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APPLICATION OF THERMAL ANALYSIS IN A PHASE COMPOSITION STUDY ON BY-PRODUCT FROM SEMI-DRY FLUE GAS DESULFURIZATION SYSTEM

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Abstract

DTA, TG and XRD methods were used for the determination of by-product – obtained during flue gas desulfurization by means of introduction of dehydration – resisting sludge from water decarbonization system. Analysis results enabled the development and application of sludge utilization technology by means of semi-dry flue gas desulfurization in ‘Siersza’ power plant.

Keywords: DTA, phase composition, sludge, TG, utilization, XRD

Introduction

The sludge disposal from water decarbonization process is an essential problem for many power plants. This is a hardly filtering mixture of $CaCO_3$, coagulant, flocculent and separated pollutants [1, 2]. Until now, sludge dehydrated on a filter-press was periodically removed at the coal yard and next loaded into the boiler. This way of sludge utilization disturbed boiler fuel balance and in consequence – caused destabilization of power plant. So, an attempt of effective application of wasted sludge as a sorbent in a semi-dry desulfurization process was undertaken. However, the realization of this project demanded the determination of sludge real sorption capacity. For this aim methodical study of sludge phase composition was carried out.

After analyzing several technological solutions it has been decided to apply spray reactor used in the process of desulfurization. The reactor was filled with a mixture of lime solution, recycle and sludge (Fig. 1). This technical solution enabled the difficult process of sludge dewatering to be avoided, assured its permanent reception from the decarbonization system and solved the problem of its utilization.

The sludge in the form of 10% suspension is pumped to a recycle preparing tank and used instead of water for preparing a sorption suspension undergoing atomization in a spray reactor of the flue gas desulfurization system.

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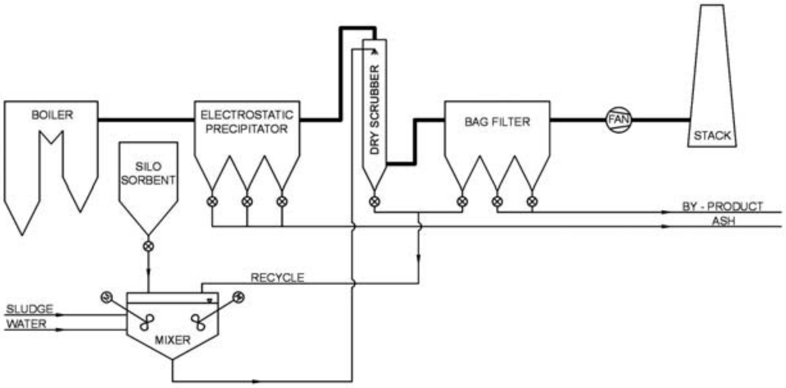

Fig. 1 Scheme of semi-dry flue gas desulfurization process with sludge utilization

The estimation of sludge addition influence both on desulfurization process and product quality was enabled by thermal analysis [3], the results of which are presented below.

Experimental

Mineralogical composition of sludge – and by-product samples was determined on the basis of chemical analysis and phase composition tests by means of thermal- and X-ray analysis [4]. 10 samples from 'Siersza' power plant flue gas desulfurization system were tested.

Chemical analysis was carried out by means of conventional methods [5]. CaO and MgO total content was determined by complexometric method in solutions obtained after hot dissolving of tested samples in 10% hydrochloric acid solution and successive separation of insoluble parts, aluminium and iron hydroxides. The SO_3^{2-} ions content was determined by iodometric method. The determination of total sulfur content in terms of SO_4^{2-} was made by gravimetric method in solutions obtained from dissolving samples in hydrochloric acid in the presence of bromine. The determination of Cl^- ions was carried out by Mohr's method. The content of active CaO, was determined in accordance to standard [6].

The differential thermal and thermogravimetric analysis was carried out by means of a Paulik–Paulik–Erdey (MOM, Hungary) type derivatograph within the range of temperatures 20–1000°C under different atmospheres (air and nitrogen). The 500 mg samples were placed in corundum crucibles; α-Al_2O_3 powder was used as a reference material for DTA experiments. Heating rate was 10 K min^{-1}.

The X-ray phase analysis of examined samples was made with the use of a XRD-3003 TT type X-ray diffractometer, CuK_α radiation and Ni filter.

Results and discussion

Table 1 presents the results of by-product samples chemical analysis including determination of the content of: MgO and CaO, SO_3^{2-} in terms of $CaSO_3{\cdot}0.5H_2O$, SO_4^{2-} ions in terms of anhydrous $CaSO_4$ (after previous allowance for sulfur to be bounded in $CaSO_3$), Cl^- in terms of anhydrous $CaCl_2$, residues undissolved in 10% HCl solution and active CaO.

Table 1 Results of chemical analysis of by-product samples

Sample No.	Content/mass%						
	CaO total	MgO	$CaSO_3{\cdot}0.5H_2O$	$CaSO_4$	$CaCl_2$	Residue	CaO active
1	50.3	6.0	45.7	6.6	3.8	0.5	20.8
2	51.4	2.2	46.1	8.1	3.4	0.4	22.3
3	51.4	2.2	46.1	8.1	3.4	0.4	22.3
4	47.7	1.4	32.3	5.4	1.9	3.6	14.8
5	47.5	1.4	32.1	6.6	2.2	3.6	14.4
6	48.0	4.3	31.0	6.1	1.9	4.1	14.1
7	49.4	2.8	47.6	18.0	1.1	3.1	16.4
8	46.1	4.3	30.5	4.7	1.9	3.0	11.4
9	50.0	1.4	29.9	8.9	2.2	3.6	14.0
10	49.9	1.4	44.5	7.7	2.8	1.1	19.2

Table 2 Quantitative phase composition of by-product samples determined on the basis of thermal analysis made in the atmosphere of air and nitrogen

Sample No.	Content/mass%			
	$CaSO_3{\cdot}0.5H_2O$	$Ca(OH)_2$	$CaCO_3$	CaO in $Ca(OH)_2$
1	42.8	28.8	7.3	21.8
2	43.6	29.6	7.1	22.4
3	43.6	29.2	8.0	22.1
4	30.7	20.1	27.3	15.2
5	33.1	19.7	28.5	14.9
6	31.9	19.7	28.9	14.9
7	46.0	21.8	7.7	16.5
8	29.1	17.7	29.6	13.4
9	30.3	20.1	30.5	15.2
10	42.4	25.7	11.8	19.4

The X-ray analysis pointed out that $CaCO_3$ was the major component of sludge (Fig. 2) but $CaSO_3 \cdot 0.5H_2O$ predominated the by-product samples next to unprocessed $Ca(OH)_2$ sorbent and $CaCO_3$ (carbonizated sorbent and sludge component) (Fig. 3). Table 2 shows the content of mineral ingredients for by-product samples as

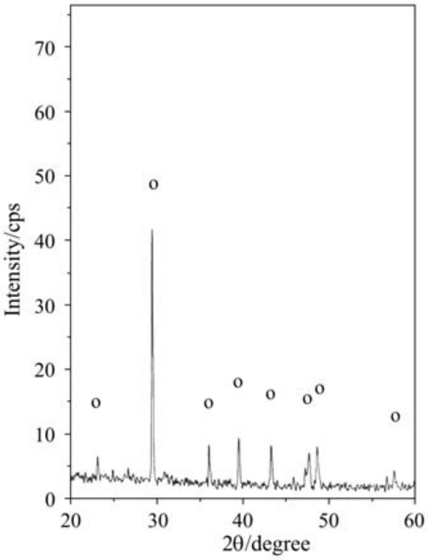

Fig. 2 XRD pattern of the dry slugde. o – calcium carbonate

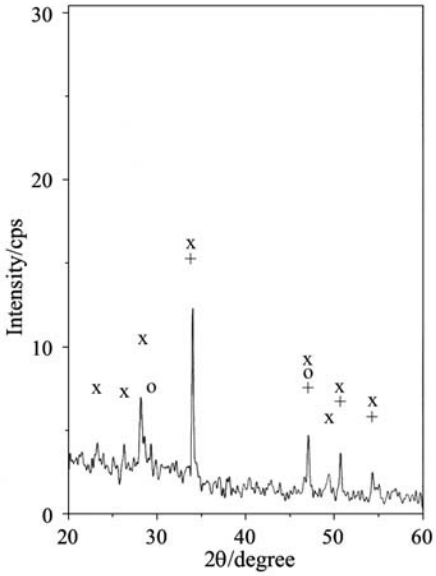

Fig. 3 XRD pattern of by-product sample No. 2. x – calcium sulfite hydrate, + – calcium hydroxide, o – calcium carbonate

above, calculated on the basis of thermogravimetric analysis performed in the atmosphere of air and nitrogen.

Exemplary curves of differential thermal analysis and gravimetric analysis of sludge are shown in Fig. 4. The thermal analysis confirmed the presence of $CaCO_3$ (strong endothermic effect with T_{max} 925°C connected with mass decrease). Besides, a weak endothermic effect with T_{max} 430°C connected with an unconsiderable mass loss on the DTA curve proved the presence of $MgCO_3$ and $Mg(OH)_2$ impurities in the sludge sample.

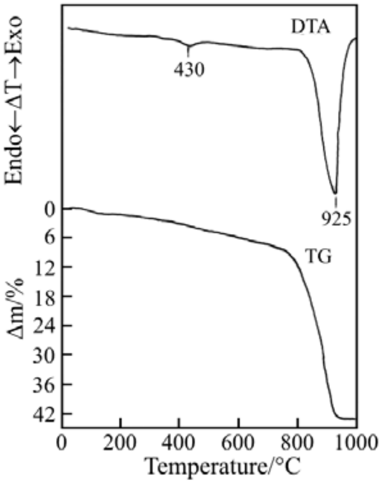

Fig. 4 The DTA/TG diagrams for the dry sludge in the atmosphere of air

According to the shape of thermal curves of by-product samples, presented in Figs 5 and 6, in the temperature range up to 200°C, the loss of moisture is observed and the loss of water chemically bounded by hydrated $CaCl_2$ and $CaSO_4{\cdot}2H_2O$ impurities is also possible. On the basis of X-ray analysis the presence of these compounds was not proved univocally.

At the temperature of about 360°C α-$CaSO_3{\cdot}0.5H_2O$ dehydration with α-$CaSO_3$ formation occurs. On the DTA curve a weak endothermic effect connected with an unconsiderable mass loss, probably caused by decomposition of $Mg(OH)_2$ or $MgCO_3$ impurities, is followed by endothermic effect of $CaSO_3{\cdot}0.5H_2O$ dehydration. The endothermic effects with maximum in the temperature range 480–510 and 760–850°C result from $Ca(OH)_2$ dehydroxylation and the $CaCO_3$ decomposition [7–10].

All specified endothermic effects appear on DTA curves recorded both in the atmosphere of air (Fig. 5) and nitrogen (Fig. 6) and are connected with mass loss visible on TG curves. Besides, a very strong exothermic effect with maximum in the temperature range 570–620°C, has been observed on DTA curves received during analysis under the atmosphere of air. This effect is connected with $CaSO_3$ oxidation to $CaSO_4$. The presence of the last compound was proved by means of X-ray analysis of samples which were subjected to the thermal analysis in the air atmosphere. The mass in-

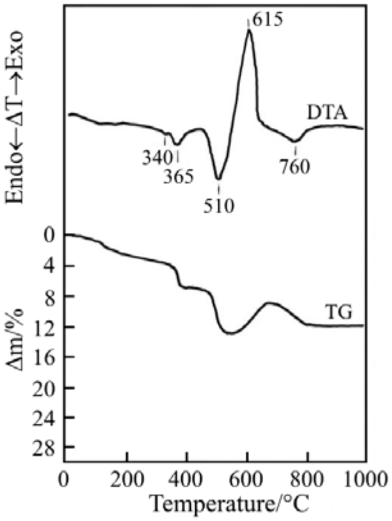

Fig. 5 DTA and TG curves of sample No. 2 under atmosphere of air

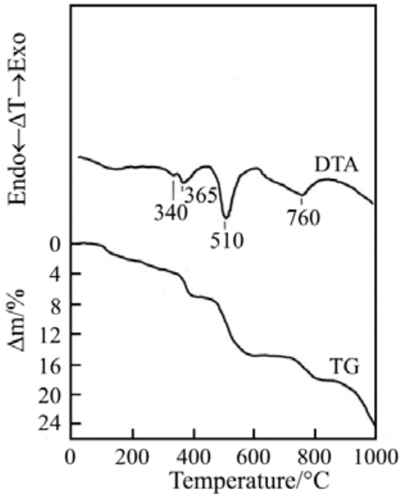

Fig. 6 DTA and TG curves of sample No. 2 under atmosphere of nitrogen

crease of samples which can be seen on TG curves. However, it is lowered owing to partial superposition of initial stage of $CaSO_3$ oxidation and final stage of $Ca(OH)_2$ decomposition accompanied by mass decrease. Furthermore, in the case of samples No. 1, 2, 3 and 7 with low $CaCO_3$ content, i.e. less than 10% (mass), in which T_{max} peak displacement of $CaCO_3$ thermal dissociation in low temperatures direction was observed, the final stage of $CaSO_3$ oxidation process overlapped with beginning of $CaCO_3$ decomposition. For this reason the real increase of samples mass related to oxygen amount necessary for $CaSO_3$ oxidation to $CaSO_4$ was calculated by comparison of the course of TG curves under different atmospheres (air and nitrogen). This enabled a determination of approximate $CaSO_3 \cdot 0.5H_2O$ contents in analyzed by-product samples (Table 2).

Thermal analysis in the atmosphere of nitrogen made possible the calculation of $Ca(OH)_2$ and $CaCO_3$ content (Table 2); in this case the $CaSO_3$ oxidation process, overlapping with $Ca(OH)_2$ dehydroxylation and $CaCO_3$ possible decomposition, did not occur. Differences in $CaSO_3 \cdot 0.5H_2O$ content evaluated from chemical and thermogravimetric analysis have been situated in the range of 0.4–2.9%. The differences in $Ca(OH)_2$ amount determined on the basis of chemical determination of active CaO content and of thermogravimetric method did not exceed 1.6%.

In the case of samples analyzed in nitrogen atmosphere, in which $CaSO_3$ oxidation did not take place, the mass loss on TG curves, probably caused by SO_2 escape, was observed in final stage of analysis, i.e. after termination of $CaCO_3$ thermal dissociation. $CaSO_3$ undergoes decomposition to $CaSO_4$ and CaS above 800°C [11, 12]. The solid-state reaction process, i.e. reaction between $CaSO_4$ and CaS with CaO and SO_2 formation, proceeds partially above 900°C. In samples analyzed in air atmosphere $CaSO_4$, formed as a result of $CaSO_3$ oxidation, is practically thermostable up to 1350°C.

Conclusions

The by-product of semi-dry desulfurization process in 'Siersza' power plant is a multicomponent mixture of inorganic matter. Samples of by-product obtained at simultaneous sludge utilization contain mainly $CaSO_3 \cdot 0.5H_2O$ (31–48% mass), unreacted $Ca(OH)_2$ sorbent (18–30% mass) and $CaCO_3$ (7–30% mass).

The partial overlapping of chemical reactions during by-product samples heat treatment under the air access makes difficult the estimation of phase quantitative composition of samples by the thermal analysis method. This fact implies the necessity of realization of two supplementary thermal analyses – one in air atmosphere, and another one, aimed at elimination of $CaSO_3$ oxidation in atmosphere of inert gas – nitrogen or argon. The temperatures at which the chemical reactions proceed, characteristic for individual sample components, depend on their content. The higher the content of a given component in the sample, the higher the temperature at which this component reacts at constant heating rate used in experiments and at constant mass of analyzed samples.

Moreover, the obtained results have shown that sludge did not possess sorptive properties with respect to SO_2, and so it is not suitable for use as sorbing agent in semi-dry flue gas desulfurization. Its utilization, by introduction into absorption solution is possible, although maintaining the required effectiveness of desulfurization is connected in this case with an increase of lime consumption. This technological application has no influence on deterioration of by-product properties, enables its economic utilization and improves transport conditions.

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