

COMPARATIVE REACTIVITY OF SOME CALCAREOUS ROCKS AS SORBENTS TOWARDS SULPHUR DIOXIDE

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Abstract. The thermogravimetric method was used for studying the SO₂ binding reactivity of Estonian limestones and dolomites from different deposits. Chemical, X-ray, BET, a.o. methods were used for the characterization of the initial samples and the products of SO₂ binding. The experimental data were processed mathematically to determine the models of the SO₂ binding mechanism for all sorbents used. The results of this study confirmed the high reactivity of Estonian limestones and dolomites towards SO₂ — in some cases it is comparable to the reactivity of the reactive grade of CaCO₃. The correlation between the reactivity of the samples and their specific surface area was observed.

Key words: limestone, dolomite, sulphur dioxide, sorption.

INTRODUCTION

The extensive use of sulphur-containing fuels induces the acidic pollution of the atmosphere with sulphur dioxide, which requires a supplementary cleaning of flue gases. It is a serious problem for Estonia where the Estonian and the Baltic Thermal Power Plants operate on Estonian oil shale which contains about 1.5% of sulphur [1].

For the removal of acidic compounds from flue gases, the most common sorbents used are lime-containing materials: natural limestones, and dolomites and their derivatives, and industrial materials — ashes containing free calcium-magnesium oxides [2–5]. The explored resources of Estonian limestones and dolomites are estimated to be 200–250 million m³, but their use in technology is confined to the cement and glass industries and the production of lime [6–8].

Our investigations were aimed at the comparative characterization of the reactivity of Estonian limestones and dolomites towards SO₂ binding from the gaseous phase by a dry method. We used the thermogravimetric (TG) method [9–16]. Earlier, the high temperature oil-shale ashes have been used for the same purpose [17].

EXPERIMENTAL

Estonian limestones and dolomites of different deposits (Adavere, Anelema, Karinu, Vasalemma, Vão, Kaarma, Maardu and shivers waste

of Maardu limestone) with different CaCO_3 and MgCO_3 content were studied. For comparison, oil-shale furnace ash formed in the fluidized bed boiler (the so-called low-temperature ash), a limestone sample from Poland and calcium carbonate of reactive grade were used.

TG studies were carried out in isothermal conditions in the derivatograph OD-103 (MOM, Hungary), the calcination taking place in the atmosphere of air, the sulphation in the mixture of SO_2 and air, with the heating rate 10 K per min. The calcination was performed up to 900°C in order to achieve a constant weight of the sample. When necessary, the sample was cooled down to the required temperature, after which the air enriched with SO_2 was led to the reaction chamber. Plate type Pt-crucibles were used. The thickness of the sample layer was 0.2–0.3 mm, the weight of the sample — 100 mg, the rate of the gas flow was 270 ml/min, and the partial pressure of SO_2 in the air— SO_2 mixture was 120 mm Hg.

The chemical composition and physical properties of the samples and their changes during the contact between the solid and gaseous phases were determined by using different methods of analysis — chemical, stereological (Videolab 2), X-ray (Dron 3M), BET-nitrogen dynamic desorption (sorptometer EMS-53), and others. The results for the initial samples are presented in Table 1.

As seen from Table 1, the sum of the contents of CaO and MgO varied from 51 to 59%, except for Maardu waste where it was 39.7%. The content of SiO_2 varied from 1 to 12%, the content of SO_4^{2-} between 0–1%, and that of CO_2 from 39.4 to 43.3% (for Maardu waste — 34.8%). The content of CaO + MgO in the oil-shale ash was 73.1%, that of free CaO was 45.1%. The density of the samples was nearly the same: it varied from 2.88 to 2.99 g/cm³. The specific surface area (SSA) for Estonian limestones and dolomites ranged from 2.3 to 5.7 m²/g, for Polish limestone it was 0.85 m²/g, and for oil-shale ash 1.6 m²/g. Two different fractions of the samples were used: the fine fraction and the coarse fraction. The mean particle size for the samples of the fine fraction ranged from 10.5 to 28 μm, for the samples of the coarse fraction it varied between 44 and 48 μm.

Two parameters were used to characterize the extent of interaction: the SO_2 binding rate (mg SO_2 /mg sample per min) and the SO_2 binding capacity (mg SO_2 /100 mg sample). The results of the TG investigations were used to determine the reaction mechanisms.

RESULTS AND DISCUSSION

The characteristic TG-curve of limestone decomposition in the dynamic heating conditions, in air, with the following sulphation of the decomposed product in isothermal conditions, in an air— SO_2 mixture, is presented in Fig. 1. The results obtained in the temperature interval from 400 to 900°C confirmed that the capacity to bind SO_2 increased for all the materials studied when the temperature was increased, and it was considerable at 700°C and above. During the first period of interaction, the SO_2 binding rate was the more intensive the higher the temperature. For example, at 500°C, the amount of the SO_2 bound by the limestone of the Karinu deposit during the first 2 min was 8.8 mg per 100 mg of sample (62% of the total amount of bound sulphur dioxide), the amount bound during the following 8 min was 5.4 mg. At 700 and 900°C, the amount of the bound SO_2 after 2 min of contact with Karinu limestone was 72.9 mg and 98.6 mg SO_2 per 100 mg of sample, respectively, or 80 and 90%, as related to the total amount of the bound SO_2 after 10 min of contact (Fig. 1).

Table 1

Parameters	Samples									
	Ada- vere D*	Karinu C**	Maardu C	Ane- lema D	Väo C	Vasa- lema C	Kaarma D	Maardu waste C	Oil- shale ash	Polish C
Content, wt. %, of:										
CaO	37.1	57.4	49.3	38.5	51.1	50.8	29.5	34.6	66.2	55.0
MgO	17.7	1.7	2.3	20.2	4.8	2.3	21.9	5.1	6.9	0.2
CaO free	≈ 0	≈ 0	1.1	≈ 0	0.5	0.7	0.3	0.7	45.1	—
SO ₂ - 4									5.8	≈ 0
SiO ₂	1.7	1.1	4.4	2.2	9.5	5.0	5.8	11.8	7.7	0.5
Fe ₂ O ₃	0.5	0.1	0.8	0.4	0.5	0.5	0.6	1.8	2.4	0.4
Al ₂ O ₃	0.3	0.2	0.8	0.8	0.8	0.8	0.4	1.2	2.8	0.4
K ₂ O	0.9	0.1	0.1	0.2	0.1	0.1	—	—	0.9	—
CO ₂	43.3	41.5	39.4	43.3	40.8	41.1	43.0	34.8	0.8	43.4
MgCO ₃	37.2	3.6	4.8	42.5	10.2	4.8	46.0	10.7	—	0.4
CaCO ₃	58.7	94.5	84.0	52.5	80.8	87.9	43.0	68.4	—	98.2
Density, g/cm ³	2.96	2.97	2.99	2.93	2.97	2.96	2.92	2.88	2.90	—
Specific surface area, m ² /g	5.1	3.5	2.7	5.7	4.6	3.5	2.3	5.1	1.6	0.9
Mean particle size, μm	10.5	19	26	11	18	26	24	25	28	—

* Dolomite, ** Calcite.

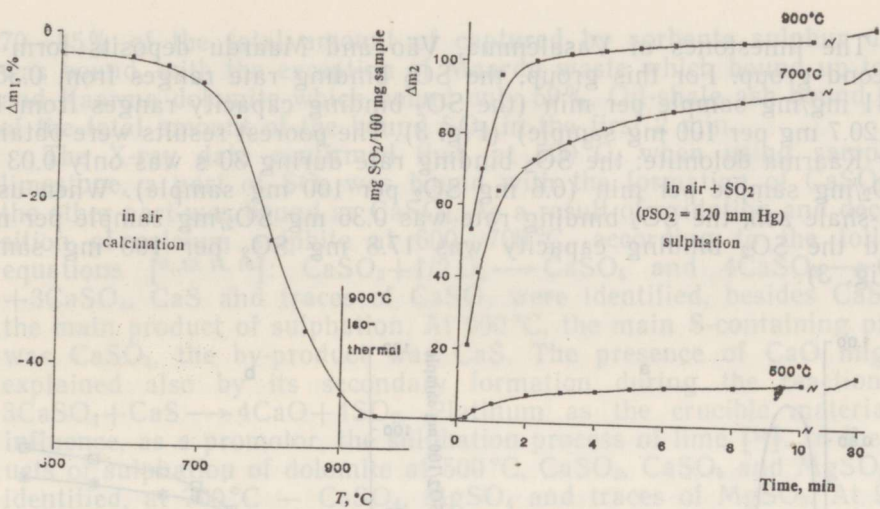


Fig. 1. Thermogravimetric curves of calcination (up to 900 °C) and sulphation of Karinu limestone at different temperatures.

The more detailed comparison of different samples was carried out at 700 °C. On the basis of the SO₂ binding activity data of the samples, for 30 s of interaction between the solid and gaseous phases, the limestones and dolomites were divided into three groups. The best results were obtained for the dolomites of Adavere and Anelema deposits: the reaction proceeded with a high SO₂ binding rate — 1.19 and 0.89 mg SO₂/mg sample per min, respectively, which means that 59.6 and 44.4 mg SO₂ per 100 mg sample were bound (Fig. 2). The binding rate of SO₂ by Maardu waste and Karinu limestone was approximately the same as that by Anelema dolomite — 0.87 and 0.81 mg SO₂/mg sample per min, and the SO₂ binding capacity was 43.4 and 40.4 mg SO₂ per 100 mg of sample, respectively (Figs. 2 and 3).

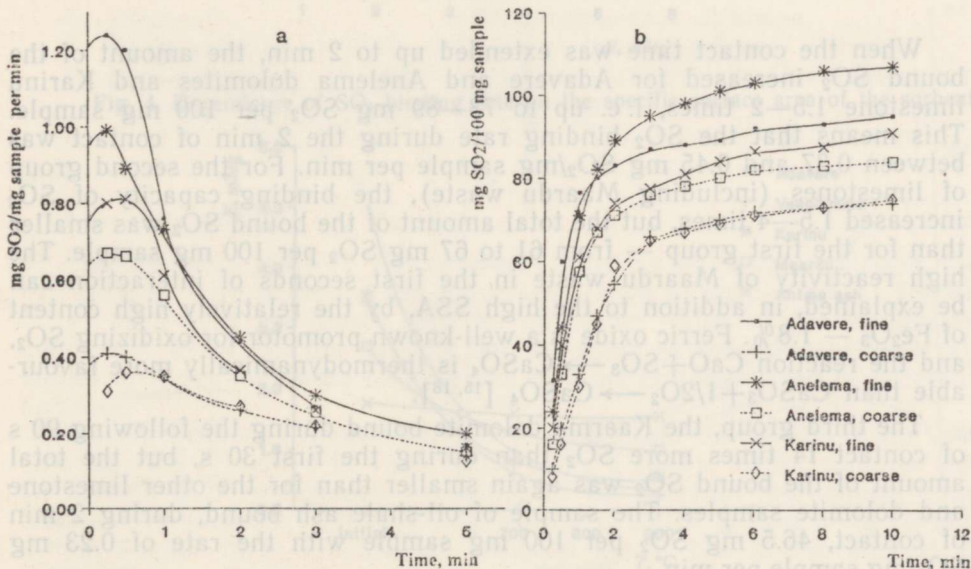


Fig. 2. SO₂ binding rate (a) and binding capacity (b) of different fractions of Adavere and Anelema dolomites and Karinu limestone at 700 °C.

The limestones of Vasalemma, Vão and Maardu deposits form the second group. For this group, the SO₂ binding rate ranges from 0.35 to 0.41 mg/mg sample per min (the SO₂ binding capacity ranges from 17.7 to 20.7 mg per 100 mg sample) (Fig. 3). The poorest results were obtained for Kaarma dolomite: the SO₂ binding rate during 30 s was only 0.03 mg SO₂/mg sample per min (6.6 mg SO₂ per 100 mg sample). When using oil-shale ash, the SO₂ binding rate was 0.36 mg SO₂/mg sample per min, and the SO₂ binding capacity was 17.8 mg SO₂ per 100 mg sample (Fig. 3).

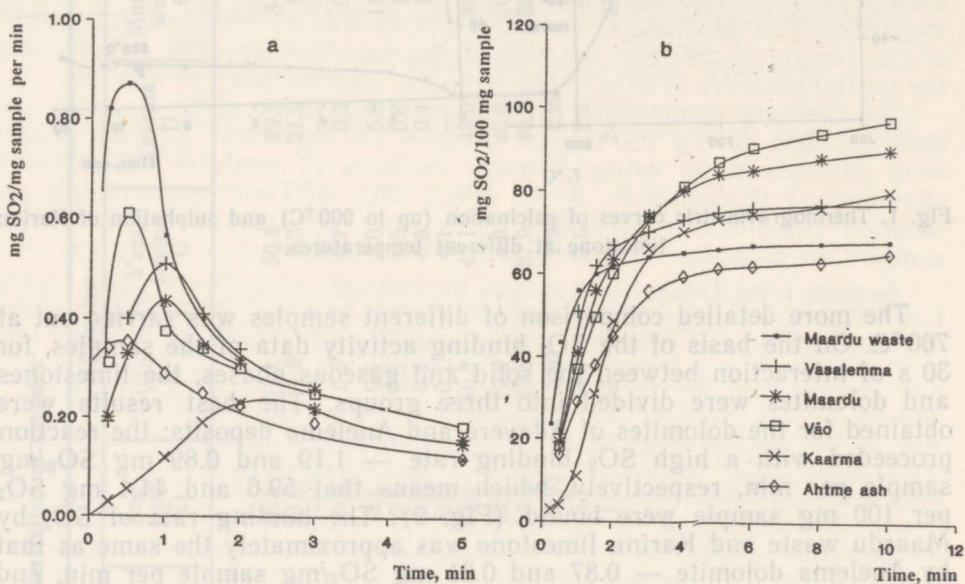


Fig. 3. SO₂ binding rate (a) and binding capacity (b) of the fine fraction of different samples at 700 °C.

When the contact time was extended up to 2 min, the amount of the bound SO₂ increased for Adavere and Anelema dolomites and Karinu limestone 1.5–2 times, i.e. up to 73–89 mg SO₂ per 100 mg sample. This means that the SO₂ binding rate during the 2 min of contact was between 0.37 and 0.45 mg SO₂/mg sample per min. For the second group of limestones (including Maardu waste), the binding capacity of SO₂ increased 1.5–4 times, but the total amount of the bound SO₂ was smaller than for the first group — from 61 to 67 mg SO₂ per 100 mg sample. The high reactivity of Maardu waste in the first seconds of interaction can be explained, in addition to the high SSA, by the relatively high content of Fe₂O₃ — 1.8%. Ferric oxide is a well-known promotor for oxidizing SO₂, and the reaction $\text{CaO} + \text{SO}_3 \rightarrow \text{CaSO}_4$ is thermodynamically more favourable than $\text{CaSO}_3 + 1/2\text{O}_2 \rightarrow \text{CaSO}_4$ [15, 18].

The third group, the Kaarma dolomite bound during the following 90 s of contact 14 times more SO₂ than during the first 30 s, but the total amount of the bound SO₂ was again smaller than for the other limestone and dolomite samples. The sample of oil-shale ash bound, during 2 min of contact, 46.5 mg SO₂ per 100 mg sample with the rate of 0.23 mg SO₂/mg sample per min.

Comparing the SO₂ binding capacity data after 2 and 10 min of contact (Figs. 2 and 3), it was concluded that during the first 2 min, as a rule,

70—85% of the total amount of captured by sorbents sulphur dioxide was bound, with the exception of Maardu waste which bound up to 91% and Kaarma dolomite which bound only 59%. Oil-shale ash bound 68.5% of the total amount of the bound SO_2 in the first 2 min.

The X-ray data confirmed that, at 500°C , when using samples of limestone, a part of SO_2 was bound with the formation of CaSO_3 , and the other part was bound as CaSO_4 . As a result of oxidation and decomposition of calcium sulphite at $600\text{--}700^\circ\text{C}$, according to the following equations [9, 13, 14, 16]: $\text{CaSO}_3 + 1/2 \text{O}_2 \rightarrow \text{CaSO}_4$ and $4\text{CaSO}_3 \rightarrow \text{CaS} + 3\text{CaSO}_4$, CaS and traces of CaSO_3 were identified, besides CaSO_4 as the main product of sulphation. At 900°C , the main S-containing product was CaSO_4 , the by-product was CaS. The presence of CaO might be explained also by its secondary formation during the reaction [16]: $3\text{CaSO}_4 + \text{CaS} \rightarrow 4\text{CaO} + 4\text{SO}_2$. Platinum as the crucible material can influence, as a promotor, the sulphation process of lime [16]. In the products of sulphation of dolomite at 500°C , CaSO_3 , CaSO_4 and MgSO_3 were identified, at 700°C — CaSO_4 , MgSO_4 and traces of MgSO_3 . At 900°C , the main products of sulphation were CaSO_4 and MgSO_4 . A certain amount of CaS, CaO and traces of MgO were also identified. These results confirmed that, in our experimental conditions, MgO took part in the binding of SO_2 not only below 800°C [12].

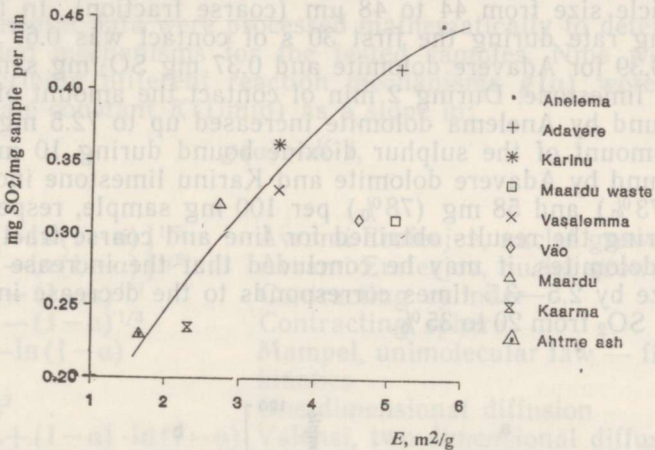


Fig. 4. Dependence of SO_2 binding rate on the specific surface area of the sorbent.

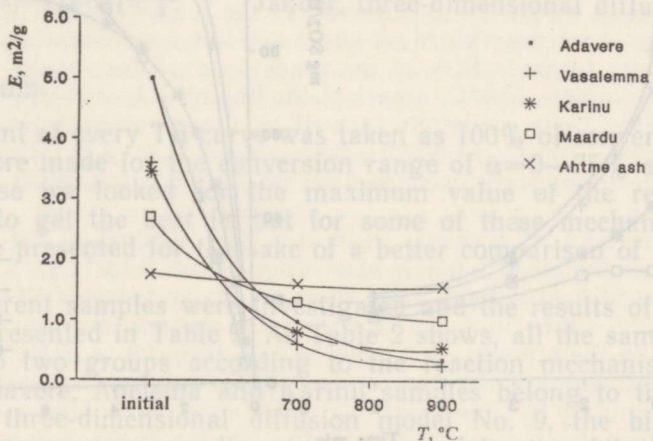


Fig. 5. Dependence of the specific surface area of processed sorbents on the temperature of the experiment.

The SSA is one of the parameters which characterizes well the natural limestones-dolomites as sorbents for the removal of SO_2 from flue gases [19, 20]. There exists a correlation between the reactivity of samples towards SO_2 binding and the SSA of the initial samples (Fig. 4). Only two of the samples have a comparatively low SO_2 binding rate, as might be expected on the basis of the SSA data. These are Vão limestone and Maardu waste which both contain twice as much insoluble residue (SiO_2) as the others and, apart from that, Maardu waste contains Ca, Mg-oxides about 10% less than the other samples. The changes in the SSA data after 10 min of processing of the samples in the atmosphere of air- SO_2 mixture are shown, for different temperatures, in Fig. 5. The SSA value decreases rapidly during the binding of SO_2 , and the higher the SSA data for the initial sample, the bigger the difference between the initial sample and the product. The SSA value for oil-shale ash did not actually change during the interaction between SO_2 and the sorbent. The stereological analysis of the samples confirmed that during calcination and sulphation the mean particle size of Estonian limestones and dolomites increased by 6–12%.

A series of experiments for studying the influence of the particle size on desulphurization of the gaseous phase was carried out by using the samples of Adavere and Anelema dolomite and Karinu limestone with a mean particle size from 44 to 48 μm (coarse fraction). In that case the SO_2 binding rate during the first 30 s of contact was 0.67 for Anelema dolomite, 0.39 for Adavere dolomite and 0.37 mg SO_2 /mg sample per min for Karinu limestone. During 2 min of contact the amount of the sulphur dioxide bound by Anelema dolomite increased up to 72.5 mg (or 85% of the total amount of the sulphur dioxide bound during 10 min), and the amount bound by Adavere dolomite and Karinu limestone increased up to 54.0 mg (73%) and 58 mg (78%) per 100 mg sample, respectively (Fig. 2). Comparing the results obtained for fine and coarse fractions of limestones or dolomites, it may be concluded that the increase in the mean particle size by 2.5–3.5 times corresponds to the decrease in the binding capacity of SO_2 from 20 to 35%.

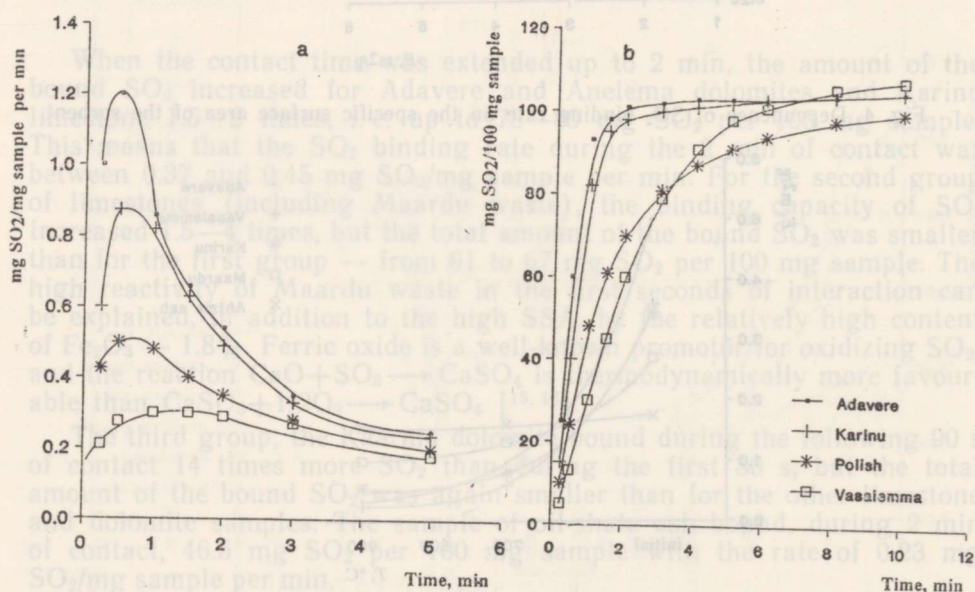


Fig. 6. SO_2 binding rate (a) and binding capacity (b) of different samples at 900 °C.

The experiments for comparing the SO₂ binding efficiency of Estonian limestones and dolomites with Polish limestone were carried out at 900 °C. The results confirmed that the SO₂ binding rate during the first minutes of contact was 2–3 times higher for Adavere dolomite and Karinu limestone and twice lower for Vasalemma limestone than for Polish limestone. The amount of SO₂ bound by these Estonian limestones during 10 min of contact exceeded by 5–10% the amount bound by the Polish limestone (Fig. 6).

The comparison of the SO₂ binding capacity of the first group of limestones and dolomites with that of reactive grade CaCO₃ was carried out in dynamic heating conditions at the rate 5 °C/min, up to 1000 °C. The samples of Adavere and Anelema dolomite had approximately the same SO₂ binding capacity as the reactive calcium carbonate — only 2.7 and 8.5% less, respectively. Karinu limestone and Maardu waste bound 15.9 and 25.4% of SO₂ less, respectively, than CaCO₃.

MATHEMATICAL PROCESSING OF THE EXPERIMENTAL DATA

The experimental data were processed mathematically to determine the possible reaction mechanisms for the tested samples. Nine well-known equations describing different reaction mechanisms $g(\alpha)$ were used to calculate the rate constant K (1/min) as a slope in:

$$g(\alpha) = K \cdot t, \quad (1)$$

where

- | | |
|----------------------------------------------------------|----------------------------------------------------|
| 1. $g(\alpha) = [-\ln(1-\alpha)]^{1/3}$ | Avrami-Erofeejev, nuclei growth |
| 2. $g(\alpha) = [-\ln(1-\alpha)]^{1/2}$ | Avrami-Erofeejev, nuclei growth |
| 3. $g(\alpha) = 1 - (1-\alpha)^{1/2}$ | Contracting cylinder |
| 4. $g(\alpha) = 1 - (1-\alpha)^{1/3}$ | Contracting sphere |
| 5. $g(\alpha) = -\ln(1-\alpha)$ | Mampel, unimolecular law — first order kinetics |
| 6. $g(\alpha) = \alpha^2$ | One-dimensional diffusion |
| 7. $g(\alpha) = \alpha + (1-\alpha) \cdot \ln(1-\alpha)$ | Valensi, two-dimensional diffusion |
| 8. $g(\alpha) = 1 - 2/3\alpha - (1-\alpha)^{2/3}$ | Ginstling-Brounshtein, three-dimensional diffusion |
| 9. $g(\alpha) = [1 - (1-\alpha)^{1/3}]^2$ | Jander, three-dimensional diffusion |

and

t — time, min.

The last point of every TG-curve was taken as 100% of conversion, the calculations were made for the conversion range of $\alpha=0-75\%$ at 700 °C.

In each case we looked for the maximum value of the regression coefficient R^2 to get the best fit but for some of these mechanisms all values of K are presented for the sake of a better comparison of different samples.

Eleven different samples were investigated and the results of the calculations are presented in Table 2. As Table 2 shows, all the samples can be divided into two groups according to the reaction mechanism. Fine fractions of Adavere, Anelema and Karinu samples belong to the group of the Jander three-dimensional diffusion model No. 9, the biggest K value of this group corresponding to Adavere dolomite. All the other limestone and dolomite samples studied, as well as the oil-shale ash, belong to the first order kinetics model No. 5, the biggest K values

corresponding to Maardu waste and Vasalemma limestone, the smallest one to Vão limestone. The highest SO₂ binding rates were achieved by Maardu waste, Adavere dolomite and Vasalemma limestone, the lowest by Vão limestone.

Table 2

Kinetic constant for samples

Sample	R ²	K, 1/min	K, 1/min for models	
			No. 5	No. 9
Model No. 5				
Maardu, waste	0.9805	1.6038	1.6038	0.4434
Vasalemma, fine	0.9708	0.9677	0.9677	0.2651
Anelema, coarse	0.9877	0.9092	0.9092	0.2572
Karinu, coarse	0.9977	0.6644	0.6644	0.1835
Adavere, coarse	0.9992	0.5838	0.5838	0.1630
Maardu, fine	0.9889	0.5580	0.5580	0.1544
Oil-shale ash	0.9981	0.4874	0.4874	0.1377
Kaarma, fine	0.9688	0.4470	0.4470	0.1200
Vão, fine	0.9941	0.4024	0.4024	0.1146
Model No. 9				
Adavere, fine	0.9519	0.2701	0.9588	0.2701
Anelema, fine	0.9831	0.2072	0.7302	0.2072
Karinu, fine	0.9409	0.1448	0.5000	0.1448

CONCLUSIONS

1. Considering the reactivity towards SO₂ binding, Estonian limestones and dolomites, investigated in this study, fall into three groups:

- Adavere and Anelema dolomites, Karinu limestone and shivers waste of crushed Maardu limestone;
- Vasalemma, Vão and Maardu limestones;
- Kaarma dolomite

The SO₂ binding efficiency of Maardu waste decreased rapidly when the contact time was prolonged over 60 s.

The samples of Adavere and Anelema dolomite have approximately the same level of SO₂ binding capacity as the reactive grade CaCO₃.

2. The low-temperature oil-shale ash has approximately the same level of reactivity towards SO₂ as the limestones of the second group.

3. Up to 500–550 °C, a part of the bound SO₂ was identified as CaSO₃ and MgSO₃; their oxidation as well as the decomposition of CaSO₃ took place at 600–700 °C. At 900 °C, the main product of sulphation was CaSO₄ when limestones were used, and CaSO₄ and MgSO₄ when dolomites were used.

4. The SSA of sorbents decreases rapidly during the sulphation; the increase in the mean particle size ranged from 6 to 12%. A correlation between the SSA of sorbents and their reactivity towards SO₂ was observed; the 2.5–3.5 times increase in the mean particle size corresponds to the decrease in the amount of the bound SO₂ from 20 to 35%.

5. Mathematical data processing confirmed that the reaction mechanism of SO₂ binding by fine fractions of Adavere and Anelema dolomite and Karinu limestone corresponds to the Jander three-dimensional diffusion model. The reaction mechanism of the other studied sorbents corresponds to the first order kinetics model.

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MÕNINGATE LUBJAKIVIMITE VÄÄVELDIOKSIIDI SIDUMISVÕIME KÕRVUTAV UURIMINE

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Kasutades termogravimeetria meetodit uuriti mõningate Eesti lubjakivide ja dolomiitide võimet siduda SO_2 . Lähteproovide ja SO_2 -sidumisproduktide iseloomustamiseks kasutati keemilist, röntgendifraktsioon-, BET eripinna määramise ja teisi meetodeid. Katsetulemusi matemaatiliselt töödeldes määrati kõikide uuritud sorbentide SO_2 sidumismehhanismi mudelid. Saadud tulemused kinnitavad Eesti lubjakivide ja dolomiitide kõrget aktiivsust vääveldioksiidi sidumisel. Mõningate proovide puhul on see võrreldav reaktiivse CaCO_3 sidumisaktiivsusega. Täheledatai head korrelatsiooni uuritud proovide SO_2 sidumisaktiivsuse ja eripinna vahel.

СРАВНИТЕЛЬНОЕ ИССЛЕДОВАНИЕ АКТИВНОСТИ СВЯЗЫВАНИЯ ДИОКСИДА СЕРЫ НЕКОТОРЫМИ ИЗВЕСТКОВЫМИ РУДАМИ

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Термогравиметрическим методом анализа изучена активность связывания диоксида серы некоторыми эстонскими природными известковыми рудами. Для характеристики исходных образцов и продуктов связывания SO_2 использованы химический, рентгенофазовый, БЭТ-десорбционный и др. методы анализа. По результатам экспериментов определены модели механизма связывания SO_2 для всех изученных сорбентов. Установлено, что активность некоторых эстонских известковых руд при связывании SO_2 сравнима с активностью реактивного CaCO_3 . Существует хорошая корреляция между активностью связывания SO_2 и удельной поверхностью образцов.