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THE ROLE OF MgO IN THE BINDING OF SO_2 BY LIME-CONTAINING MATERIALS

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The results of investigation of MgO participation in the binding of SO_2 with lime-containing materials as sorbents are presented. Experiments of SO_2 binding into solid phase using model samples of reactive grade MgO and CaO varying the mole ratio of MgO/CaO from 9:1 to 1:9 were carried out. Besides, dolomite and limestone samples with different MgO/CaO mole ratio (from 1.24 to 0.13) and samples of ashes formed at combustion of Estonian oil shale (containing 35–40% of carbonates) and its semicoke were studied

Initial samples, intermediate and final products were subjected to chemical, IR-spectroscopy, X-ray and BET specific surface area analyses.

The results of the present study confirmed the active participation of MgO in the binding of SO_2 into the solid phase. In addition to $CaSO_4$ the formation of Ca,Mg-double sulphate $CaMg_3(SO_4)_4$ and β-$MgSO_4$ was observed. The presence of $CaMg_3(SO_4)_4$ was fixed in a large temperature range 400–900°C and that of β-$MgSO_4$ in between 500–700°C. The optimum temperature range for formation and durability of $CaMg_3(SO_4)_4$ was 700–800°C.

Keywords: *calcite, calcium oxide, dolomite, magnesium oxide, oil shale ash, sulphur dioxide*

Introduction

Natural carbonaceous rocks like limestone and dolomite are the most common sorbents for the removal of acidic gaseous compounds from flue gases. The mechanism of decarbonisation of limestone and sulphation of lime formed at that has been studied by many authors [1–8]. Some papers are also dealing with the decarbonisation of dolomites [9–13], but there are quite few and contradicting data on the participation of MgO formed at that in the binding of SO_2. In general, the concept is that MgO does not take part in the binding of SO_2 into solid phase or if it occurred at lower temperatures, then over 800°C the magnesium and sulphur containing compounds formed have decomposed [14–20]. Thermodynamic calculations showed that SO_2 binding by MgO with the formation of $MgSO_4$ should be the most effective in between 650 and 840°C [21] or, depending on the SO_2 concentration in the gaseous phase, in the range of 740–885°C [22]. In [23] the catalytic effect of Fe_2O_3 on the binding of SO_2 by MgO was studied and the formation of $MgSO_4$ was fixed at temperatures as high as 700–850°C.

Analysing the filter cakes from pressurised fluidized bed combustion of coal with dolomite as a sorbent for SO_2 removal from flue gases [24] a new phase – $CaMg_2(SO_4)_3$ – was identified by means of X-ray diffraction analysis. Later, the FTIR spectroscopy method for identification and quantitative analysis of $MgSO_4$, $CaSO_4$ and $CaMg_2(SO_4)_3$ in the mixtures of these compounds as well as in filter cakes was developed [25].

The participation of MgO in the binding of SO_2 was proved also in our earlier works [26, 27].

The aim of the present work was the clarification of the role of MgO in the binding of SO_2 by different lime-containing materials.

Experimental

Materials

The following lime-containing samples were studied (Table 1):

- model samples based on reactive grade MgO and CaO with the mole ratio of MgO/CaO from 9:1 to 1:9
- dolomite and dolomitic limestone samples from different deposits (Estonia)
- bottom (BA), cyclone (CA) and bag filter (BFA) ashes formed at low-temperature (800–850°C) combustion of lumpy Estonian oil shale semicoke (SC) at laboratory BFBC conditions
- BA formed at high-temperature (1200–1300°C) combustion of pulverised Estonian oil shale (OS) at Baltic power plant (Baltic PP)

The initial samples as well as the products of sulphation were subjected to chemical, XRD (CuK_α radiation, 40 kV, 20 mA) (DRON-4), FTIR spectros-

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Table 1 Main characteristics of the samples

Samples	Mole ratio of MgO/CaO	Content%					SSA/m^2 g^{-1}
		CaO	MgO	CO_2	Insoluble residue in aqua regia	free CaO	
			Dolomites, limestone				
Hellamaa	1.240	28.8	25.5	45.7	0.5	–	0.91
Tagavere	1.232	27.3	24.1	41.6	4.6	–	3.36
Mundi	1.241	26.3	23.3	37.5	13.7	–	4.62
Rostla	1.003	30.3	21.7	44.7	2.5	–	0.82
Pajusi	1.017	25.3	18.4	38.2	19.3	–	2.19
Anelma	0.742	38.5	20.2	43.2	2.2	–	5.70
Adavere	0.668	37.1	17.7	43.3	1.7	–	5.11
Arina	0.232	46.3	7.7	41.8	1.5	–	1.23
Maibaum	0.130	44.8	4.2	36.9	11.7	–	2.67
			Ashes				
Semicoke, BFBC							
Bottom ash (BA)	0.232	38.7	6.4	6.8	22.4	14.9	3.90
Cyclone ash (CA)	0.240	32.7	5.6	3.8	26.2	13.0	5.68
Bag filter ash (BFA)	0.195	28.0	3.9	3.2	33.7	4.2	4.14
Oil shale, Baltic PP							
Bottom ash (BA)	0.139	58.6	5.8	3.1	21.7	20.5	1.45

copy (Interspec 2020, Interspectrum Ltd.) and BET specific surface area (SSA) (Kelvin 1042, Costech International) analyses. For identification of the phase composition of the samples by XRD data, the ICDD (International Centre for Diffraction Data) PDF database (year 2000 version) was used.

Methods

The experiments were carried out with thermogravimetric equipment (Q-Derivatograph, MOM) as described in [27]. Calcination of dolomite and dolomitic limestone samples was performed under dynamic heating conditions (10 K min^{-1}) in the atmosphere of air up to 850°C, sulphation under isothermal conditions at temperatures 400–900°C in the mixture of air and SO_2. The multiplate Pt crucibles were used, the mass of sample was ≈100 mg and the thickness of sample layer 0.2–0.3 mm. The rate of gas flow was 270 mL min^{-1} and the concentration of SO_2 in the gas mixtures was 80 ppm or 25 vol%. The main parameter used for characterisation of the extent of interaction between gaseous and solid phases was the SO_2 binding efficiency (%) per content of total CaO and MgO (CaO·MgO), besides that the SO_2 binding rate (mg SO_2/mg sample·min) and the SO_2 binding capacity (mg SO_2/100 mg sample) were calculated. The temperature dependencies of the Gibbs energy changes were calculated using HSC Chemistry® 4.0 software [28]. Unfortunately, this software does not contain the thermodynamic data of CaMg-double sulphate and these data are missing also in the literature.

Results and discussion

The Gibbs energy changes show the preference of Ca, Mg-oxides in SO_2 binding at atmospheric pressure as compared to carbonates as well as of Ca-compounds compared to corresponding Mg-compounds (Fig. 1).

Experiments with model blends

Actually, the results of our experiments indicated the active participation of MgO in the binding of SO_2. At lower temperatures (400 and 500°C) the SO_2 binding took place at a low but almost constant rate and during 30 min of contact between solid and gaseous phase (25% SO_2) there was bound 38 and 90 mg SO_2 per 100 mg sample, respectively, or, otherwise, 23.6 and 55.9% of MgO contained in the sample was utilised. At 700 and 900°C during the initial period of interaction (1–2 min) the mean SO_2 binding rate was quite high – 0.345 and 0.130 mg of SO_2 per mg sample·min^{-1}. At 900°C the equilibrium between gaseous and solid phases was established after 12 min of contact on the level of 51 mg SO_2 per 100 mg sample which correspond to 31.6% of MgO utilisation. At 700°C during 30 min contact the equilibrium was not reached and the

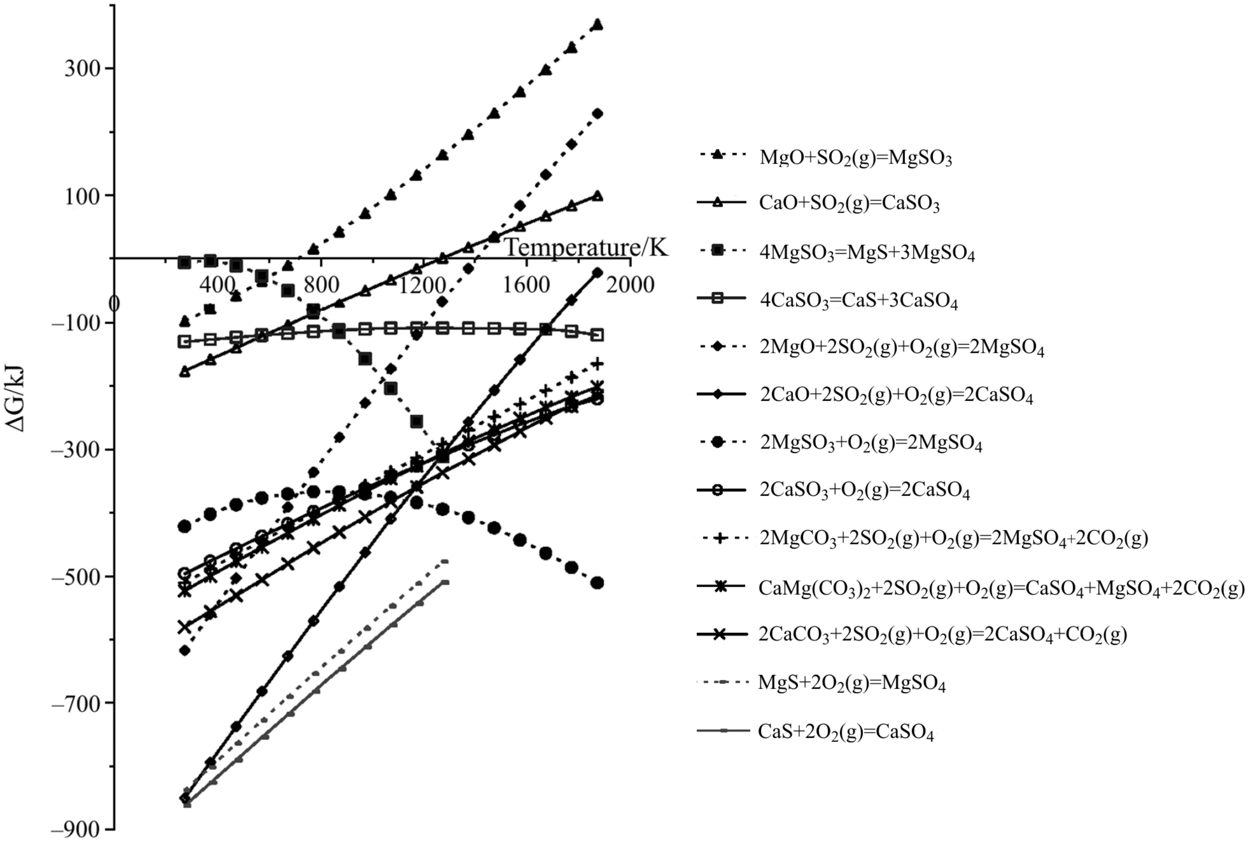

Fig. 1 The Gibbs energy value changes with the temperature for different reactions

amount of SO_2 bound at that was 115 mg SO_2 per 100 mg sample or 66.8% (Fig. 2) of MgO contained was utilised. In comparison, with a CaO sample at 700°C during 30 min of contact 54.8 mg SO_2 per 100 mg sample was bound or 47.2% of CaO contained was utilised (Fig. 2). A model sample with MgO/CaO mole ratio 3:1 bound SO_2 more intensively than that with mole ratio 9:1, but less than pure MgO. All blends with mole ratio of MgO/CaO≥1.0 bound more and with mole ratio <1.0 less SO_2 than it was bound by CaO (Fig. 2). The dependence of the SO_2 binding efficiency (BE) of Ca, Mg-oxides on the MgO/CaO mole ratio in the model blends is well demonstrated in Fig. 3.

The results of XRD analysis confirmed the formation of anhydrite, β-$MgSO_4$ and CaMg-double sulphate which by the ICDD database (card 19-0241) has a formula $CaMg_3(SO_4)_4$ and the presence of unreacted MgO and CaO in the products of sulphation (in 25% SO_2) in all the model blends studied. At 500 and 700°C also the formation of γ-$CaSO_4$ was fixed. In Figs 4 and 5 the variation in intensities of the respective peaks, especially of these characteristic for anhydrite, β-$MgSO_4$ and CaMg-double sulphate on XRD patterns depending on the temperature of experiment and the MgO/CaO mole ratio in the blends can be seen. The characteristic peaks for CaMg-double sulphate were

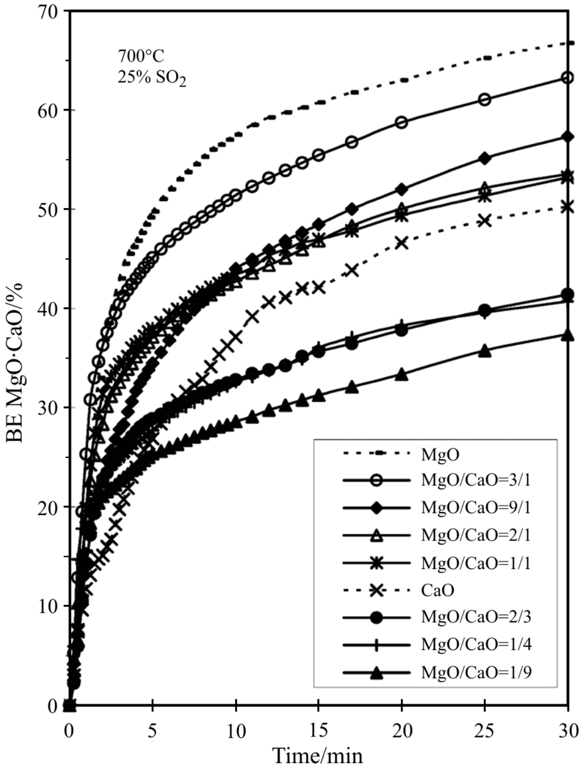

Fig. 2 SO_2 binding efficiency (BE) per MgO·CaO in blends with different MgO and CaO mole ratio sulphated at 700°C

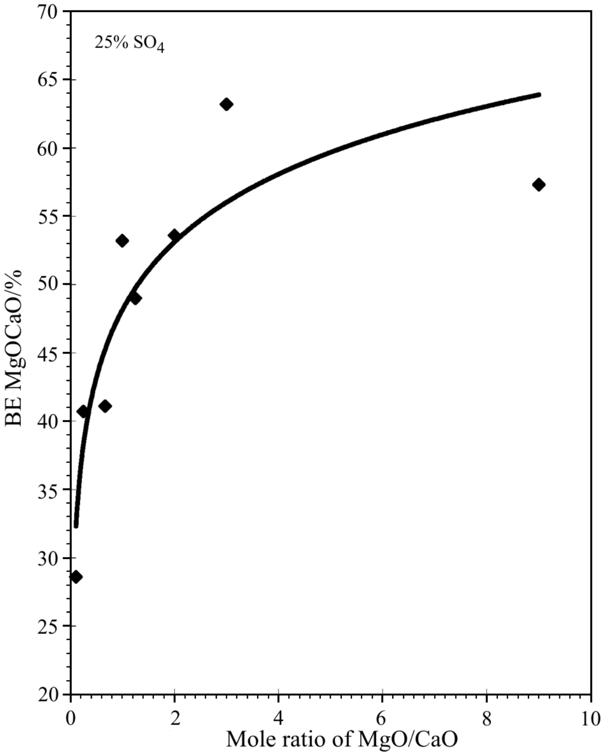

Fig. 3 Dependence of SO_2 binding efficiency (BE) per the content of MgO and CaO in model blends on the mole ratio of MgO/CaO after 30 min contact at 700°C

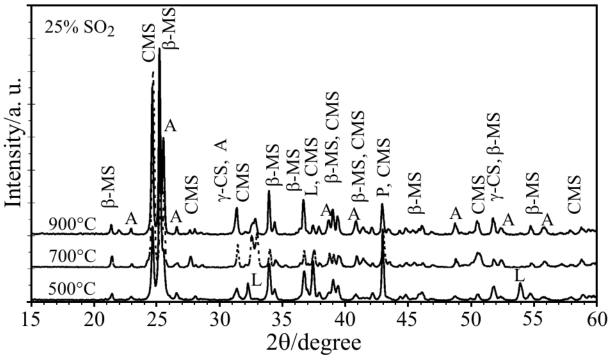

Fig. 4 XRD patterns of model blends at mole ratio of MgO/CaO=3:1 sulphated at different temperatures; CMS – $CaMg_3(SO_4)_4$, β-MS – β-$MgSO_4$, A – anhydrite, γ-CS – γ-$CaSO_4$, L – lime, P – periclase

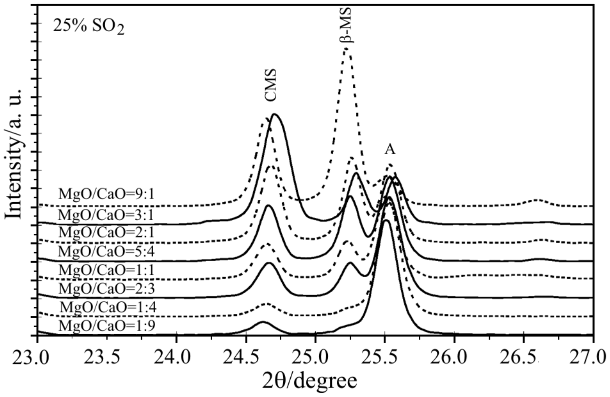

Fig. 5 XRD patterns of model blends at different mole ratio of MgO/CaO sulphated at 700°C; CMS – $CaMg_3(SO_4)_4$, β-MS – β-$MgSO_4$, A – anhydrite

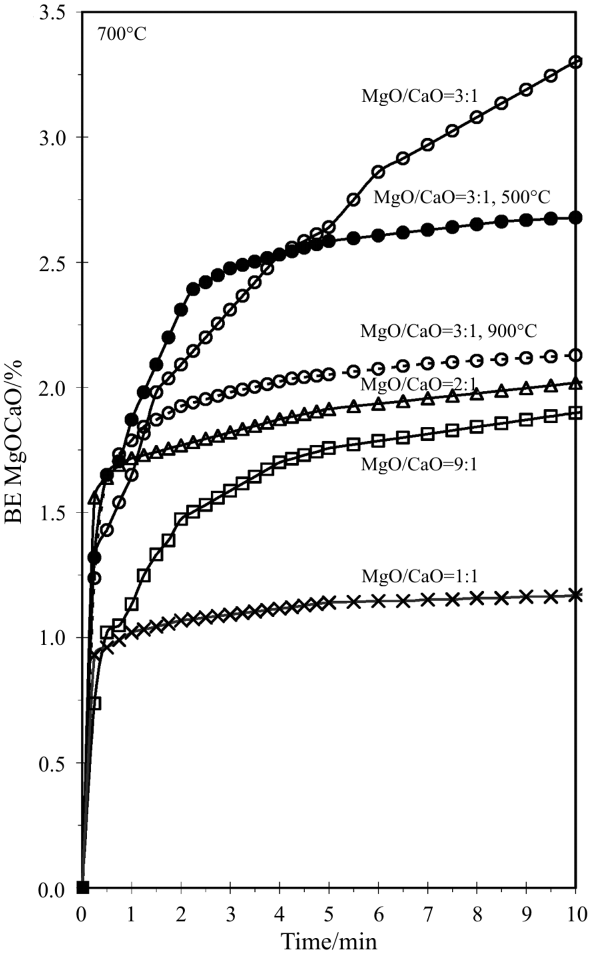

Fig. 6 SO_2 binding efficiency (BE) per MgO·CaO in blends with different MgO and CaO mole ratio sulphated at different temperatures (SO_2 – 80 ppm)

the most intensive at 700°C and, for example, for the blend with MgO/CaO mole ratio 3:1 these were approximately 1.5 times more intensive than these with mole ratio 2:1. This could indicate that the formula $CaMg_3(SO_4)_4$ for CaMg-double sulphate is more probable than $CaMg_2(SO_4)_3$ proposed by Smith *et al.* [24].

The experiments carried out with model blends in the atmosphere with low SO_2 concentration (80 ppm) showed that the equilibrium was practically established in 1–2 min of contact between gaseous and solid phases (except for the blend with MgO/CaO mole ratio 3:1) and at that 2–5 mg SO_2 per 100 mg sample was bound or only 1.2–3.3% of MgO·CaO contained was utilised (Fig. 6). The highest value was obtained with the blend with MgO/CaO mole ratio 3:1. The results of

XRD data confirmed that at 700°C in addition to anhydrite as a main product of sulphation, the formation of $CaMg_3(SO_4)_4$ took place on the level of traces when the blends with MgO/CaO mole ratio of 3:1, 2:1 and 1:1 were used and at 9:1 the only product was anhydrite. The presence of β-$MgSO_4$ was not fixed which means that all β-$MgSO_4$ formed took immediately part in the following formation of $CaMg_3(SO_4)_4$.

Experiments with dolomite and dolomitic limestone samples

Depending on the origin (chemical composition, mole ratio of MgO/CaO, etc.) of natural dolomite and limestone samples and on the temperature of sulphation, the efficiency of SO_2 binding by MgCa-oxides contained in the decarbonised sample was on the level of 30–70% and, as a rule, this value was higher for the samples which had higher level of insoluble in aqua regia residue. The additives influence the crystallinity and SSA of the samples and together with this also the SO_2 binding efficiency.

For example, comparing Mundi (MgO/CaO= 1.241, insoluble residue 13.7%), Tagavere (MgO/CaO=1.232, insoluble residue 4.6%) and Hellamaa (MgO/CaO=1.240, insoluble residue 0.5%) dolomites indicated that the SO_2 binding efficiency of MgCa-oxides of Mundi dolomite exceeded this value of Hellamaa and Tagavere dolomite depending on temperature of sulphation 10–16 and 4–5%, respectively, being the highest at 900°C. The SO_2 binding efficiency of Tagavere dolomite exceeded that of Hellamaa dolomite 10–14% being the highest at 700°C (Fig. 7).

The formation of $CaMg_3(SO_4)_4$ was observed with all the dolomite and limestone samples studied (Fig. 8) and the characteristic peaks on XRD patterns were like in the case of model blends the most intensive at 700°C and only for Mundi dolomite at 900°C (Fig. 9). For Pajusi dolomite (which has a high content of additives) no differences were observed in the intensities of these peaks at 700 and 900°C. At 500 and 900°C the characteristic peaks of anhydrite prevailed on XRD patterns (Fig. 9). At 700°C on XRD patterns of Hellamaa, Tagavere (both with MgO/CaO mole ratio >1.2) and Pajusi dolomite (MgO/CaO mole ratio 1.02, but with high content of additives) the intensities of the characteristic peaks of $CaMg_3(SO_4)_4$ and anhydrite were approximately on the same level (Fig. 9), for the other samples with MgO/CaO mole ratio ≤1.0 the peaks of anhydrite were more intensive. At 500°C in the product of sulphation Pajusi and Mundi dolomite the presence of CaS was fixed on the level of traces. The formation of β-$MgSO_4$ was clearly observed with all the samples at 500, at 700°C its content remained on the level of

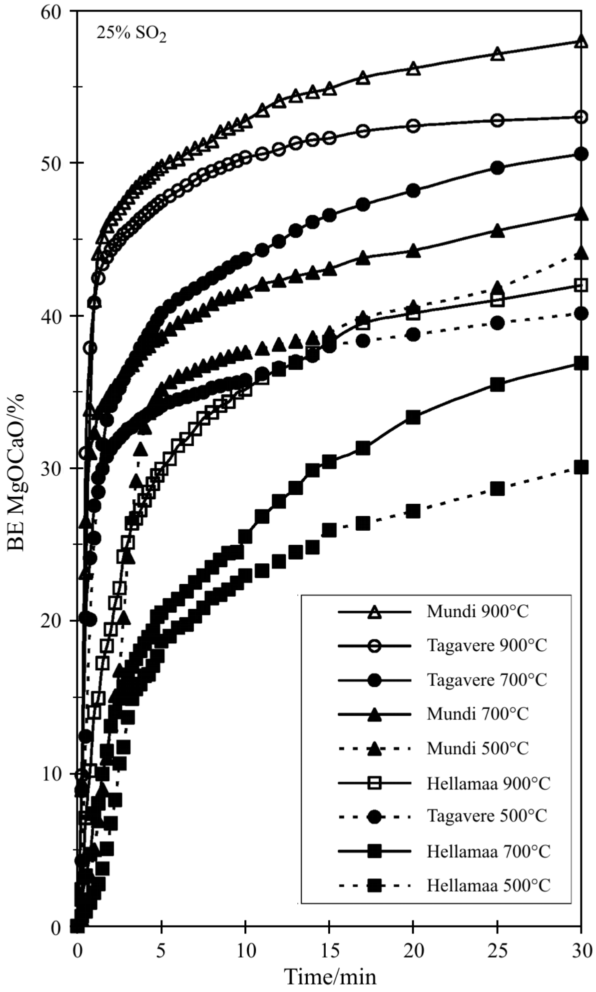

Fig. 7 SO_2 binding efficiency (BE) per MgO·CaO of Mundi, Tagavere and Hellamaa dolomites sulphated at different temperatures

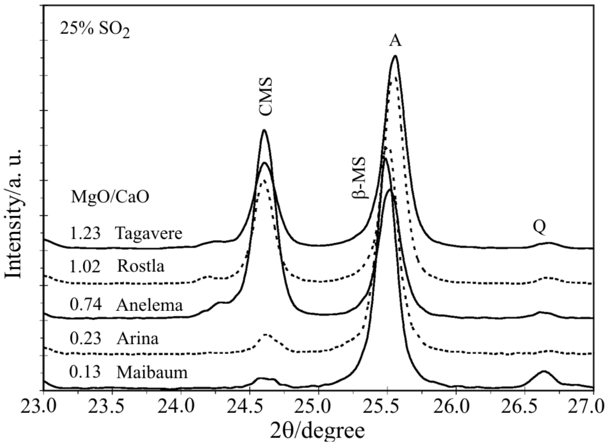

Fig. 8 XRD patterns of dolomite and limestone samples with different mole ratio of MgO/CaO sulphated at 700°C (previously calcinated at 850°C); CMS – $CaMg_3(SO_4)_4$, β-MS – β-$MgSO_4$, A – anhydrite, Q – quartz

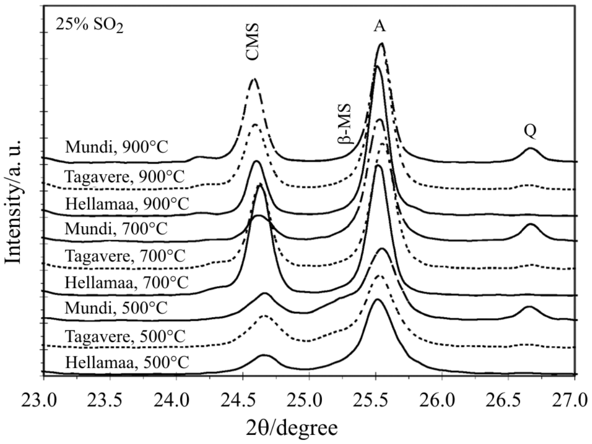

Fig. 9 XRD patterns of Mundi, Tagavere and Hellamaa dolomites sulphated at different temperatures (previously calcinated at 850°C); CMS – $CaMg_3(SO_4)_4$, β-MS – β-$MgSO_4$, A – anhydrite, Q – quartz

traces (Fig. 9). At 500 and 700°C also the formation of γ-$CaSO_4$ was noticed which at higher temperatures transformed to anhydrite.

In the atmosphere containing 80 ppm of SO_2 at 700°C during 30 min of contact 7–9% of MgCa-oxides were utilised, the equilibrium between the phases was not reached. The formation of anhydrite and $CaMg_3(SO_4)_4$ was observed, the last one at least on the level of traces. The presence of β-$MgSO_4$ was not fixed.

In the combustion experiments with SC in a 50 kW_{th} laboratory-scale BFBC device the only compound formed in SO_2 binding with BA and CA was anhydrite, in BFA also $CaMg_3(SO_4)_4$ and traces of β-$MgSO_4$ were detected (Fig. 10). On the XRD patterns of these ashes which were supplementary sulfated, the increase in the content of anhydrite and the formation of $CaMg_3(SO_4)_4$ was followed. The formation of β-$MgSO_4$ at that was not fixed (Fig. 10). On the XRD patterns of BA formed at combustion of OS in Baltic Power Plant only the presence of anhydrite was observed, but after supplementary sulphation of BA also the formation of $CaMg_3(SO_4)_4$ was detected on the level of traces.

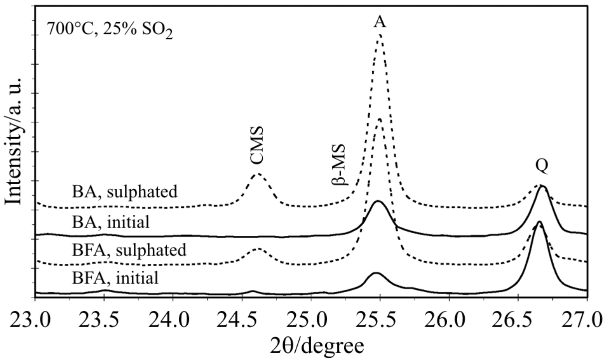

Fig. 10 XRD patterns of initial and sulphated bottom (BA) and bag filter ash (BFA) formed at combustion of semicoke at BFBC; CMS – $CaMg_3(SO_4)_4$; β-MS – β-$MgSO_4$; A – anhydrite; Q – quartz

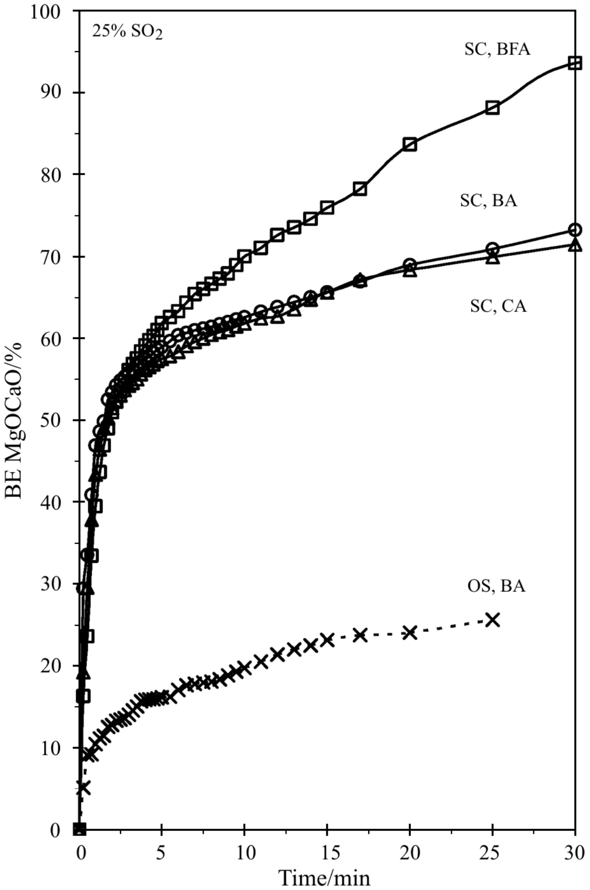

Fig. 11 SO_2 binding efficiency (BE) per MgO·CaO of different semicoke (SC) and oil shale (OS) ashes sulphated at 700°C; BA – bottom ash; CA – cyclone ash; BFA – bag filter ash

In the case of low-temperature ashes at 700°C during 30 min of contact between gaseous and solid phases 35–60 mg SO_2 per 100 mg sample was bound or 70–95% of MgO·CaO contained in the ash was utilised (Fig. 11) which exceeded the respective values of natural dolomite and limestone samples (Fig. 7). It could be due to the higher content of additives in ash samples which diluted the oxides in the sample and improved the diffusion of SO_2 into the sample layer and into the CaO·MgO particles. In high-temperature BA only 25.2% of MgO·CaO was utilised (Fig. 11), which is caused by the shell formed during high-temperature combustion of fuel and surrounding ash particles hindering the diffusion of SO_2 into the particles.

Conclusions

The results of the studies of sulphation of different lime-containing samples (model blends, dolomite and limestone samples, ashes) confirmed that in addition to anhydrite also CaMg-double sulphate $CaMg_3(SO_4)_4$ is formed in a wide temperature range 400–900°C. The optimum temperature for formation and durability of $CaMg_3(SO_4)_4$ is 700–800°C and its formation occurs over the formation of anhydrite and $MgSO_4$. At 400–700°C also the presence of β-$MgSO_4$ was fixed, but only at high SO_2 partial pressure in gaseous phase. At low partial pressure (80 ppm) all the β-$MgSO_4$ formed took immediately part in the formation of $CaMg_3(SO_4)_4$.

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