

## PROPERTIES OF THE WASTES PRODUCED IN THE SEMI-DRY FGD INSTALLATION

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In this paper the examination results of chemical and phase composition as well as wastes graining from the semi-dry flue gas desulfurization (FGD) have been presented. The wastes contain mainly semi-hydrate calcium sulfite and calcium sulfate. The phase composition changes of wastes at the temperature of 350 and 600°C have been determined. On the basis of carried out examinations, possibilities of flue gas desulfurization wastes utilization in building materials production (sulfite and anhydrite cement) are proposed.

**Keywords:** DTA, phase composition, semi-dry FGD products utilization, TG, XRD

### Introduction

Impetuous development of civilization effected intensive growth of economy has an unquestionable influence for changes in ecosystem. Emission many types of pollutants as by products in industrial processes and current human activity are the reasons that relevant in national economy are created. In Poland the power industry is the major source of pollution into the atmosphere resulting largest changes in environment. During ten last years emission of sulfur was considerably reduced as a result of structural changes in Polish economy as well as increasing of capital expenditures for investment projects towards environmental protection but further decreasing emission of sulfur is the fundamental target Polish proecological policy. In 1994 as result of signing by Polish Republic's Government document called 'Second Sulfur Protocol' the limit values of SO<sub>2</sub> in 2010 were settled. In order to achieve this target the investment program for flue gas desulfurization installation in Polish power industry was initiated. Sustainable development of flue gas desulfurization installations as well as implementation of fluidized bed combustion furnaces in electric and thermal power plants led to the production of new type of wastes [1].

After wet lime/limestone flue gas desulfurization (FGD) with gypsum as end product, the semi-dry FGD process using lime as sorbent is the most used FGD technology in power and thermal industry [1–5]. The final product of semi-dry absorption is called semi-dry absorption product (SDAP). Compared with lime/limestone scrubbers with gypsum as product, the semi-dry absorption process offers the following advantages:

- no waste water
- straightforward operation
- no or little reheating
- low space requirements
- lower investment

Semi-dry FGD products consist of different calcium compounds, mainly calcium sulfite, but typically also a few percent of sulfate, hydroxide, carbonate and small amounts of chloride, as well as varying amounts of fly ash [1, 5]. The chemical composition of the SDAP is influenced by the following factors:

- properties of the reagents i.e. coal, lime (ash, sulfur and chlorine contents)
- existence of a pre-separator for the fly ash and its efficiency
- sulfur dioxide removal efficiency
- recirculation rate
- load level

According to the EU's environmental legislation most of the by-products from power plants are categorized as non-hazardous waste [1]. The US EPA has also made this classification of the semi-dry FGD products as non-hazardous in 1993. Thus it has a similar status as coal fly ash. However, the wet FGD product, FGD-gypsum, is a special by-product not classified as waste at all, due to its well-defined chemical composition, but defined as a 'product' already as produced at power plant. To become a 'product' the semi-dry FGD 'waste' product must be mixed, treated or undergo some kind of 'conversion'. In the European Waste Catalogue EWC, passed on 1993-08-31, the semi-dry FGD product is classified under code 10 01 05 (and 10 05 06): cal-

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cium-based reaction wastes from flue gas desulfurization in solid form.

While for the wet FGD process there already existed a market demand for gypsum and the FGD by-product could gradually replace the use of natural gypsum, the establishment of recycling and utilization of semi-dry FGD product has been more difficult [1, 5]. The semi-dry FGD product is not utilized so far in Poland but only stored. This solution a problem has to be considered as not satisfactory one from the ecological point of view.

In this paper the properties of material produced in semi-dry FGD installation in one of national power and heating station will be given. Basing on the chemical and mineralogical characterization of this material the possibilities of utilization in building materials production will be presented.

## Experimental

3 samples of SDAP with a mass of 2 kg each, sampled during the period from 12 to 21.04.2006 were subjected to examination. The SDAP is a dry, fine grained powder of cream colour, odorless. Graining test of samples was made using laser grain analyzer 'Analysette 22' (Fritsch).

Content of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO and CaO (the total one) was determined according to [6]. The principle of SiO<sub>2</sub> determination consists in establishing the loss of mass after etching with hydrofluoric acid. Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO and MgO content was determined by complexometric method at an adequate pH using a solution of sodium versenate and proper indicators. The content of sulfates in terms of SO<sub>3</sub> was determined using gravimetric method according to [7]. The content of total sulfur in terms of SO<sub>3</sub> was also determined using gravimetric method after previous oxidizing the sulfite with bromine and nitric acid [8]. The content of sulfite sulfur in terms of SO<sub>3</sub> was calculated as a difference between content of total sulfur and sulfate sulfur.

The determination of Cl<sup>-</sup> ions were carried out by Volhard method according to [9]. The content of an active CaO was determined according to [10].

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 20–900°C under different atmospheres (air and nitrogen). Corundum crucibles were used, mass of samples was 500 mg. During the measurement in the atmosphere of air, TG sensitivity was 50 mg, in nitrogen atmosphere 100 mg. Alumina powder was used as a reference material for DTA experiments. Heating rate was 10°C min<sup>-1</sup>.

The X-ray phase analysis of examined samples was made with the use of a XRD-3003 TT type X-ray diffractometer (Seifert), CuK<sub>α</sub> radiation and Ni filter.

Then, to check the usability of SDAP as a raw material for the production of sulfite and anhydrite binders, samples were subjected to calcination at a temperature 350 and 600°C over 60 min.

## Results and discussion

Table 1 presents parameters of semi-dry FGD. Table 2 presents results of samples chemical analysis, and Table 3 contains their approximate mineralogical composition, determined on the basis of chemical analysis and examinations of phase composition using the method of thermal analysis and X-ray analysis. Information about the particle size of the samples is given in Fig. 1. Figure 2 shows DTA, TG and DTG curves of the sorbent Ca(OH)<sub>2</sub> applied in semi-dry FGD installation. Figures 3 and 4 present thermal curves of sample 2 recorded in air and nitrogen atmospheres. Results of X-ray phase analysis of SDAP before and after thermal treatment are listed in Table 4 (results for samples 1, 2 and 3 were similar).

Thermal analysis confirmed presence of Ca(OH)<sub>2</sub> in the sorbent (a great mass loss with an endothermic effect with  $T_{\max} \sim 520^\circ\text{C}$ ). The weak endothermic effect

**Table 1** Work parameters of semi-dry FGD installation

Date	12.04.06	18.04.06	21.04.06
Measurement (sample)	1	2	3
Waste gases flow/nm <sup>3</sup> h <sup>-1</sup>	455440	440050	450060
SO <sub>2</sub> concentration at inlet/mg nm <sup>-3</sup>	3500	3500	3450
HCl concentration at inlet/mg nm <sup>-3</sup>	210	255	295
Wastes gases dustiness before entering installation/mg nm <sup>-3</sup>	100	90	85
Temperature of waste gases before entering installation/°C	130	128	129
Sorbent consumption Ca(OH) <sub>2</sub> /kg h <sup>-1</sup>	2300	2220	2240
SO <sub>2</sub> concentration at outlet/mg nm <sup>-3</sup>	390	350	345
Temperature of waste gases after leaving the installation/°C	92	94	93

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**Table 2** Chemical composition of SDAP

Content/mass%	Sample		
	1	2	3
SiO <sub>2</sub>	0.32	0.33	0.26
Al <sub>2</sub> O <sub>3</sub>	0.41	0.42	0.40
Fe <sub>2</sub> O <sub>3</sub>	0.24	0.28	0.24
MgO	0.20	0.20	0.20
CaO total	39.54	39.45	39.10
CaO active	4.16	4.87	4.79
Cl <sup>-</sup>	5.06	5.11	5.28
SO <sub>3</sub> <sup>2-</sup> in terms of SO <sub>3</sub>	18.74	19.90	19.83
SO <sub>4</sub> <sup>2-</sup> in terms of SO <sub>3</sub>	22.19	20.25	19.79

**Table 3** Mineralogical composition of SDAP

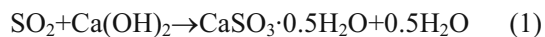
Content/mass%	Sample		
	1	2	3
CaSO <sub>3</sub> ·0.5 H <sub>2</sub> O	30.2	32.1	32.0
CaSO <sub>4</sub>	37.7	34.5	33.7
CaCl <sub>2</sub>	7.9	8.0	8.3
Ca(OH) <sub>2</sub>	5.5	6.4	6.3
CaCO <sub>3</sub>	4.8	4.3	4.3

**Table 4** Results of X-ray phase analysis of SDAP before and after thermal treatment

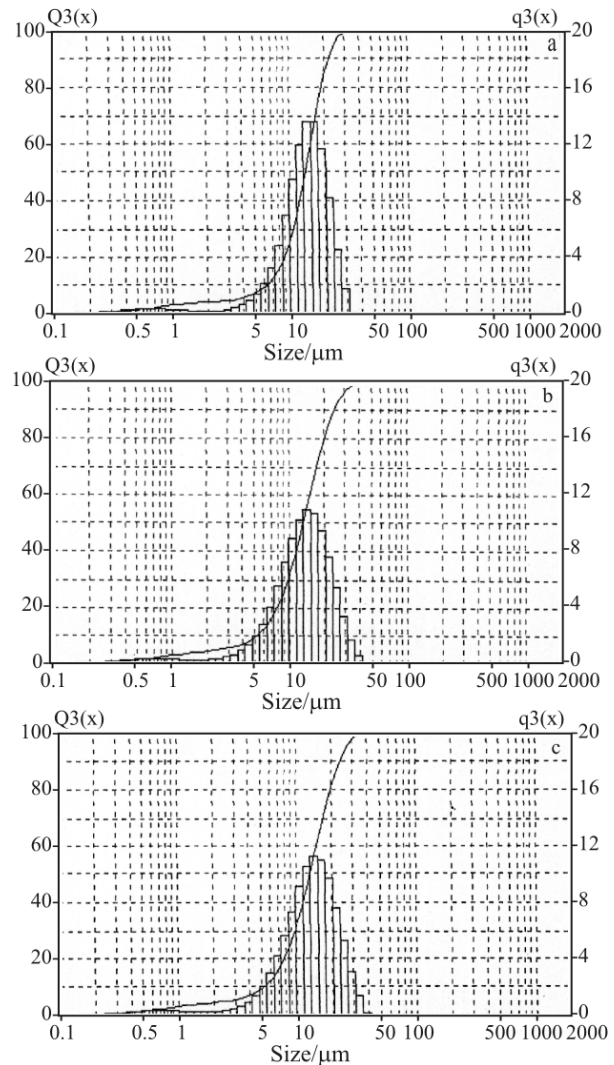
Thermal treatment/°C	Major phases detected
—	CaSO <sub>3</sub> ·0.5H <sub>2</sub> O, CaSO <sub>4</sub> , Ca(OH) <sub>2</sub> , CaCO <sub>3</sub> , CaCl <sub>2</sub> ·2H <sub>2</sub> O
350	CaSO <sub>3</sub> , CaSO <sub>4</sub> , Ca(OH) <sub>2</sub> , CaCO <sub>3</sub> , CaCl <sub>2</sub>
600	CaSO <sub>4</sub> , CaCO <sub>3</sub> , CaO

with  $T_{max} \sim 720^\circ\text{C}$  is related to the calcite (CaCO<sub>3</sub>) decomposition to form calcium oxide and CO<sub>2</sub> degassing (Fig. 2). The sorbent contained about 90% Ca(OH)<sub>2</sub> and 3.5% of CaCO<sub>3</sub> and 2% of moisture.

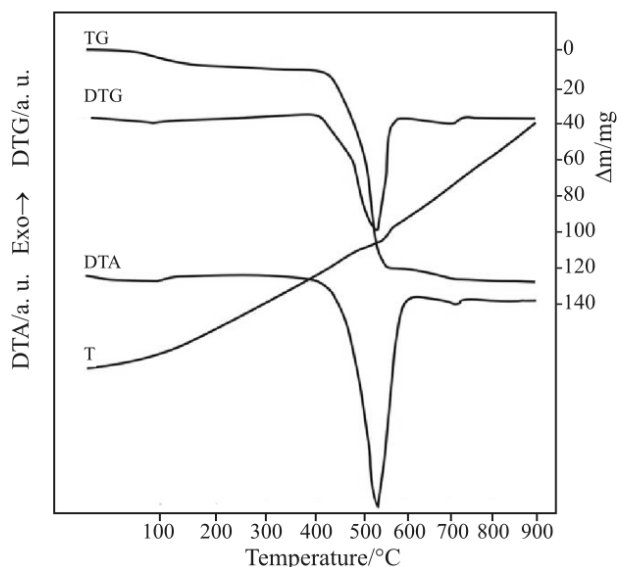
It was found using the X-ray analysis that SDAP samples contain  $\alpha$ -CaSO<sub>3</sub>·0.5H<sub>2</sub>O (hannebachite), CaSO<sub>4</sub>, Ca(OH)<sub>2</sub> (unreacted sorbent), CaCO<sub>3</sub> (carbonized sorbent) and CaCl<sub>2</sub>·2H<sub>2</sub>O (Table 4). The SDAP consist of the following overall reactions products:



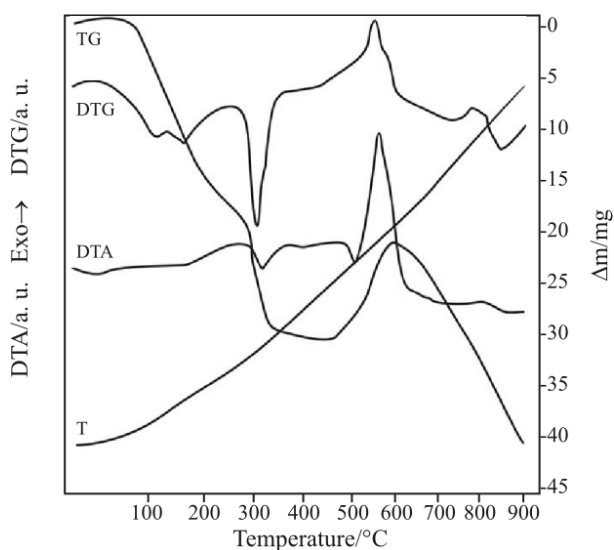
Besides the anhydrite CaSO<sub>4</sub> is obtained in the semi-dry FGD method [1, 5]. To obtain a high absorption efficiency, an excess of Ca(OH)<sub>2</sub> is required. Consequently the conversion of Ca(OH)<sub>2</sub> is incomplete. Calcium hydroxide will be converted to CaCO<sub>3</sub> by CO<sub>2</sub> in the air.



**Fig. 1** Particle – size distribution: a – sample 1, b – sample 2 and c – sample 3

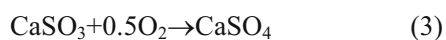


**Fig. 2** DTA, TG and DTG curves of the sorbent under atmosphere of air

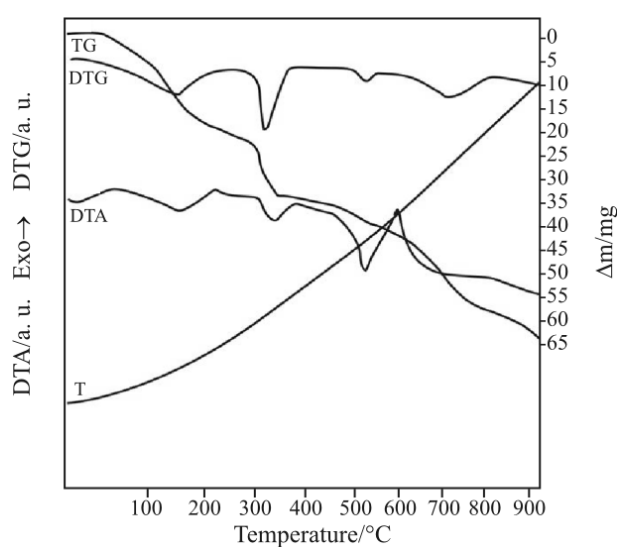
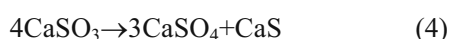


**Fig. 3** DTA, TG and DTG curves of sample 2 under atmosphere of air

According to the shape of thermal curves of samples, presented in Figs 3 and 4, in the temperature range up to about 240°C, the loss of moisture is the observed and the loss of water chemically bounded by hydrated  $\text{CaCl}_2$ . At the temperature of about 320°C  $\alpha\text{-CaSO}_3 \cdot 0.5\text{H}_2\text{O}$  dehydration with  $\alpha\text{-CaSO}_3$  formation occurs. Decomposition of admixture of magnesium hydroxide and magnesium carbonate is possible within the range of temperatures 340–440°C. The endothermic effect with maximum in the temperature of about 510°C result from  $\text{Ca}(\text{OH})_2$  dehydroxylation. All specified endothermic effects appear on DTA curves recorded both in the atmosphere of air (Fig. 3) and nitrogen (Fig. 4) and are connected with mass loss visible on TG curves. Besides, a very strong exothermic effect with maximum in the temperature 580°C, has been observed on DTA curve received during analysis under the atmosphere of air (Fig. 3). This effect is connected with  $\text{CaSO}_3$  oxidizing to  $\text{CaSO}_4$  according to the reaction:



The TG curve indicates that there is a mass gain between 480 and 600°C, because the sulfite takes up oxygen, and calcium sulfate  $\text{CaSO}_4$  is obtained. However, it is lowered owing to partial superposition of initial stage of  $\text{CaSO}_3$  oxidizing and final stage of  $\text{Ca}(\text{OH})_2$  decomposition accompanied by mass loss. Decomposition of calcite  $\text{CaCO}_3$  starts at temperature above 600°C [11–15]. Loss of samples mass above 800°C results possibly from  $\text{SO}_2$  escape. According to [16, 17], if calcium sulfite shall not completely be oxidized at lower temperatures it will disproportionate to  $\text{CaSO}_4$  and  $\text{CaS}$  according to the reaction:



**Fig. 4** DTA, TG and DTG curves of sample 2 under atmosphere of nitrogen

At the temperature above 800°C  $\text{CaO}$  and  $\text{SO}_2$  are formed via the reaction:



The SDAP is fine-grained (Fig. 1) and contains mainly semi-hydrate calcium sulfite and calcium sulfate (Table 3), hence trials were undertaken to obtain sulfite and anhydrite binders. Anhydrous calcium sulfite is rather rare in wastes from the semi-dry method of gases desulfurization i.e. only when gas temperature in the process of desulfurization exceeds 330–360°C [18].

As X-ray analysis has shown (Table 4), SDAP after calcination at the temperature of 350°C contained anhydrous calcium sulfite.  $\text{CaSO}_4$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  phases were unchanged. The sample after calcination did not show symptoms of being sintered, and after adding some water it started to bond and harden as gypsum binder.

In the SDAP sample calcined at the temperature of 600°C,  $\text{CaSO}_4$  anhydrite was dominant,  $\text{CaO}$  was also present as a result of  $\text{Ca}(\text{OH})_2$  decomposition (Table 4). The sample has shown the symptoms of being sintered i.e. as a result of calcination an agglomeration of fine grains into granules occurred. Formation of fusible chloride or chloride–sulfate eutectic mixture was the probable cause of sintering. The SDAP contains small amounts of substances, primarily sodium and potassium oxides, which form eutectic mixtures with melting points about 600°C [1, 5]. Obtained product after grinding and adding some water has shown the ability to bond and harden just like other gypsum and anhydrite binders. In order to limit the sintering, one should carry out trials of thermal oxidizing  $\text{CaSO}_3$  into  $\text{CaSO}_4$  at lower temperatures i.e. 500°C. However,

anhydrite binder obtained from SDAP does not show parameters consistent with obligatory standards due to chlorides content. In order to obtain anhydrite binder consistent with standards, the SDAP should be washed off from chlorides and the washery effluent containing chlorides should be utilized.

Continuing the thermal process of anhydrite decomposition one can obtain calcium oxide as well as  $\text{SO}_2$ , which, after catalytic oxidation transforms into  $\text{SO}_3$  i.e. sulfuric acid anhydride, which can be used for production of  $\text{H}_2\text{SO}_4$  and oleum.

## Conclusions

The semi-dry flue gas desulfurization (FGD) methods are the most frequently used desulfurization technologies in power and thermal industry, apart from the wet lime ones. The semi-dry absorption product (SDAP) was sampled on periodical basis in the intervals which took into consideration proper settings resulting from changes of parameters of the semi-dry FGD installation. Samples are fine-grained like a fly ash and contain mainly  $\text{CaSO}_3 \cdot 0.5\text{H}_2\text{O}$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{OH})_2$  (unreacted sorbent),  $\text{CaCO}_3$  (carbonized sorbent) and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ . At the temperatures between 320 and 360°C calcium sulfite releases its water of crystallization. The SDAP after thermal treatment at the temperature of 350°C can be used to manufacture the sulfite binder of properties similar to properties of gypsum binder used in finishing construction works. As a result of thermal oxidizing of the SDAP to form calcium sulfate, e.g. at 500 to 600°C, one obtains product with properties similar to natural anhydrite.

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