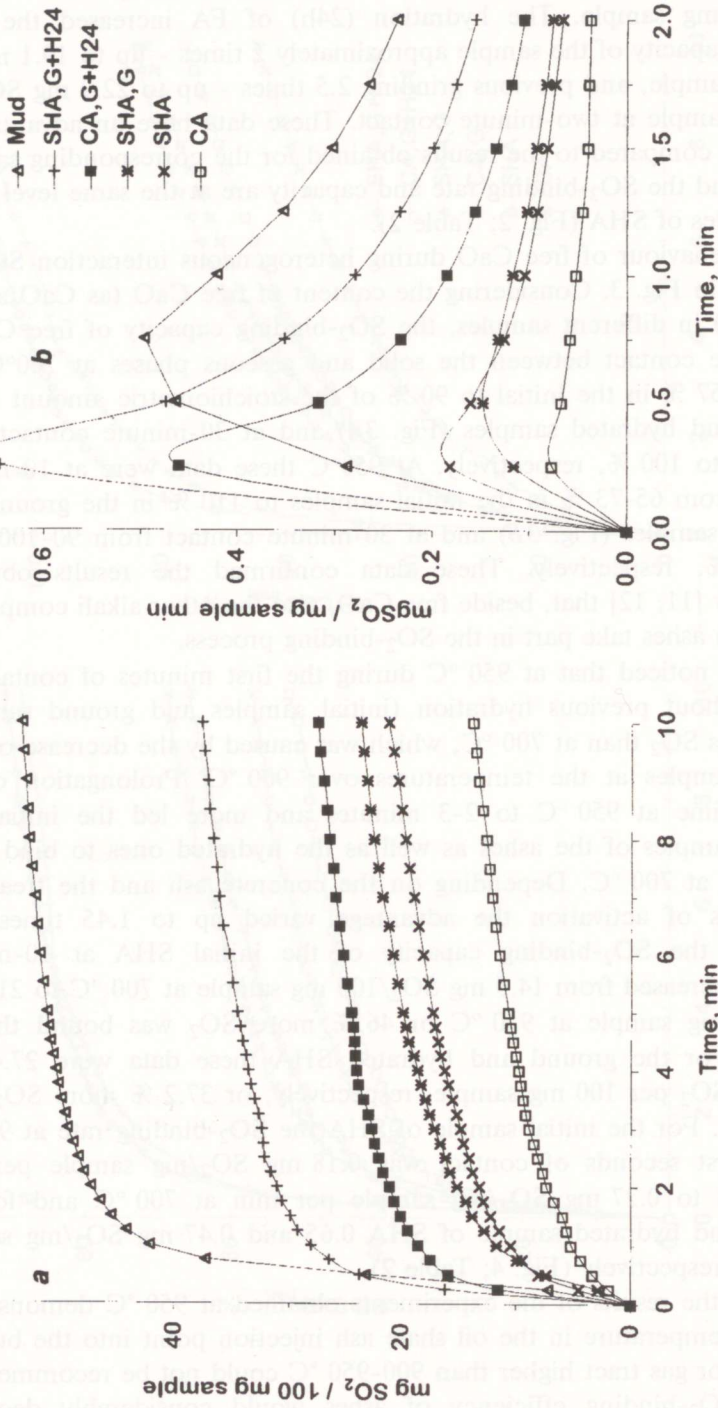


Fig. 4. SO<sub>2</sub> binding capacity (a) and binding rate (b) of different sorbents at 950 °C



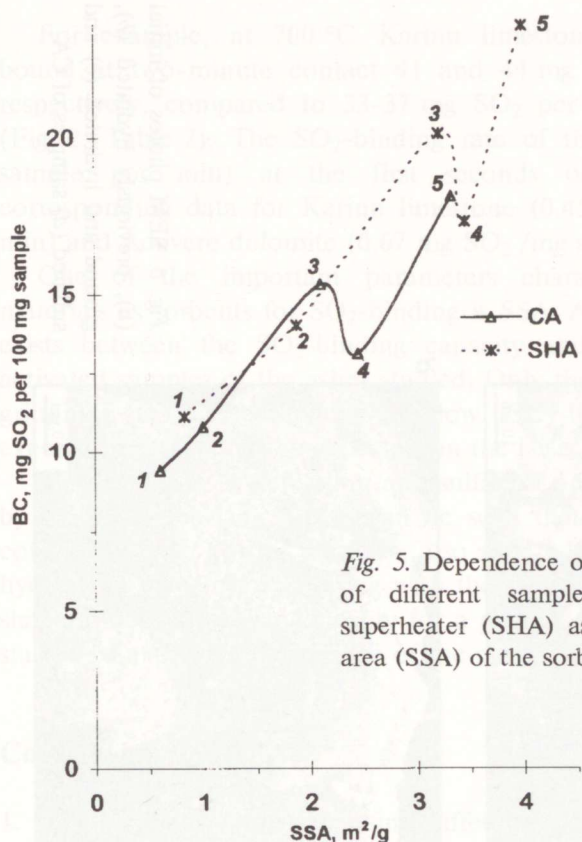


Fig. 5. Dependence of SO<sub>2</sub>-binding capacity (BC) of different samples of cyclone (CA) and superheater (SHA) ashes on the specific surface area (SSA) of the sorbent

Dried muds from the sediment ponds of the hydraulic ash separation system are very effective sorbents towards SO<sub>2</sub>. The SO<sub>2</sub>-binding rate at 700 °C at the first seconds of contact was 0.74 mg SO<sub>2</sub> per 100 mg sample and the SO<sub>2</sub>-binding capacity at two-minute contact was 36.6 mg SO<sub>2</sub> per 100 mg sample, which exceeded the corresponding data for the initial CA and SHA 3.9 and 3.3 times and for ground and hydrated CA and SHA 2 and 1.6 times, respectively (Fig. 2; Table 2). At 950 °C at two- and ten-minute contact 47.3 and 55.4 mg SO<sub>2</sub> per 100 mg sample was bound or 31 and 17 % more SO<sub>2</sub> than at 700 °C, respectively. At 950 °C the SO<sub>2</sub>-binding capacity of the muds exceeded that of the ground and hydrated samples of CA 2.5 times and of SHA 1.9 times (Fig. 4; Table 2). The high reactivity of the muds is caused by their fine granulometric composition, high SSA and the content of very active compound towards SO<sub>2</sub>-binding - Ca(OH)<sub>2</sub> (Table 1). The reactivity of muds is comparable to the reactivity of natural Estonian dolomites and limestones [14].

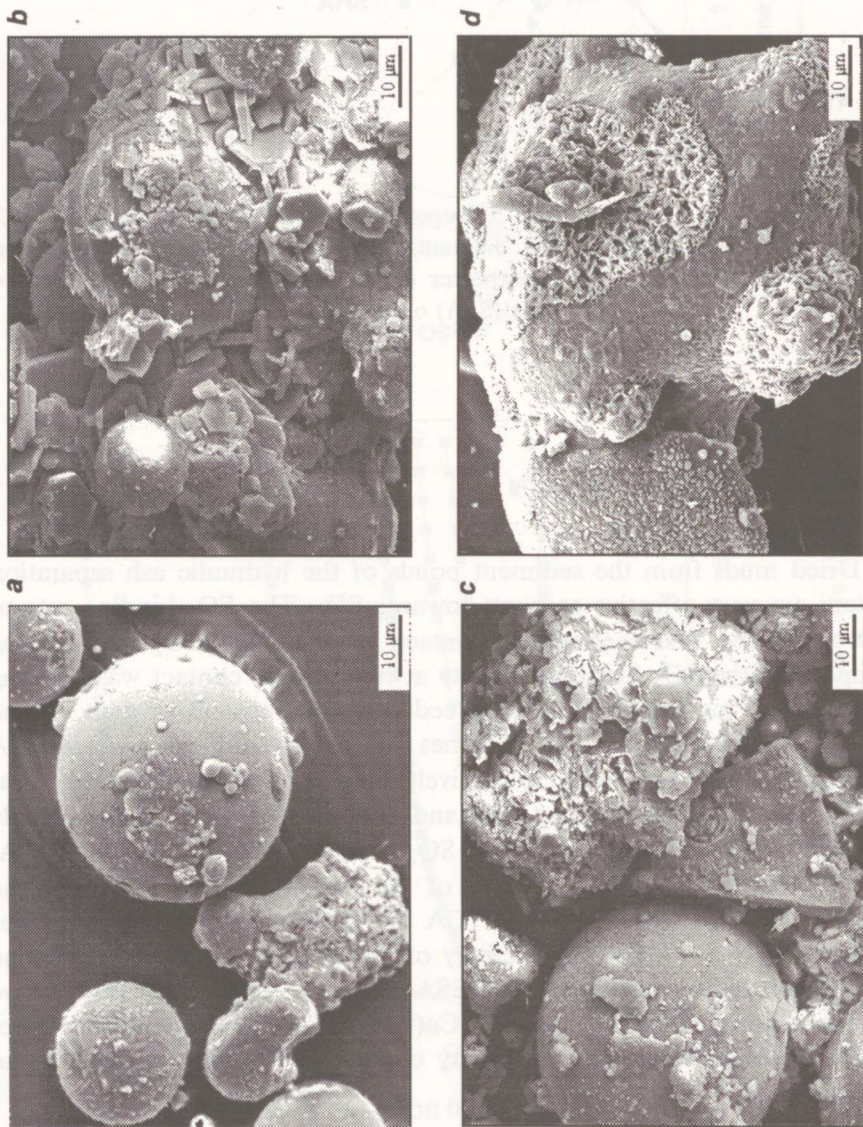


Fig. 6. SEM photos of initial (a), previously hydrated (b), ground and hydrated (c) and sulfated (d) samples of CA



For example, at 700 °C Karinu limestone and Adavere dolomite bound at two-minute contact 41 and 44 mg SO<sub>2</sub> per 100 mg sample, respectively, compared to 33-37 mg SO<sub>2</sub> per 100 mg sample by muds (Fig. 2; Table 2). The SO<sub>2</sub>-binding rate of the mud (0.74 mg SO<sub>2</sub>/mg sample per min) at the first seconds of contact exceeded the corresponding data for Karinu limestone (0.45 mg SO<sub>2</sub>/mg sample per min) and Adavere dolomite (0.67 mg SO<sub>2</sub>/mg sample per min).

One of the important parameters characterizing lime-containing materials as sorbents for SO<sub>2</sub>-binding is SSA. A well observed correlation exists between the SO<sub>2</sub>-binding capacity and SSA of the initial and activated samples of the ashes studied. Only the samples activated by wet grinding had a comparatively low SO<sub>2</sub>-binding capacity in our experiments, as could be expected on the basis of the SSA data (Fig. 5).

The influence of activation and sulfation processes has been visualised by SEM studies (Fig. 6). It can be seen that the initial sample of CA contains, beside porous particles, also sintered particles (Fig. 6a). During hydration (Fig. 6b) or grinding with the following hydration (Fig. 6c) the shape and fracture changed only for a part of the particles. The sulfation started primarily on the surface of the particles (Fig. 6d).

## Conclusions

1. It has been shown that using different methods of activation of the HTAs formed at the Baltic TPP it is possible to increase the SO<sub>2</sub>-binding capacity of the initial samples (their SO<sub>2</sub>-binding capacity at 2-minute contact was in the range of 7.6-14.5 mg SO<sub>2</sub> per 100 mg sample) up to 2 times. Dry grinding increased the SO<sub>2</sub>-binding capacity of the samples by 15-25 %, wet grinding and dry grinding with the following short-time (0.5h) hydration 30-50 %, long-time (24h) hydration 60-80 % and grinding with the following long-time hydration 90-110 %.
2. An increase in the temperature from 700 to 950 °C corresponds to the increase in the SO<sub>2</sub>-binding capacity of the samples and, depending on the concrete sample, the raise was 10-45 %. During the first two minutes contact between the solid and gaseous phases 70-90 % of the total amount of SO<sub>2</sub> removed in 10 minutes was bound. A good correlation between SSA and the SO<sub>2</sub>-binding capacity of the samples was observed.
3. Previously dried muds from the sediment ponds of the hydraulic ash separation system bound 3.3-3.9 times more SO<sub>2</sub> (in 2-minute contact 33-48 mg SO<sub>2</sub> per 100 mg sample) compared to the initial samples of HTA and 1.6-2 times more compared to the ground and hydrated samples of HTA. The SO<sub>2</sub> removal efficiency of the muds is

- comparable to that of the samples of natural limestones and dolomites used.
4. The results of these experiments confirm good possibilities for using the oil shale ashes and muds in recycle to reduce the SO<sub>2</sub> pollution during high-temperature combustion of powdered Estonian oil shale at the Estonian and Baltic Thermal Power Plants.

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## Introduction

A number of physical and chemical indicators of ash reactivity are required in considering its use as a sorbent for sulfur dioxide. Experimental investigations have shown that the effect of dust may be both positive and negative [1], depending on the type of dust and its composition. In this respect, the level of its deposition, and meteorological conditions

Dust aimed by the burning material industry is classified as non-essential dust or only relatively low reactivity. Some other authors have recommended the use of limestone or dolomite as sorbents for sulfur dioxide [2, 3]. Since the reactivity of limestone and dolomite is low, the use of these materials as sorbents is not recommended [4].