

DECARBONIZATION OF NATURAL LIME-CONTAINING MATERIALS AND REACTIVITY OF CALCINED PRODUCTS TOWARDS SO₂ AND CO₂

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Abstract

The results obtained by studying decarbonization of different samples of Estonian limestone and dolomite and the following sulphation or carbonation of calcined products to estimate their SO₂ and CO₂ binding ability were presented. Experiments were carried out with thermogravimetric equipment (Q-Derivatograph, MOM and Labsys™, SETARAM) - calcination of the samples in the atmosphere of air with the heating rate 10 K per minute using multiplate crucibles, the following sulphation or carbonation of the calcined products after cooling to the fixed temperature (temperature range 400–900°C) under isothermal conditions in the flow of air-SO₂ or air-CO₂ mixture. Chemical, X-ray, BET nitrogen dynamic desorption, etc. methods for the characterization of the initial samples, intermediate and final products were used.

In addition, the possibilities of recurrent use of oil shale ashes taken from different technological points at operating thermal power plants (Estonian and Baltic TTPs, Estonia) as sorbents for SO₂ binding from gaseous phase were studied, as well as the possibilities of activation of these ashes towards SO₂ binding.

The results of these studies confirmed the high reactivity of Estonian limestone and dolomite towards SO₂ and CO₂. Dependence of SO₂ binding mechanism on the SO₂ concentration has been established. Modelling of SO₂ capture of dolomite and limestone was carried out to establish the kinetic parameters of these processes. The possibilities of activation of oil shale ashes and their effective recurrent use for binding SO₂ and CO₂ from gaseous phase were confirmed.

Keywords: air pollution, carbon dioxide, dolomite, limestone, oil shale, oil shale ash, sulphur dioxide

Introduction

The intensive use of fossil fuels in energy production causes the pollution of the atmosphere with SO₂, CO₂, NO_x and other toxic and environmentally unfriendly compounds. To remove the acidic compounds from flue gases, preferably SO₂, the most common sorbents used are lime-containing materials: natural limestone and dolomite, their derivatives and industrial materials – ashes that contain free calcium and magnesium oxides [1–6].

Estonia is rich in limestone and dolomite resources – their explored resources are estimated to be 200–250 million m³, but their technological use is confined to the

cement and glass industries and the production of lime [13, 14]. However, about 20 000 tons per year of calcite of Vasalemma deposit is exported for cleaning flue gases in Finland.

Energy production in the Republic of Estonia is based on the burning of low quality local solid fuels – Estonian oil shale (OS). This accounts for 67% of the Estonian primary energy and 98% of the electricity production in Estonia is based on the use of OS [7–9]. About 90% of the OS based energy is produced at two big thermal power plants (TPP) – Estonian and Baltic ones, which are the major air polluters with SO₂ and CO₂ in the Baltic Sea region. These TPPs are operated on the combustion technology based on pulverized firing (PF) of OS at atmospheric pressure at temperatures 1200–1400°C. The ashes formed during the combustion of OS in boilers (high-temperature ashes – HTA) are removed in different technological points – furnace (furnace or bottom ash – FA; 10–15% of total ash formed), superheater (SHA, 15–25%), cyclone (CA, 35–50%) and electrostatic precipitator (ESPA, 15–20%) [10, 11]. The ashes removed differ from each other in chemical composition and in physical and chemical properties [10,11]. They contain 15–25% of free CaO (as free CaO or/and Ca(OH)₂) and are potential sorbents for the recurrent use for binding SO₂ and other acidic compounds from flue gases [2–5, 12], independently either in or without combination with dolomites and limestone.

The aim of the present work was a comparative determination of the SO₂ and CO₂ binding efficiency of calcined Estonian limestone and dolomite from different deposits and different oil shale ashes formed at exploited TPPs as well as ashes formed in a fluidized bed conditions (CFBC, low-temperature ashes – LTA, at 800–850°C). Also, the possibilities of activation of ashes were studied. An attempt to calculate the parameters of calcination and sulphation of the calcinated limestone and dolomite samples was made.

Experimental

Materials

About 50 samples of limestone and dolomite from different Estonian deposits and 30 samples of ashes from different technological points formed during PF or CFBC oil shale were studied. Samples that were more closely under investigation in this work are presented in the Table: dolomite from Hellamaa, Pajusi and Adavere deposits, limestone from Karinu and Maardu deposits. FA, SHA, CA, ESPA as well as hydrotransported ash from open air deposit (wet ash – WA) and mud (M) from the transport-water sedimentation pond (by X-ray data the mud contains a noticeable amount of secondary calcium and magnesium carbonates), all these from the Baltic TPP and furnace ash (LFA) formed in the 1MW-th Ahlström Pyroflow test facility in Hans Ahlström Laboratory (Karhula, Finland) were used. The activation of ashes was carried out by grinding (G) or by grinding and subsequent hydrating of the samples (G+H) [12].

Table 1 Main characteristics of the samples

Parameters	Samples											
	Oil shale ashes						Dolomites			Limestone		
	FA	SHA	CA	ESPA	WA	Mud	LFA	Hellamaa	Adavere	Pajusi	Maardu	Karinu
Content (mass%) of:												
CaO _{total}	54.9	52.5	49.1	36.5	42.0	52.6	45.0	28.8	37.1	25.3	49.3	52.6
CaO _{free} for												
initial samples	20.8	14.8	13.1	10.6	5.5	1.1	23.8	–	–	–	–	–
activated samples (G)	22.7	23.6	18.7	–	–	–	30.0	–	–	–	–	–
MgO	5.7	5.4	5.1	–	–	0.3	9.4	25.5	17.7	18.4	2.3	1.5
SO ₄ ²⁻	4.5	7.1	6.9	8.8	0.9	3.9	18.4	0.5	0.0	1.4	1.1	0.0
Al ₂ O ₃ +Fe ₂ O ₃	10.3	11.2	12.6	10.5	7.8	1.3	6.5	0.6	0.8	1.4	1.6	0.3
SiO ₂	21.1	22.3	23.5	36.5	19.8	1.2	12.9	0.5	1.7	19.3	4.4	1.1
Mole ratio of MgO/CaO	–	–	–	–	–	–	–	1.24	0.67	1.02	0.07	0.04
BET surface area (m ² g ⁻¹) for the												
initial samples	0.76	0.83	0.62	0.45	7.40	8.64	1.91	0.91	5.10	2.19	2.71	2.98
activated samples	4.84	4.02	3.33	–	–	–	3.87	–	–	–	–	–
Content (mass%) of the fractional class –45 μm for the												
initial samples	23.7	42.1	58.5	98.3	28.1	99.1	3.1	100	99.5	100	99.6	99.5
activated samples	89.3	90.8	89.8	–	–	–	92.3	–	–	–	–	–

Methods

The experiments were carried out with thermogravimetric equipment (Q-Derivatograph, MOM), calcination at dynamic heating conditions (10 K min^{-1}) in the atmosphere of air, sulphation or carbonization at isothermal conditions (temperature interval $400\text{--}900^\circ\text{C}$) in the atmosphere of SO_2 -air or CO_2 -air mixture.

The calcination was performed by heating up to 900°C in order to achieve a constant mass of the sample, when necessary, the sample was then cooled down to the required temperature, after which the air enriched with SO_2 or CO_2 was led to the reaction chamber. Multiplate Pt crucibles were used, thickness of the sample layer was $0.2\text{--}0.3 \text{ mm}$, sample mass about 100 mg , rate of gas flow 270 ml min^{-1} and partial pressure of SO_2 or CO_2 in the gas mixture 190 mm Hg .

Three parameters were used to characterize the extent of interaction: the SO_2 (CO_2) binding capacity (mmol or mg of SO_2 (or CO_2) per 100 mg sample), SO_2 (CO_2) binding rate (mmol or mg of SO_2 (CO_2) per $\text{mg sample}\cdot\text{min}^{-1}$) and SO_2 (CO_2) binding efficiency (%) per content of total CaO and MgO (CaMgO), or for ash samples per content of free CaO. The results of the TG investigations of the samples of Estonian limestone and dolomite were used to determine the reaction mechanism of calcination and sulphation of them.

Different methods of analysis for the characterization of initial samples as well as of treated products (chemical, BET nitrogen dynamic desorption, X-ray, IR-spectroscopy, etc.) were used.

Results and discussion

The characteristic TG and DTG curves of limestone and dolomite decomposition during dynamic heating in air with the following carbonization or sulphation of the calcined product under isothermal conditions in air- SO_2 (CO_2) mixture are presented in Figs 1 and 2, respectively.

Different samples of dolomite studied bound CO_2 (and SO_2) quite differently. For example, at 700°C the dolomite sample of Hellamaa deposit (very few impurities, mole ratio of $\text{MgO}/\text{CaO}=1.24$, but with low specific surface area $\text{SSA}=0.91 \text{ m}^2 \text{ g}^{-1}$) bound CO_2 from gas phase in the first seconds of contact very intensively – 0.50 mmol CO_2 per 100 mg sample during $45\text{--}60 \text{ s}$ (about 90% from the total amount of CO_2 bound). The process stopped in ten min, when 0.58 mmol of CO_2 was bound or 67.6% of total CaO was utilized (Fig. 2). Analogically, but not so intensively CO_2 was bound by Pajusi dolomite (high content of SiO_2 – 19.3%, $\text{MgO}/\text{CaO}=1.02$, $\text{SSA}=2.19 \text{ m}^2 \text{ g}^{-1}$) – during 2 and 10 min of contact it was bound 0.40 and 0.46 mmol of CO_2 per 100 mg sample or 49.0 and 57.2% of total CaO was utilized. Quite differently CO_2 was bound by Adavere dolomite (pure, but $\text{MgO}/\text{CaO}=0.67$ and $\text{SSA}=5.1 \text{ m}^2 \text{ g}^{-1}$) – in 2 min contact as well as in case of Pajusi dolomite it was bound 0.41 mmol of CO_2 per 100 mg sample, but only 36.2% of total CaO contained took part in the binding up to then and the process stopped in 20 min (0.64 mmol of CO_2 or 55.9% of total CaO) (Fig. 2).

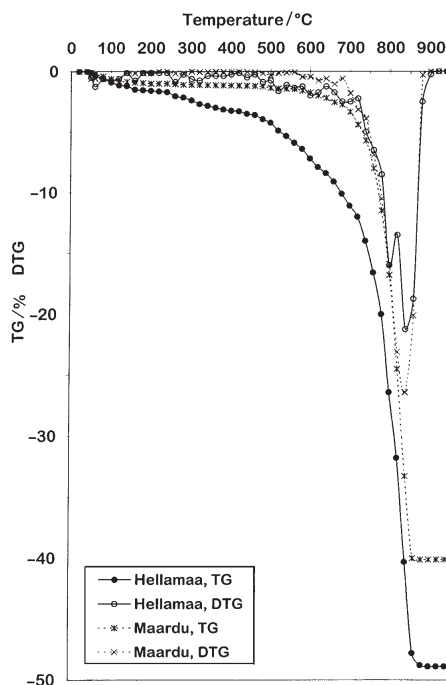


Fig. 1 TG and DTG curves of Hellamaa dolomite ($m=108.5$ mg) and Maardu limestone ($m=103.7$ mg): 10 K min^{-1} in the flow of air, plate crucibles

So, as only CaO, and not MgO contained in dolomite took part in the binding of CO_2 then, the higher the mole ratio of MgO/CaO in the sample and the lower the SSA of the sample are, the faster the binding of CO_2 stopped resulting in the formation of CaCO_3 shell on the surface of the particles, hindering the later diffusion of CO_2 into the grains of sample.

Results of X-ray analysis of the carbonization products of dolomite samples confirmed that MgO, formed during calcination of dolomites, did not take part in the binding of carbon dioxide – the only product of the carbonization of calcined dolomites was CaCO_3 .

Limestone did not bind CO_2 as actively in the first minutes of contact as dolomite and the binding was not completed in 30 min of contact. For example, in case of limestone from Karinu and Maardu deposits in 2 min contact it was bound 0.38 (16.9% of total CaO) and 0.28 mmol (18.6% of total CaO) of CO_2 and in 30 min contact 0.89 mmol (51.3% of total CaO) and 0.73 mmol (49.2% of total CaO) of CO_2 per 100 mg sample, respectively (Fig. 2).

For both types of samples – dolomite and limestone – impurities influence the binding of CO_2 : increasing the content of impurities decreased the CO_2 binding rate as well as the BC of the samples.

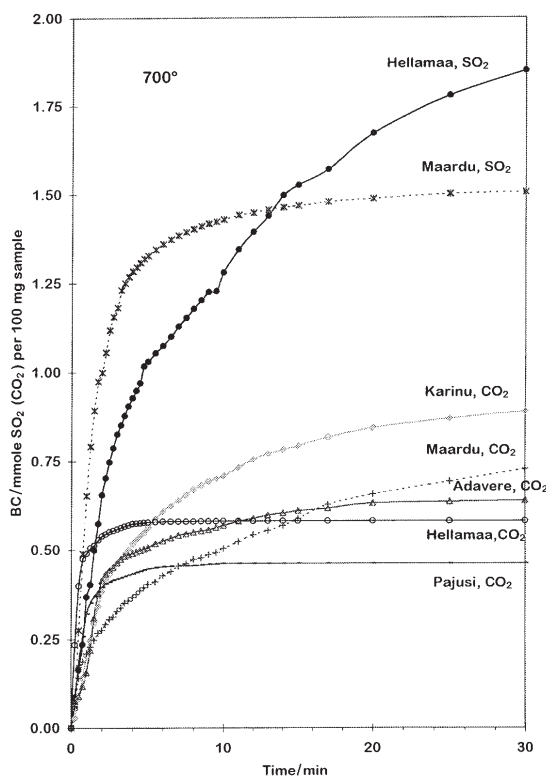


Fig. 2 SO₂ and CO₂ binding curves of Hellamaa, Adavere and Pajusi dolomites and Maardu and Karinu limestones at 700°C

In the binding of SO₂ both MgO and CaO took part and the results obtained in the temperature interval from 400 to 900°C confirmed that the SO₂ binding capacity of the samples increased for all the samples studied when the temperature was increased, but as a rule, it was considerable at 700°C and above (Fig. 3A). At 900°C there were observed some changes in the SO₂ binding rate – it was lower than at 700–800°C during the initial period of contact (30–120 s), especially, when using dolomite samples (Fig. 3B). Considering the content of CaO and MgO in the samples, at 700–900°C up to 80–95% of it took part in the binding of SO₂ from gas phase (Fig. 3C).

X-ray data confirmed that at 500°C after 30 min of contact when using samples of limestone the main products of sulphation were CaSO₄ (anhydride) and γ -CaSO₄. Also, the formation of CaSO₃ was observed. At 700°C, besides CaSO₄ and γ -CaSO₄ traces of CaS were identified, but not CaSO₃, which might be the result of the following transformations [15–18]:



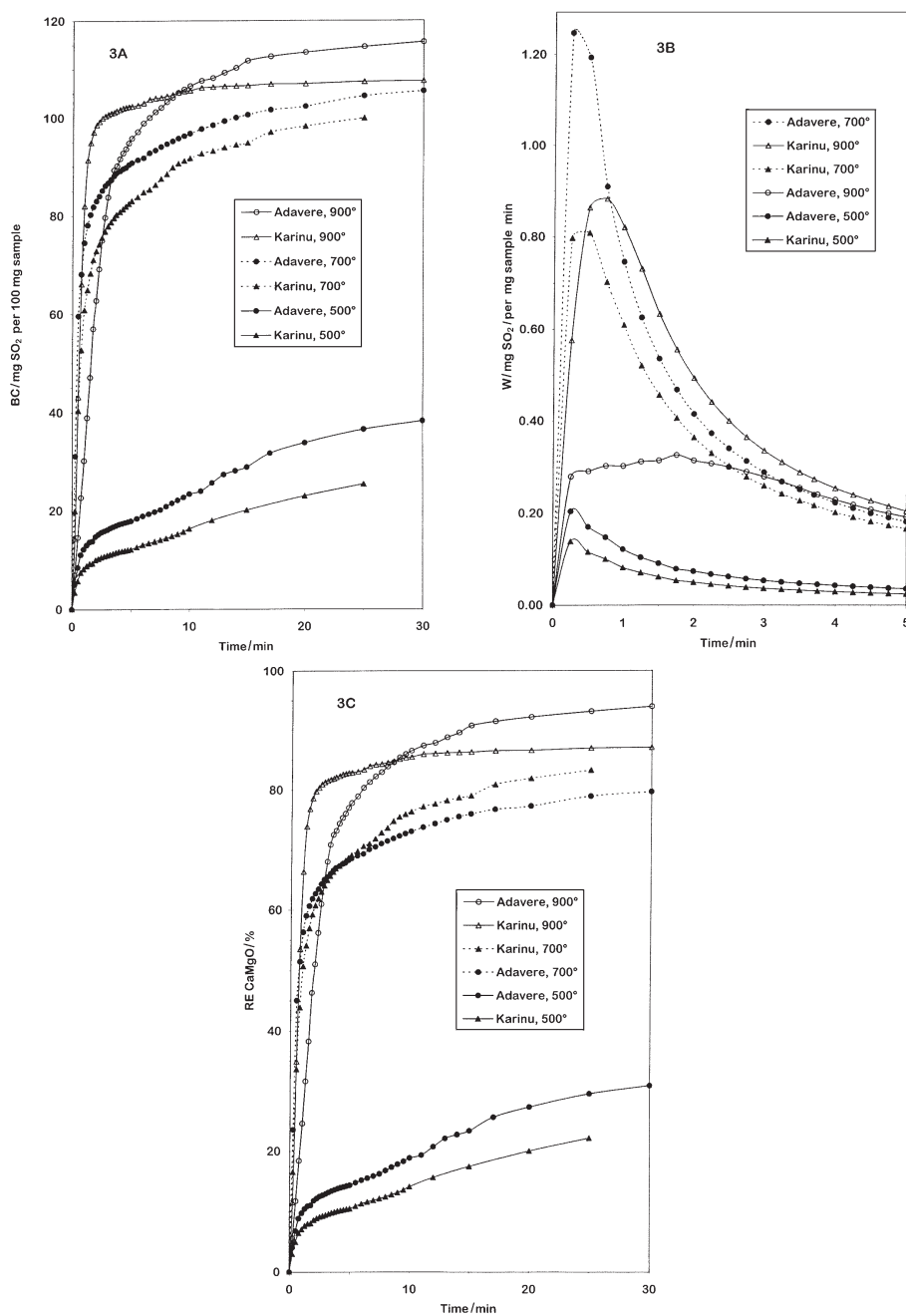


Fig. 3 Dependence of SO₂ binding capacity (*BC*) (3A), SO₂ binding rate (*W*) (3B) and SO₂ removal efficiency per the content of total CaO and MgO in samples (RE CaMgO) (3C) of Adavere dolomite and Karinu limestone on temperature



At 900°C the only sulphur-containing product was CaSO₄ and some amount of CaO, the formation of which might be explained by the following reactions [18]:



When using samples of dolomite, the main products of sulphation at 500 and 700°C were CaSO₄, CaMg₃(SO₄)₄ and γ-CaSO₄. At 900°C – CaSO₄ and CaMg₃(SO₄)₄. At 700°C also traces of MgO were present, whereas at 900°C the replicas at X-ray diffractograms characterizing MgO were more intensive than these at 700°C, which might be explained by the beginning of decomposition of CaMg₃(SO₄)₄ at higher temperatures.

It must be pointed out that carrying out the sulphation of dolomite samples from Hellamaa and Pajusi deposit during 30 min at 700°C in the gas atmosphere, which contained 100 ppm of SO₂, the products of sulphation identified by X-ray analysis were CaSO₄ and γ-CaSO₄. CaMg₃(SO₄)₄ was not identified. By using the limestone sample of Karinu deposit the product of sulphation was CaSO₄ and in case of the sample of pure MgO (99.6%) – β-MgSO₄. It means, that during sulphation of dolomite samples in a gas atmosphere with a low SO₂ concentration, SO₂ preferably reacts with CaO (not with MgO) forming a CaSO₄ shell on the surface of particles, which hinders the diffusion of SO₂ into the particles.

Comparing the CO₂ and SO₂ binding capacities of limestone and dolomite (at 700°C, after 30 min of contact), the *BC* of SO₂ for dolomite samples studied was 2.5–3 times higher than the *BC* of CO₂ and for limestone samples 1.8–2 times higher. The first possible reason is that MgO does not take part in the binding of CO₂ and the second that the CaCO₃ shell formed on the surface of particles hinders the diffusion of CO₂ into the particle more than CaSO₄–CaMg₃(SO₄)₄ shell the diffusion of SO₂.

Figure 4 presents the results of investigation of the reactivity of different wastes formed at an OS firing power plant, including the activated forms of ashes and, for comparison, ashes formed by using CFBC technology as well as calcined dolomite and limestone samples from Adavere and Karinu deposits. The SO₂ binding capacity was used as a parameter of comparison. At 700°C and 2 min of contact between the solid and gaseous phases, the initial samples of HTA bound 9.6–10.9 mg SO₂ per 100 mg sample and the initial samples of LFA and WA 17.3 and 21.8 mg SO₂ per 100 mg sample, respectively, or 1.6 and 2.1 times more than HTAs. Previous activation of LFA by grinding, as well as activation of HTA by grinding and subsequent hydration, increased the *BC* of the ashes approximately two times – up to 32.6 and 23.0 mg of SO₂ per 100 mg sample, respectively. The *BC* of M (36.5 mg of SO₂ per 100 mg sample) is comparable to the *BC*s of natural limestone and dolomite (41.0 and 44.2 mg of SO₂ per 100 mg sample, respectively) (Fig. 4).

So, the reactivity of wastes formed at the operating TPPs depends on the technological point of their removal, dry ashes can be activated towards acidic compounds in the gas phase, wet ashes are already activated and carbonaceous mud is highly re-

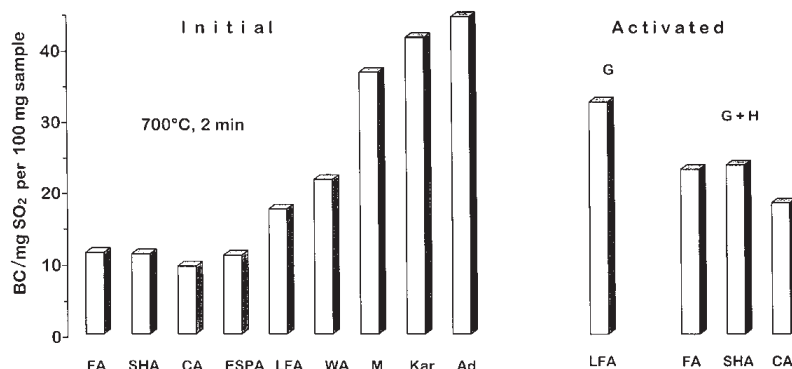


Fig. 4 SO₂ binding capacity (*BC*) of different lime-containing materials at 700°C after 2-min contact (Legend: FA – furnace ash, SHA – superheater ash, CA – cyclone ash, ESPA – electrostatic precipitator ash, LFA – low-temperature FA, WA – wet ash, hydrotransported ash from open air deposit, M – mud from the transport-water sedimentation pond; G – ground, G+H – ground+hydrated)

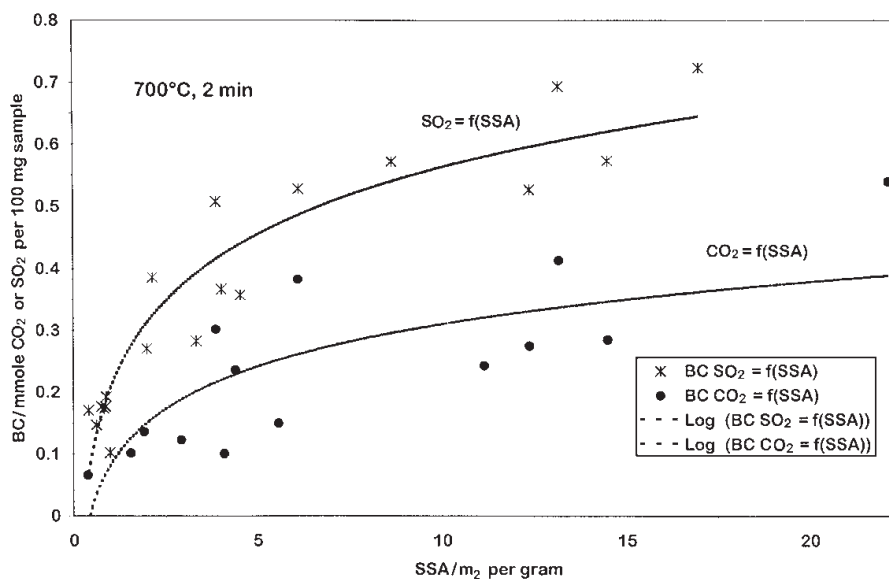


Fig. 5 Dependence of CO₂ and SO₂ binding capacity (*BC*) of different lime-containing materials on specific surface area (*SSA*) of samples after 2-min contact at 700°C

active towards these compounds. Higher binding ability of WA and M could be explained also by their higher *SSA*, the activation of ashes increased the *SSA* of the samples as well (Table). The influence of *SSA* of the samples studied on the binding of CO₂ and SO₂ is well demonstrated in Fig. 5.

Mathematical modelling of sulphur capture

Several experiments were carried out in a mixture of 15% of CO₂ and air at dynamic heating conditions to obtain kinetic parameters for the limestone and dolomite decomposition reactions. Activation energy (E_A) for CaCO₃ and MgCO₃ decomposition was determined by Ozawa method [19] using three runs with 2, 5 and 10 K min⁻¹ heating rates. For limestone samples, the values of E_A of CaCO₃ decomposition in these conditions were in the range of 514–577 kJ mol⁻¹. For dolomite samples, the values of E_A for CaCO₃ decomposition were higher 723–750 and the values of E_A for MgCO₃ decomposition were in the range of 450–458 kJ mol⁻¹.

Sulphation of several different limestone and dolomite samples (particle size 125–160 μm) was carried out isothermally at 850°C in a gas mixture of 4% O₂, 15% CO₂, 0.5% SO₂ and N₂ at 1 or 15 bar pressure using a pressurized TG equipment (DMT, Germany). An attempt was made to apply an unreacted shrinking core (USC) model with variable effective diffusivity to the CaO and CaCO₃ sulphation data [20, 21]. In this extended model diffusion inside the sorbent particle has been made conversion dependent and it includes two sequential processes: diffusion in pores and diffusion through the product layer.

It was shown that at atmospheric pressure sulphation starts at a high speed (values of the rate constants 2–90 cm s⁻¹) and in 200–300 s up to 25–44% of conversion was achieved. Then a sharp shift from chemical kinetics control to intra-particle diffusion control was observed. Although special sample holders and high flow rates were used to diminish the external mass transfer limitations, the obtained values for the rate constants due to the extremely high reactivity of the calcined limestone should be treated with certain caution. Under 15 bar pressure the initial sulphation rates were significantly lower (values of the rate constants 0.02–0.1 cm s⁻¹) and the shift from chemical kinetics control to diffusion control took place at remarkably lower conversion values, especially for the limestone samples. Under pressure, the increase in the degree of conversion of CaO or CaCO₃ into CaSO₄ during the second hour of experiment was remarkably higher compared to the values obtained at atmospheric pressure. The increase in the intra-particle diffusion resistance predicted by the extended USC model was higher than in the real process, especially in the experiments at atmospheric pressure. Therefore, in this case the modelling was carried out in two steps, assuming that up to a certain degree of conversion the sulphation process was not diffusion controlled. The extended USC model was successfully applied to the sulphation data obtained under pressure. Calculated product layer diffusivities were in the range of 3.2·10⁻¹⁰–3.7·10⁻⁹ m² s⁻¹ and the final values of the degree of conversion at these conditions and experiment duration of 2 h remained in the range of 32–66% (BC 15.5–34 mg SO₂ per 100 mg of initial sample).

There was no well-established relationship between the chemical composition or any physical properties and parameters in the USC model. However, the best binding results were obtained with samples that had high initial porosities and pore surface areas as well as a higher content of impurities. These samples also had a bit higher E_A values of CaCO₃ decomposition.

Conclusions

1. In the binding of CO₂ from gaseous phase ($p_{\text{CO}_2} = 190$ mm Hg) in the temperature interval 400–800°C by using previously calcined dolomite and limestone samples only calcitic part of the samples (CaO) and not MgO took part with the formation of CaCO₃. In the binding of SO₂ by high partial pressure of it ($p_{\text{CO}_2} = 190$ mm Hg) both MgO and CaO took part with the formation, when using limestone at 400–700°, of CaSO₄ and γ -CaSO₄, and at 800–900°C of CaSO₄, mainly. When using dolomite at temperatures $\leq 700^\circ\text{C}$ CaSO₄, CaMg₃(SO₄)₄ and γ -CaSO₄ were formed and at 800–900°C CaSO₄ and CaMg₃(SO₄)₄ were the main products.
2. Carrying out the sulphation in the gas atmosphere with low SO₂ content 100 ppm of SO₂ at 700°C during 30 min the products of sulphation of the calcined dolomites were CaSO₄ and γ -CaSO₄, which means that in a gas atmosphere with low SO₂ concentration preferably, with SO₂ reacts CaO and not MgO with the formation of a CaSO₄ shell on the surface of particles hindering the later diffusion of SO₂ inside the particles.
3. Comparing the CO₂ and SO₂ binding ability of the samples studied, indicated that dolomites bound 2.5–3 times more SO₂ than CO₂ and limestone 1.8–2 times more SO₂ compared to CO₂. This is caused, firstly, by the very low reactivity of MgO towards CO₂ and, secondly, by the CaCO₃ shell formation on the surface of particles that hinders the diffusion of CO₂ inside the particles more than CaSO₄–CaMg₃(SO₄)₄ shell hinders the diffusion of SO₂.
4. An attempt was made to apply an unreacted shrinking core model with variable effective diffusivity to the sulphation data of several limestone and dolomite samples at atmospheric pressure as well as under pressure. The rate parameters were calculated for the sulphation reaction and the limiting stages for the binding process were established. Activation energies for the decomposition reactions of limestone and dolomite in the air CO₂ mixture were calculated using the standard Ozawa method.
5. The ashes formed at the oil shale pulverized firing power plants have considerably high remaining reactivity towards acidic gaseous compounds, therefore, they could be accepted as potential sorbents for deeper cleaning of flue gases by dry method. By using different methods of activation, it is possible to double the SO₂ binding capacity of the initial samples.

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