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A THERMOGRAVIMETRIC METHOD FOR COMPARING THE SO_2-BINDING ABILITIES OF DIFFERENT LIME-CONTAINING MATERIALS

R. Kuusik and A. Trikkel

Laboratory of Inorganic Technology, Tallinn Technical University, Ehitajate tel 5, EE-200108 Tallinn, Estonia

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Abstract

A thermogravimetric method based on dynamic heating and the use of an internal source of SO_2 (metal sulfates with a suitable range of decomposition temperatures) was used to compare the SO_2-binding abilities of various lime-containing materials.

By means of this method, furnace and cyclone ashes formed in the combustion of oil-shale in the Baltic Power Station, their differently activated (grinding, hydrating) forms and some carbonaceous materials were investigated to estimate their suitability for exhaust gas purification in thermal power stations.

Keywords: environment, TG

Introduction

The acidification of the environment in industrial regions has become a serious problem during recent years. The result of the combustion of oil shale in the Baltic and the Estonia Thermal Power Stations in North-East Estonia is the emission of SO_2 amounting to 150.000 tons per year. The exhaust gases from these two power stations contain up to 1500–2000 mg/Nm^3 of SO_2 [1]. At the same time, the solid waste (ash) contains free Ca and Mg oxides due to the high content of carbonates in Estonian oil shale, and can be used for purification of the flue gases by dry desulfurization.

The investigation of SO_2-binding ability is rather difficult due to the toxicity and corrosiveness of SO_2, and special apparatus is therefore needed (special furnaces for TG apparatus, etc.) to perform experiments in SO_2 medium [2–4]. A simple method for preliminary comparison of the different sorbents is described and some results of the evaluation of the SO_2-binding abilities of oil shale ashes and some carbonaceous materials are presented in this paper.

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Methods and materials

A simple and quick method to compare the SO_2-binding abilities of different materials and lessen the damage of scaling caused by the condensation of SO_3 on the surfaces of the system is to subject them to dynamic heating with an internal source of sulfur dioxide (Fig. 1). The lower layer in the crucible is a metal sulfate with a suitable range of decomposition temperatures. A small amount of SiO_2 is strewn on it as an inert material to achieve a better distribution of SO_2 in the volume of the crucible. The sorbent under investigation forms the upper layer.

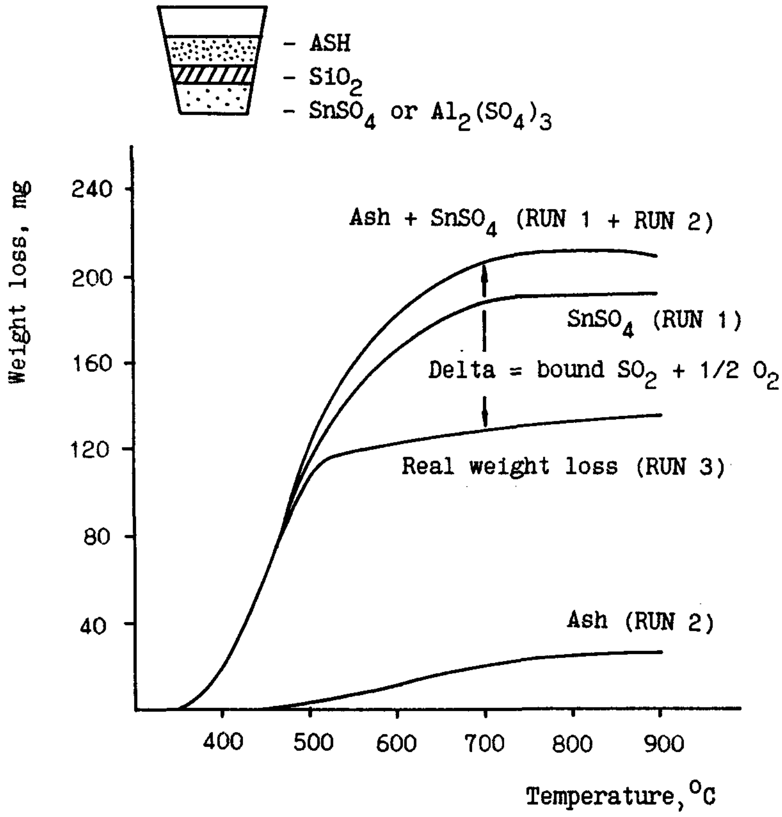

Fig. 1 Experiments with the inner source of SO_2.Dynamic heating 10 deg·min^{-1}

Three runs (with sorbent itself, the sulfate alone and the two together) must be performed under the same conditions (the same furnace, heating rate and amount of material) to obtain the required information, supposing that the difference between the total loss in mass of the sorbent and the sulfate and the real loss in mass from the third run will describe the amount of SO_2 bound by the

Table 1 Characterization of the samples

Sample	BET surface / $m^2 \cdot g^{-1}$	CaO^F /%	CaO^T /%	MgO /%
CaO	0.735	98.0	98.2	
$CaCO_3$	0.086	53.9	54.0	
$Ca(OH)_2$	3.48	74.5	74.6	
MgO	13.70			98.60
$Mg(OH)_2$	136.50			67.90
cyclone ash*	0.82	17.56	52.9	5.01
furnace ash*	0.98	27.46	58.6	5.83
dolomite of the Advere deposit	5.00		27.8	20.90
calcite of the Karinu deposit	3.29		53.3	0.21

* formed in the Baltic Power Station

material. The calculations are made on the assumption that the final product is $CaSO_4$ and/or $MgSO_4$:

$$CaO(s)+SO_2(g)+1/2O_2(g)=CaSO_4(s) \tag{1}$$

$$MgO(s)+SO_2(g)+1/2O_2(g)=MgSO_4(s) \tag{2}$$

However, it must be noted that some $CaSO_3$ or $MgSO_3$ may be formed at lower temperatures, but in the oxidative atmosphere these are not stable over 500–600°C [5] and, when the heating rate is relatively low and the final temperature high enough, the calculations can be considered to be acceptable. The decomposition of $MgSO_4$ above 800–850°C must be taken into consideration [2, 6].

$SnSO_4$ (decomposes at 400–600°C), $Al_2(SO_4)_3$ (decomposes at 750–950°C) and their mixture in a ratio corresponding to the equal amount of SO_2 liberated in the lower and higher temperature intervals (65.3% of $SnSO_4$ and 34.7% of $Al_2(SO_4)_3$), were used as the internal source of SO_2 in these series of experiments. The amount of free CaO (CaO^F: CaO from $CaCO_3$, $Ca(OH)_2$ and free CaO itself) or total CaO (CaO^T: all calcium-containing compounds) was kept at the same level for different materials (changing the sample mass, the differences in the CaO contents of the samples resulting in the sample amount varying from 0.3 up to 1.5 g) and this was also the basis for calculating the theoretical SO_2-binding ability. In most experiments, the mole ratio $CaO(MgO)/SO_2$ was >1. The amounts of $SnSO_4$, $Al_2(SO_4)_3$ and the mixture were kept at the same level and were about 660, 350 and 400 mg, respectively.

The experiments were carried out in a MOM (Hungary) derivatograph, at a heating rate of 10 deg·min^{-1} up to 1000°C in air. The sorbents used are presented in Table 1.

The BET surfaces of CaO and the ashes are close; calcite, dolomite and $Ca(OH)_2$ form the next group, with BET surfaces a little higher. MgO and particularly $Mg(OH)_2$ have high, and $CaCO_3$ quite low BET surfaces.

Results and discussion

To establish the temperature region in which the binding takes place, several runs were made with the mixture of $SnSO_4$ and $Al_2(SO_4)_3$ (Fig. 2). The mole ratio $CaO(MgO)/SO_2$ was chosen to be relatively high in order to avoid the total loss of the binding ability of the sorbents during the run. Since these sulfates decompose in different ways:

$$SnSO_4(s)=SnO_2(s)+SO_2(g) \tag{3}$$

$$Al_2(SO_4)_3(s) = Al_2O_3(s) + 3SO_2(g) + 3/2O_2(g) \quad (4)$$

only the amount of bound SO_2 (m_{SO_2}, mg) is presented. The reactions of SO_2 with CaO and MgO attain an observable rate at 450–500°C and the decomposition curves resemble that of the mixture. This indicates that the rate of binding is higher than the rate of decomposition of the mixture. Nevertheless, the SO_2-binding ability of MgO exceeds that of CaO, especially at higher temperatures, when aluminium sulfate starts to decompose. In these experiments, the decomposition temperature of $MgSO_4$ was relatively high, because of the high partial pressure of SO_2 in the volume of the crucible, and became noticeable at temperatures over 920°C, when the amount of bound SO_2 began to decrease. The reactions of SO_2 with $Ca(OH)_2$ and $Mg(OH)_2$ start at lower temperatures and

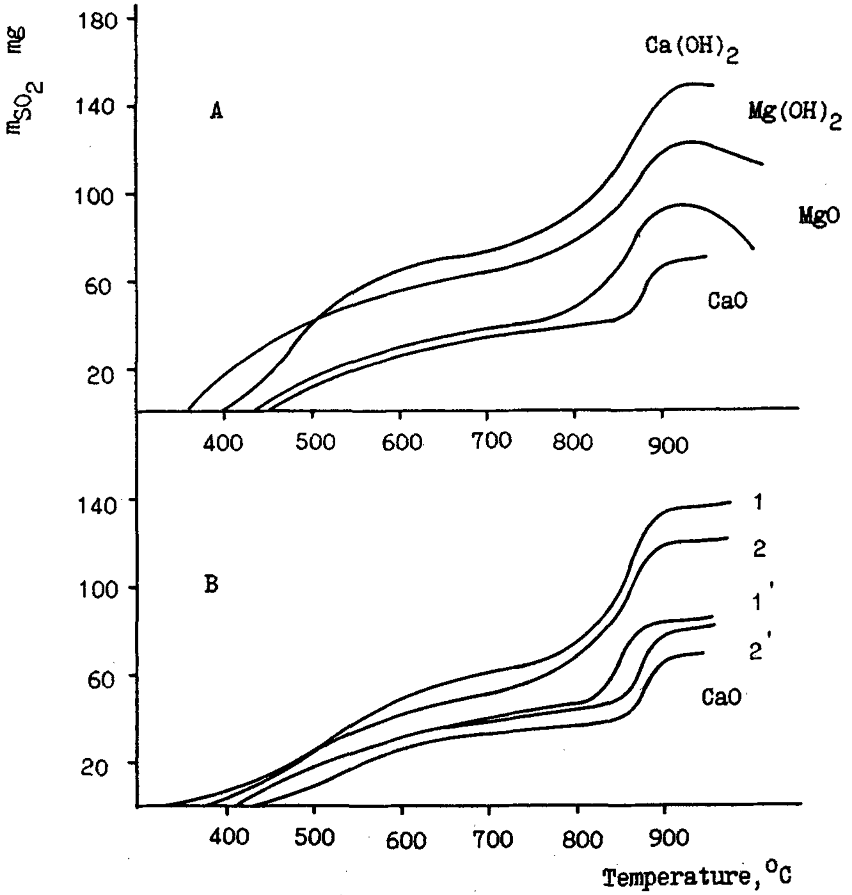

Fig. 2 The amount of SO_2 (m_{SO_2}, mg) bound by different materials: 1 - cyclone ash, 2 - furnace ash. $CaO^F(MgO)/SO_2 = 2$(A, B - 1,2) or $CaO^T/SO_2 = 2$(B - 1',2')

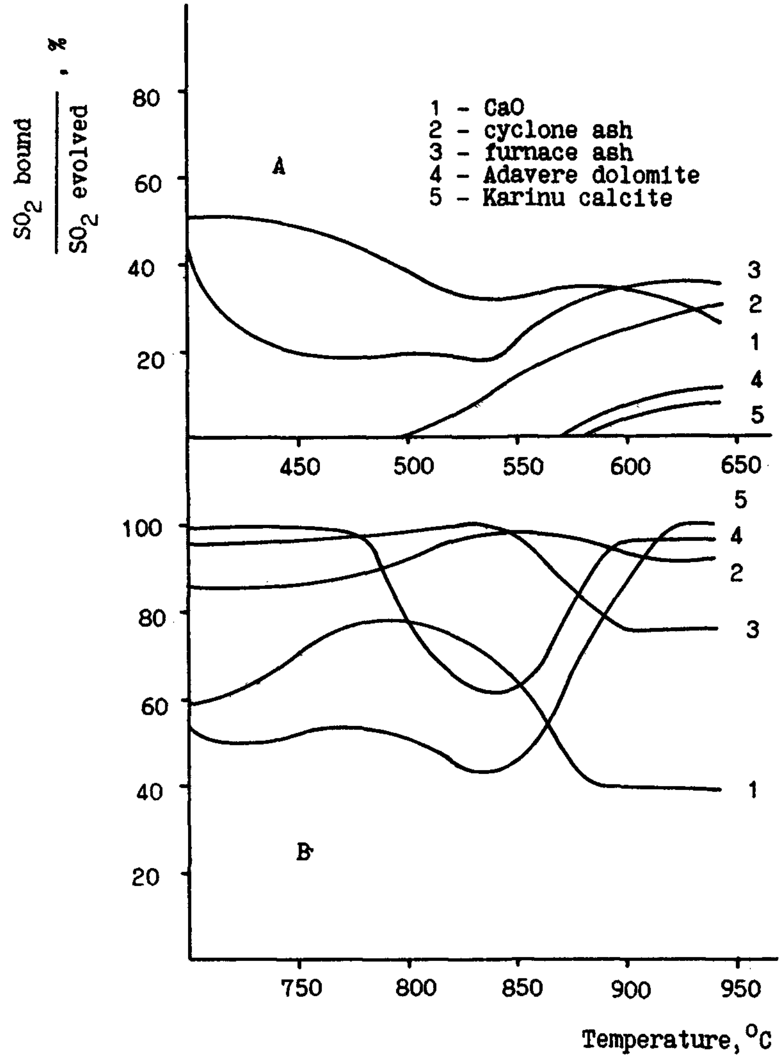

Fig. 3 Changes in the SO_2-binding ability of different materials in the range of 400–600°C ($SnSO_4$) - A, or 750–950°C ($Al_2(SO_4)_3$) - B, $CaO^F(MgO)/SO_2 = 1.6$

the rate increases at 450–500°C the SO_2-binding abilities considerably exceeding those of the other materials used.

The corresponding curve for $CaCO_3$ is not shown here, because its decomposition temperature in the run with the mixture decreased and the decomposition curve itself differed significantly from that for the run with $CaCO_3$ alone, leading to essential errors. This can be explained by the change in the conditions (partial pressure of O_2, SO_2 and CO_2) in the volume of the crucible when

Table 2 SO_2 removal efficiency of different materials. $CaO^F/SO_2=1.6$

Bound SO_2	Materials				
	CaO	Cyclone ash	Furnace ash	Adavere dolomite	Karinu calcite
			$SnSO_4$ (400–600°C)		
%	28.5	35.1	39.7	21.6	24.2
$mg \cdot mg^{-1}$mat.	0.196	0.043	0.075	0.080	0.080
$mg \cdot mg^{-1}$ CaO^F	0.196	0.243	0.273	–	–
$mg \cdot mg^{-1}$ CaO^T	0.196	0.081	0.128	0.149*	0.165*
			$Al_2(SO_4)_3$ (750–950°C)		
%	38.6	92.4	76.4	98.0	96.0
$mg \cdot mg^{-1}$mat.	0.291	0.115	0.147	0.368	0.315
$mg \cdot mg^{-1}$ CaO^F	0.291	0.653	0.534	–	–
$mg \cdot mg^{-1}$ CaO^T	0.291	0.217	0.250	0.688*	0.647*

*here CaO^T expresses the sum of CaO and MgO only $CaCO_3$ decomposes or when two decomposition reactions ($CaCO_3$ and $Al_2(SO_4)_3$) and the binding of SO_2 by the CaO formed take place at the same time. However, it may be noted that the reaction with SO_2 starts at 560°C (which can be explained by the beginning of formation of CaO from $CaCO_3$) and the final value of m_{SO_2} is somewhat higher than that for CaO. The reaction with the ashes starts at 400°C and the cyclone ash retains better SO_2-removal ability for $CaO^F/SO_2 = 2$ as well as for $CaO^T/SO_2 = 2$.

More information can be obtained by using $Al_2(SO_4)_3$ or $SnSO_4$ alone [Table 2].

The best results as concerns the percentage of SO_2-bound in the lower temperature region are obtained with the two ashes, but, due to their relatively low CaO^F contents, calcite and dolomite give even better results when these are expressed in mg of SO_2 to mg of material. In the higher temperature region, the best results are obtained with carbonaceous materials. Cyclone ash is slightly better at higher temperatures, and furnace ash at lower temperatures.

In the lower temperature region, furnace ash and CaO begin to react with SO_2 from the beginning of the decomposition of $SnSO_4$, cyclone ash at 500°C and the carbonaceous materials at 560–570°C (Fig. 3A). At the same time, the degree of SO_2-binding to the ashes also remains evenly high in the whole decomposition range of $Al_2(SO_4)_3$ (85–95% of the SO_2 evolved up to that temperature) (Fig. 3B), while the binding ability of CaO increases up to 800°C and subsequently starts to decrease, probably because of the formation of a new solid phase on the surface of the grains, hindering the diffusion of SO_2 towards the unreacted oxide [7]. Adavere dolomite reacts intensively with SO_2 at the beginning of decomposition of aluminium sulfate (this may be related to the decomposition of $MgCO_3$); the reaction then slows down, and a new increase in reaction rate occurs over 850°C (the decomposition of $CaCO_3$ with the formation of CaO starts, and an additional amount of SO_2 is bound). Karinu calcite starts to react more intensively at 840°C (its $MgCO_3$ content is negligible).

Series of experiments have been carried out with this method to determine the possibility of activating the oil shale ashes. In these runs, a mole ratio $CaO^F/SO_2 = 1$ was applied to attain better separation of the curves. The results for furnace ash are presented in Table 3 and Fig. 4.

It can be seen that grinding and hydrating increase the BET surface of the material. At the same time, grinding affects the SO_2-binding ability to a small extent, while hydration (addition of water in excess and drying at 150°C) considerably increases the reaction ability of the furnace ash, especially at lower temperatures. As for $Ca(OH)_2$ and $Mg(OH)_2$, this can be explained by their decomposition and by the role of water vapor in the process. The influence of the increased BET surfaces must also be taken into consideration.

Table 3 SO_2 removal efficiency of the activated furnace ash. $CaO^F/SO_2=1$, ($SnSO_4$)

Sample	BET surf. /	Bound SO_2			
	$m^2 \cdot g^{-1}$	%	$mg \cdot mg_{mat.}^{-1}$	$mg \cdot mg_{CaO^F}^{-1}$	$mg \cdot mg_{CaO^T}^{-1}$
Furnace ash	0.98	32.6	0.0997	0.363	0.170
ground	1.22	45.2	0.138	0.504	0.236
hydrated	2.50	81.8	0.234	0.922	0.432
ground and hydrated	2.75	89.4	0.255	1.008	0.472

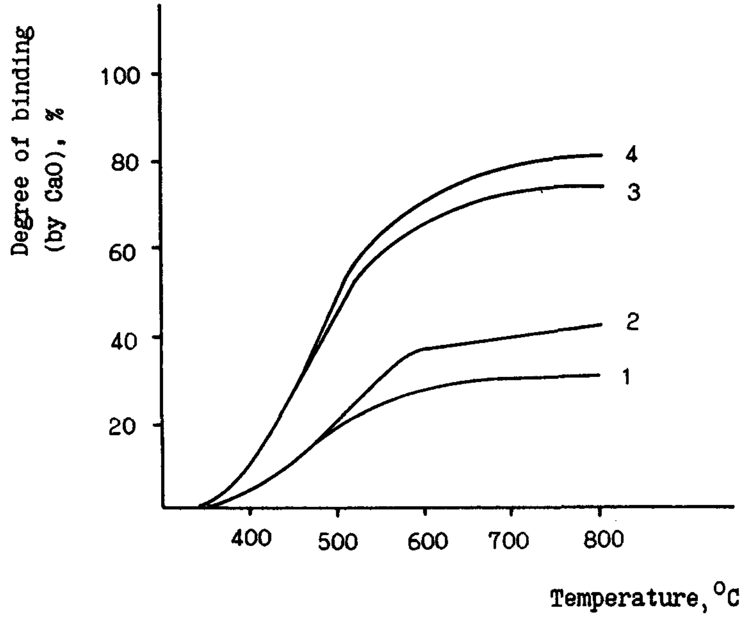

Fig. 4 The effect of various activation methods on the SO_2 binding ability of furnace ash: 1 - initial probe, 2 - ground, 3 - hydrated, 4 - ground and hydrated. CaO^F/SO_2 = 1 ($SnSO_4$)

Conclusions

The method described here is convenient for preliminary and comparative investigations of the SO_2-binding abilities of various oil shale ashes in order, to be able to plan more exact experiments and estimate possible activation methods for them. For carbonaceous materials, simultaneous registration of the evolved CO_2 may be recommended, to eliminate errors. It is difficult to draw any conclusions on the kinetics of these reactions, because the decomposition of the source of SO_2 appeared to be the limiting factor under these conditions. Thus, experiments in pure SO_2 must be performed to obtain reliable results.

The SO_2-binding abilities of the samples that contained hydroxides proved to be essentially higher than those of the other materials, and therefore the best activation method is hydration of the ashes to increase the SO_2-removal efficiency in the cooler parts of the exhaust gas tract. The effect of grinding of the materials was found to be of lesser importance. Carbonaceous materials will be good in the temperature region 850–950°C. In this case, the decomposition of $MgSO_4$ must be taken into consideration.

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Zusammenfassung — Zum Vergleich der Fähigkeit verschiedener kalkhaltiger Materialien, SO$_2$ zu binden, wurde eine thermogravimetrische Methode eingesetzt, die auf dynamischem Aufheizen und einer internen SO$_2$-Quelle basiert (Metallsulfate mit geeigneten Intervallen von Zersetzungstemperaturen).

Mittels dieser Methode wurden Ofen- und Wirbelscheideraschen aus der Verbrennung von Ölschiefer im Baltischen Kraftwerk, deren verschiedene aktivierte (Mahlen, Hydratieren) Formen und einige kohlenstoffhaltige Materialien untersucht, um deren Eignung zur Abgasreinigung von Wärmekraftwerken abzuschätzen.