

BEHAVIOUR OF MAGNESIUM COMPOUNDS AT SULPHATION OF LIME-CONTAINING SORBENTS

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Abstract

Investigation of the SO₂ binding ability of natural dolomite and limestone as well as of the ashes formed at combustion of Estonian oil shale (containing 65.70% of mineral matter including carbonates) or its semi-coke indicated that the amount of SO₂ bound under certain conditions exceeds the stoichiometric amount of SO₂ that could be bound by CaO (or by free CaO in the case of ashes). However, the role of Mg-oxide in the binding of SO₂ is not clear, clarification of this problem was the aim of the current study.

Experiments with model samples were carried out using thermogravimetric equipment (QDerivatograph, MOM). Calcination of the samples was performed under dynamic heating conditions (10K per min) in the atmosphere of air, sulphation under isothermal conditions at 400-900°C in air – SO₂ mixture. Initial samples, intermediate and final products were subjected to chemical, X-ray, IR-spectroscopy, etc. methods of analysis.

The results of these studies confirmed the high SO₂ binding ability of the samples used and the formation in addition to CaSO₄ as of the main product also CaMg - double sulphate CaMg₃(SO₄)₄ in the large temperature range 400-900°C. The optimum temperature range for formation and durability of CaMg₃(SO₄)₄ was 700-800°C. The mechanism of binding SO₂ into the solid phase by Mg-compounds during sulphation of lime-containing materials and at combustion of fuels containing carbonates was proposed.

Introduction

The most known sorbents for binding acidic gaseous compounds from flue gases are dolomite, limestone and lime-containing ashes formed at combustion of solid fossil fuels. The total amount of these sorbents used is huge – millions of tons annually. The mechanism of decarbonisation of limestone and sulphation of lime formed at that has been studied by many authors. Some papers are also dealing with the decarbonisation of dolomites, but there is quite few and contradicting data on the participation of MgO formed at that in the binding of SO₂ (1-5). Interesting data was obtained by analysing the filter cakes from pressurised fluidized bed combustion of coals by means of infrared spectroscopy (6). Dolomite was used as a sorbent for binding SO₂ from flue gases and a new phase – Mg₂Ca(SO₄)₃ - was identified in these cakes. The participation of Mg compounds in the binding of SO₂ was proved also in our earlier works (7,8).

In this work an attempt to determine the mechanism of SO₂ binding from gaseous phase by Mg-compounds was made.

Methods

The experiments were carried out with thermogravimetric equipment (QDerivatograph, MOM) according to (8). The multiplate Pt crucibles were used, the thickness of sample layer was 0.20.3 mm, the weight of sample was ≈100 mg, the rate of gas flow was 270 ml per min and the concentration of SO₂ in the gas mixtures was 80ppm or 25% (Vol.). Based on the data obtained, the following parameters were calculated to characterise the extent of interaction: SO₂ binding rate (mg SO₂/mg sample*min), the SO₂ binding capacity (mg SO₂/100 mg sample) and SO₂ binding efficiency (%) per content of total CaO and MgO (CaO+MgO) in the samples.

Different lime-containing samples were studied (Table):

- model samples based on reactive grade MgO and CaO, the mole ratio of MgO/CaO was varied from 9:1 to 1:9,
- dolomite and (dolomitic) limestone samples from different deposits (Estonia),
- bottom ash (BA) formed at high-temperature (1200-1300°C) combustion of pulverised Estonian oil shale (OS) at Baltic Power Plant (Baltic PP),

- 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.

The initial samples as well as the products of sulphation were subjected to chemical, XRD (Cu K α radiation, 40kV, 20 mA) (DRON-4), FTIR spectroscopy (Interspec 2000, Interspectrum Ltd.) and BET specific surface area (SSA) (Kelvin 1042, Costech International) analyses. For identification of the phase composition of samples by XRD data, the ICDD (International Centre for Diffraction Data) PDF database (1997 year version) was used.

Table. Main characteristics of samples

Samples	Mole ratio of Mg/CaO	Content, %					SSA, m ² /g
		CaO	MgO	CO ₂	Insoluble residue in aqua regia	free CaO	
<u>Dolomites, limestone:</u>							
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
Adavere	0.668	37.1	17.7	43.3	1.7	-	5.10
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
<u>Ashes:</u>							
<i>Semicoke, BFBC:</i>							
Bottom ash (BA)	0.156	38.7	6.4	6.8	224	14.9	3.90
Cyclone ash (CA)	0.167	32.7	5.6	3.8	26.2	13.0	5.68
Bag filter ash (BFA)	0.133	28.0	3.9	3.2	33.7	4.2	4.14
<i>Oil shale, Baltic PP:</i>							
Bottom ash (BA)	0.100	58.6	5.8	3.1	21.7	20.5	1.45

Results and discussion

The experiments with MgO showed that at lower temperatures (400° and 500°C), the SO₂ binding took place at a low but almost constant rate and during 30 minutes of contact between solid and gaseous phases (25% SO₂) there was bound 26 mg and 90 mg SO₂ per 100 mg sample, respectively. At 700° and 900°C during the initial period of interaction (1-2 min) the mean SO₂ binding rate was quite high – 0.345 mg and 0.130 mg SO₂ per mg sample*min⁻¹. During 30 minutes of contact it was bound 120 mg and 57 mg SO₂, respectively (or, otherwise, 66.8% and 31.6% of MgO contained was utilised as can be seen in Figure 1). It means that at 900°C the decomposition rate of MgSO₄ exceeded the formation rate of it. In comparison, with CaO at 700°C during 30 minutes 54.8 mg SO₂ per 100 mg sample was bound or 47.2% of CaO contained was utilised (Figure 1). The model samples with MgO/CaO mole ratio 3:1 and 2:1 bound SO₂ more intensively than these at mole ratio 9:1 but less than MgO. All blends with mole ratio of MgO/CaO >1.0 bound more or on the same level and with mole ratio <1.0 less SO₂ than it was bound by CaO (Figure 1).

The results of XRD analysis confirmed the formation of anhydrite, β -MgSO₄ and CaMg-double sulphate which by the ICDD database (card 190241) has a formula CaMg₃(SO₄)₄ and unreacted MgO and CaO in the products of sulphation (25% SO₂) in all the model blends studied. In Figure 2 the variation in intensities of the respective peaks on XRD patterns depending on the MgO/CaO mole ratio in the blends can be seen.

The experiments carried out with model blends in the atmosphere with low SO₂ concentration (80ppm) showed that the equilibrium was obtained in 1-2 minutes of contact between gaseous and solid phases and at that 2-5 mg SO₂ per 100 mg sample was bound. 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(SO₄)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 formation of β -MgSO₄ was not fixed which could mean that the formation of CaMg₃(SO₄)₄ proceeded over the formation of anhydrite

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 SO₂ binding by MgCa-oxides contained in the decarbonised sample was on the level of 25-70% and, as a rule, this value

was higher for the samples which had higher level of insoluble residue. The additives influence the crystallinity and SSA of the samples together with this also on the SO₂ binding efficiency.

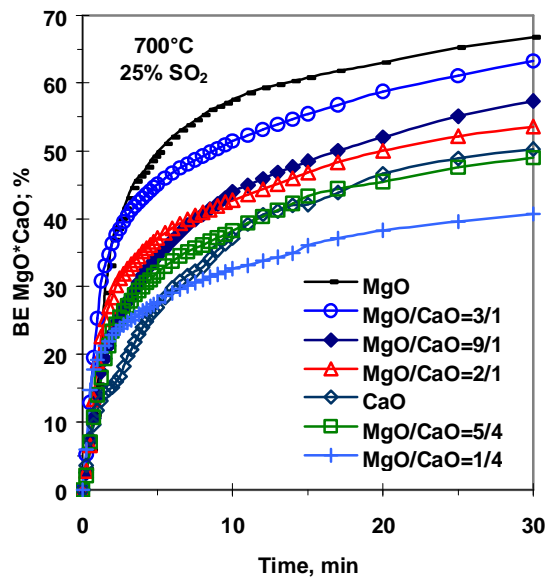


Figure 1. SO₂ binding efficiency per MgO*CaO in blends with different MgO and CaO mole ratio

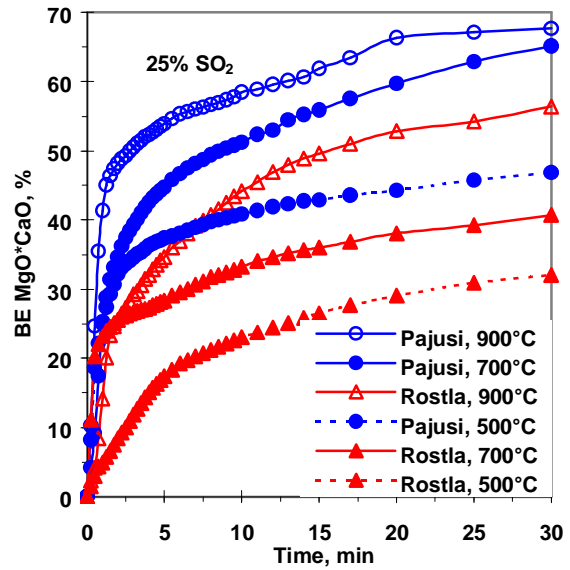


Figure 3. SO₂ binding efficiency per MgO*CaO in Pajusi and Rostla dolomites at different temperatures

For example, comparing Pajusi (MgO/CaO=1.017; insoluble residue 19.3%) and Rostla (MgO/CaO =1.003, insoluble residue 2.54%) dolomites indicated that the SO₂ binding efficiency per MgCa-oxides of Pajusi dolomite exceeded this value for Rostla dolomite depending on temperature of sulphation 11-23%, being the highest at 700°C (Figure 3).

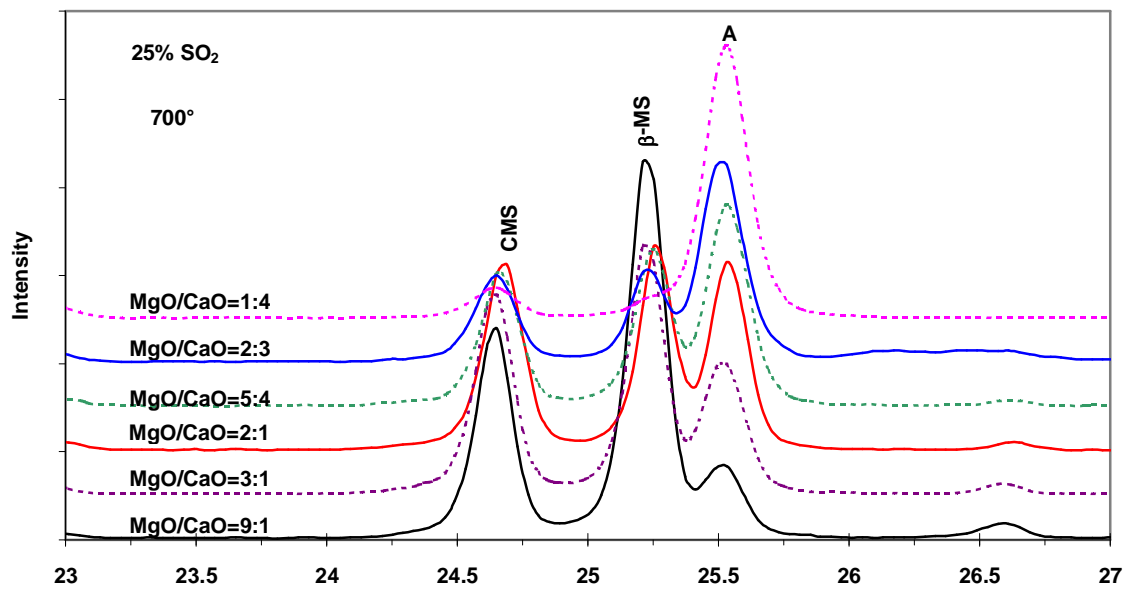


Figure 2. XRD patterns of model blends at different mole ratio of MgO/CaO (CMS -CaMg₃(SO₄)₄; β-MS - β-MgSO₄; A - Anhydrite)

The characteristic peaks of CaMg₃(SO₄)₄ on the XRD patterns were more intensive for Pajusi and these of anhydrite for Rostla dolomite (Figure 4). The formation of CaMg(SO₄)₄ was fixed with all the dolomite and limestone sample studied (Figure 4) and the characteristic peaks on XRD patterns were most intensive at 700°C (Figure 5). The formation of β-MgSO₄ was clearly fixed at 500°C, at 700°C its content remained on the level of traces. At 500° and 700°C also the formation of γ-CaSO₄ was fixed which at higher temperatures transformed to anhydrite. At 500°C and with Pajusi and Munddolomites (both with high content of additives) the presence of CaS was fixed on the level of traces.

In the atmosphere containing 80ppm of SO₂ at 700°C during 30-minutes of contact 7-10% of MgCa-oxides were utilised, the equilibrium between the phases was not reached. The formation of anhydrite and CaMg₃(SO₄)₄ was fixed, the last one at least on the level of traces. The formation of β-MgSO₄ was not fixed.

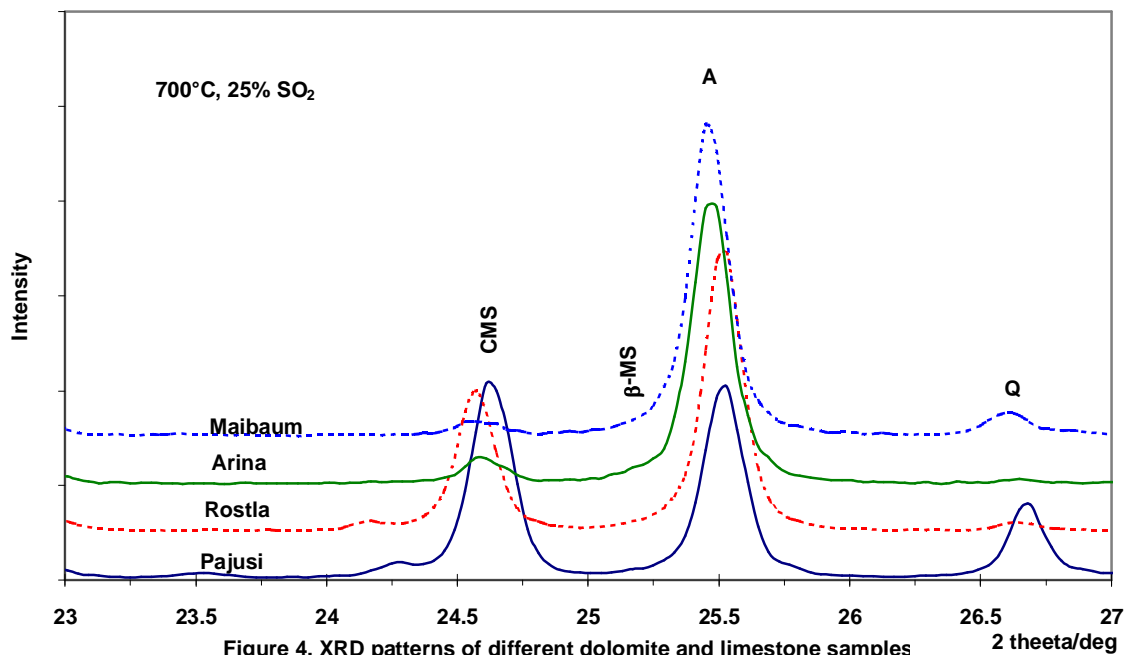


Figure 4. XRD patterns of different dolomite and limestone samples (previously calcinated) sulphated at 700°C (CMS - CaMg₃(SO₄)₄; β-MS - β-MgSO₄; A - Anhydrite; Q-Quartz)

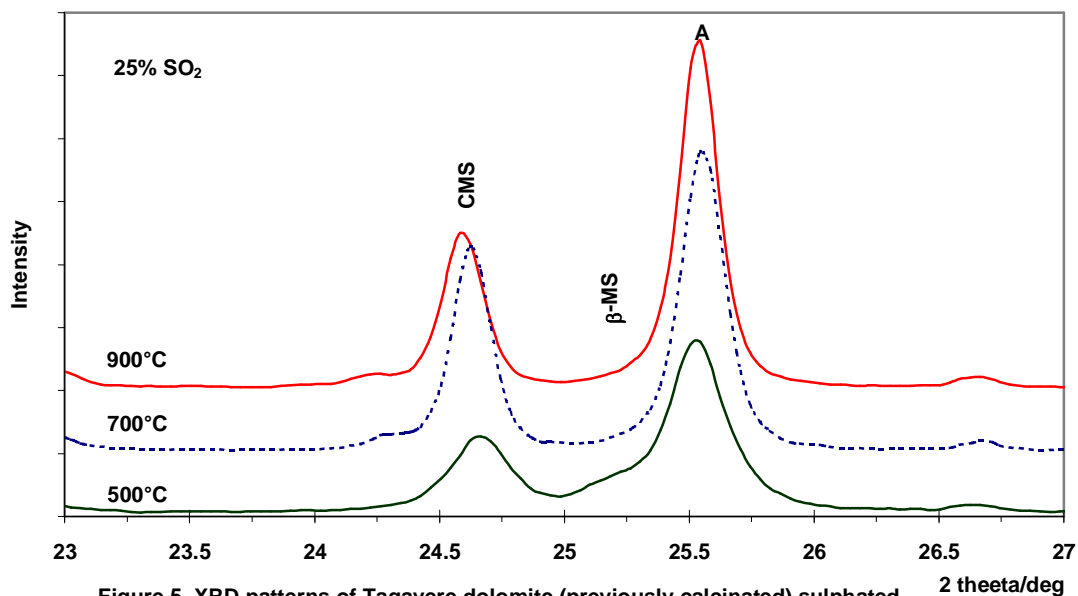
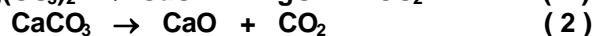


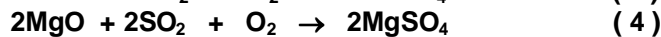
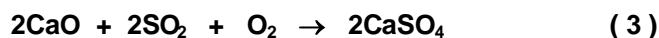
Figure 5. XRD patterns of Tagavere dolomite (previously calcinated) sulphated at different temperatures (CMS - CaMg₃(SO₄)₄; β-MS - β-MgSO₄, A - Anhydrite)

At combustion of SC in a 50kW_{th} laboratory-scale BFBC device the only product of SO₂ binding with BA and CA was anhydrite, in BFA also CaMg₃(SO₄)₄ and traces of β-MgSO₄ were fixed. On the XRD patterns of these ashes which were supplementary sulphated, the increase in the content of anhydrite and the formation of CaMg₃(SO₄)₄ was detected. The formation of β-MgSO₄ at that was not observed. On the XRD patterns of BA formed at combustion of OS in Baltic Power Plant only the content of anhydrite was fixed, but after supplementary sulphation of BA also the formation of CaMg₃(SO₄)₄ on the level of traces.

So, considering the results of experiments, the following transformations would occur:
decomposition of carbonates:



binding of SO₂:



formation of CaMg double sulphate:



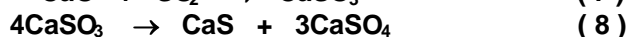
or



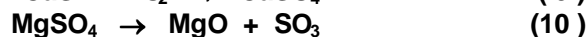
The presence of traces of CaS in the solid phase at temperatures ≤600-650°C could be explained by the occurrence of reactions:



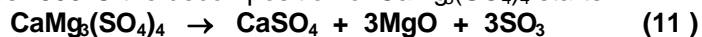
and



At temperatures >650°C the transformation of γ-CaSO₄ into anhydrite, the oxidation of CaS and the decomposition of MgSO₄ take place:



and at temperatures >800°C the decomposition of CaMg₃(SO₄)₄ starts:



and SO₃ formed at that reacts with CaO:



Conclusion

The results of sulphation of the samples studied (model blends, dolomite and limestone samples, ashes) confirmed that in addition to anhydrite as the main product of sulphation CaMg-double sulphate CaMg₃(SO₄)₄ is formed in the large temperature range 400-900°C. At temperatures 400-700°C also β-MgSO₄ is formed. The optimum temperature of formation and durability of CaMg(SO₄)₂ is 700-800°C. The mechanism of binding SO₂ into the solid phase by CaMg-oxides during sulphation of lime-containing materials is proposed.

Acknowledgement

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References

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