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MARTA PLASKACZ-DZIUBA*, MARCIN CICHOSZ, BARTŁOMIEJ IGLIŃSKI, ROMAN BUCZKOWSKI

AUTOCLAVED AERATED CONCRETE WITH AN ADDITION OF WASTE FROM SEMI-DRY FLUE GAS DESULFURIZATION PROCESS – THERMAL STABILITY AND XRD INVESTIGATIONS

AUTOKLAWIZOWANY BETON KOMÓRKOWY Z DODATKIEM ODPADU Z INSTALACJI PÓŁSUCHEGO ODSIARCZANIA SPALIN – ANALIZA TERMOGRAWIMETRYCZNA ORAZ RENTGENOGRAFICZNA

A b s t r a c t

The article presents the results of research on autoclaved aerated concrete (AAC) produced according to the manufacturer recipe and modified AAC with the addition of waste from the semi-dry flue gas desulfurization installation. Produced cubes of concrete were analysed using thermogravimetry in a temperature regime of 0–1200°C in order to determine thermal stability. Samples were also tested using X-ray diffractometer to determine the differences in the content of tobermorite 1.1 nm, the compound which is responsible for the mechanical properties of tested concrete.

Keywords: autoclaved aerated concrete, semi-dry flue gas desulfurization, x-ray diffraction, termogravimetry

S t r e s z c z e n i e

W artykule przedstawiono wyniki badań autoklawizowanego betonu komórkowego (ABK) wyprodukowanego według przepisu producenta oraz zmodyfikowanego ABK z dodatkiem odpadu z instalacji odsiarczania spalin metodą półsuchą. Wyprodukowane kostki betonu poddano analizie termicznej w reżimie temperaturowym 0–1200°C w celu określenia stabilności termicznej oraz badaniu dyfraktometrem rentgenowskim w celu określenia różnic w zawartości tobermorytu 1.1 nm, składnika odpowiedzialnego za parametry wytrzymałościowe betonu komórkowego.

Słowa kluczowe: autoklawizowany beton komórkowy, odsiarczanie metodą półsuchą, dyfraktometria rentgenowska, termograwimetria

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* MSc. Marta Plaskacz-Dziuba, PhD. Marcin Cichosz, PhD. Bartłomiej Igliński, Assoc. Prof. Roman Buczkowski, Department of Chemical Proecological Processes, Faculty of Chemistry, Nicolaus Copernicus University in Toruń.

Signatures

FGD – flue gas desulfurization
AAC – autoclaved aerated concrete
AACS – autoclaved aerated concrete standard
AACM – autoclaved aerated concrete modified
ABKS – autoklawizowany beton komórkowy standardowy
ABKM – autoklawizowany beton komórkowy modyfikowany

1. Introduction

The waste from the semi-dry flue gas desulfurization (FGD) is currently inapplicable, what makes it an useless material, whose utilization is associated with additional costs. Unlike the waste from wet FGD, where the product is a synthetic gypsum, widely used in industry, mainly in the production of building materials [1]. The applicability of waste from semi-dry FGD in the production of autoclaved aerated concrete could be an interesting alternative for manufacturers [2]. However, the composition of the analyzed, unstable waste whose main component is calcium sulfite, requires tests before usage as a substitute for gypsum.

2. Experiment

2.1. Waste from the semi-dry flue gas desulfurization

The waste obtained in the semi-dry FGD method consists of calcium sulfite – 2CaSO3 · H2O (15–75%), calcium sulfate – CaSO4 · 2H2O (2–30%), unreacted lime – CaO, Ca(OH)2 (0–25%), limestone – CaCO3 (1–30%), calcium chloride – CaCl2 · nH2O (1–15%), moisture (1–10%) and others (e.g. chlorides, sulfates, silicates of sodium, potassium, magnesium, iron, aluminum). The exact composition depends on a wide range of factors, e.g. type of sorbent, type of fuel used in power station, operating conditions during desulfurization process, and composition of fumes. Due to the high content of sulfate (IV) calcium any possible use as a synthetic gypsum must be subjected to a detailed analysis because of the instability of sulphates on the IV oxidation degree.

2.2. Autoclaved aerated concrete production

The studied autoclaved aerated concrete blocks (AACS and AACM) were obtained in the industrial conditions with retaining the existing manufacturer production process parameters [3].

The test product was produced as follows: to 4600 kg of slime with a 64% average content of silica 545 kg of cement was added, 180 kg of lime and 200 kg of gypsum or waste product from the FGD installation. Samples were taken from both the surface and the center of prepared blocks. Collected research material was triturated in a mortar, and then placed in a hermetic vessel with a capacity of 200 ml.

Samples with a signature G were taken from the top of a particular cube, whereas samples with signature D and S were taken from the center of a tested block. Figure 1 shows a diagram of sampling for analysis.

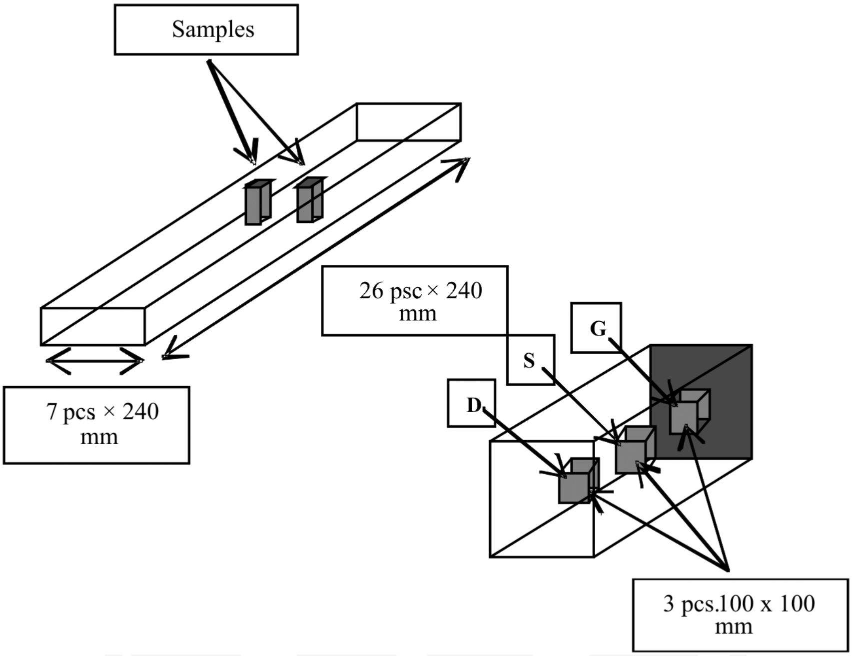

Fig. 1. Diagram of samples for analysis

2.3. Termogravimetric analysis

The thermal analysis was performed, for four randomly selected samples of AACS and AACM, to estimate the thermal stability of the produced building materials. Thermograms of the two samples are given in Figure 2. Beton 1 is the sample of AACS, while beton 2 is the sample of AACM.

Thermograms shown in Figure 2 illustrate that the material marked as beton1 and beton 2 have a low moisture content (approximately 3%). The minimal endothermal effect within a temperature range 500–550°C is a result of dehydration of calcium hydroxide. The loss of mass at a temperature of about 650–700°C is caused by decarboxylation. A significant exothermal effect at about 800–850°C is related to transformation of calcium silicate into wollastonite, and there is no change in weight during this process. Decomposition of sulphates occurs only at temperatures of about 1000 °C. For the above reasons, it is allowed to conclude that the tested materials made of AAC are characterized by high thermostability.

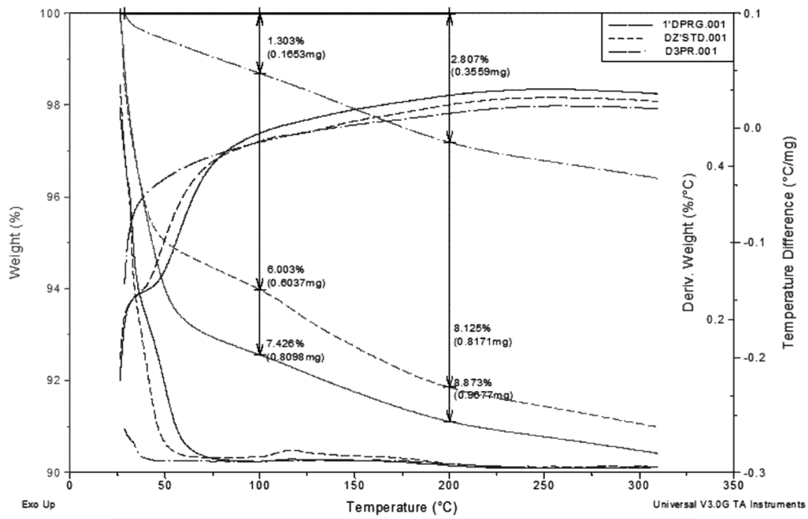

Fig. 2. Thermogram of two randomly selected samples, AACS (beton1) and AACM (beton2)

Figures 3–5 show the results of thermal analysis for the various samples marked as D, S, G respectively for AACS (STD) and AACM (PR and PRG). Analyses confirmed the results for dried material (marking 3) as well as for the material 1 and 2 (1-AACM and 2-AACS).

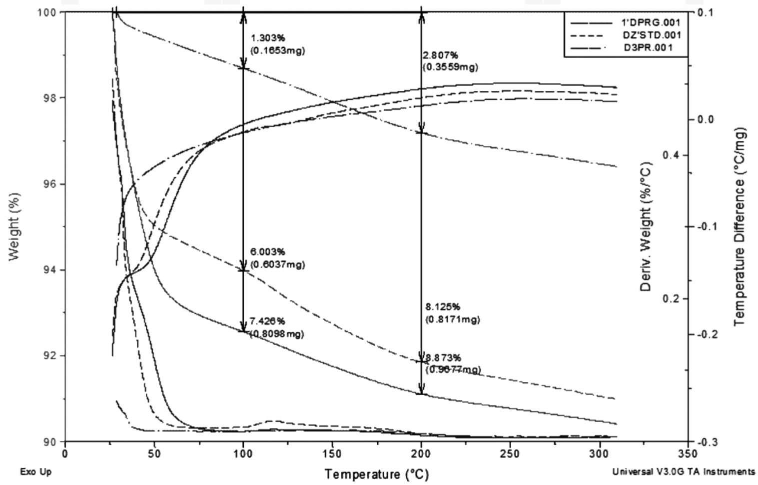

Fig. 3. Thermogram for sample D

Typical flow of thermal processes characterizes the analyzed materials. The release of weakly bound water appears at temperature about 100°C. Afterwards, dehydration of tobermorite and other forms of hydrated calcium silicates occures at temperature range of 150–200°C.

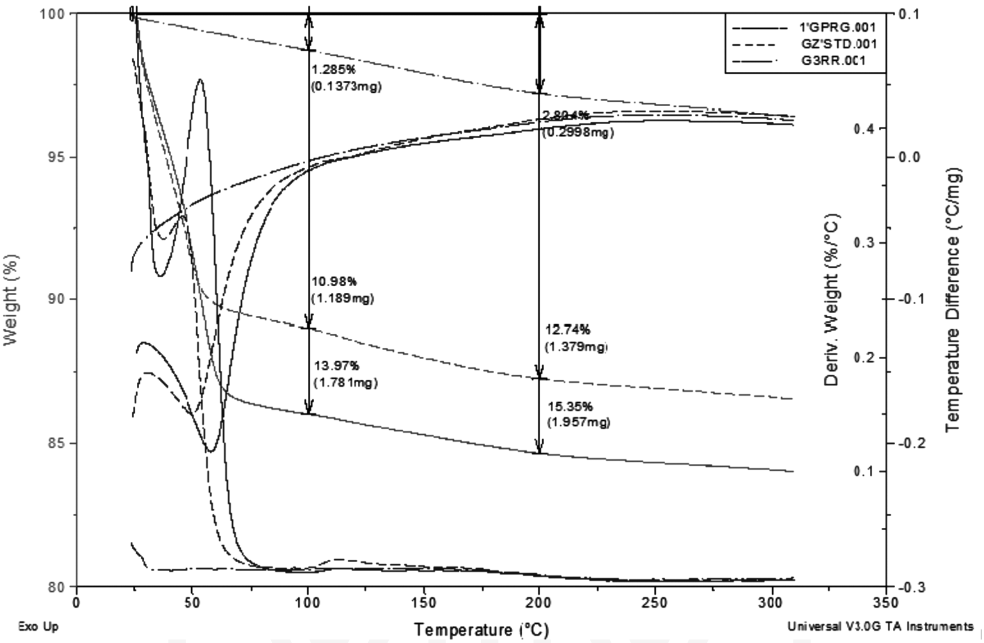

Fig. 4. Thermogram for sample G

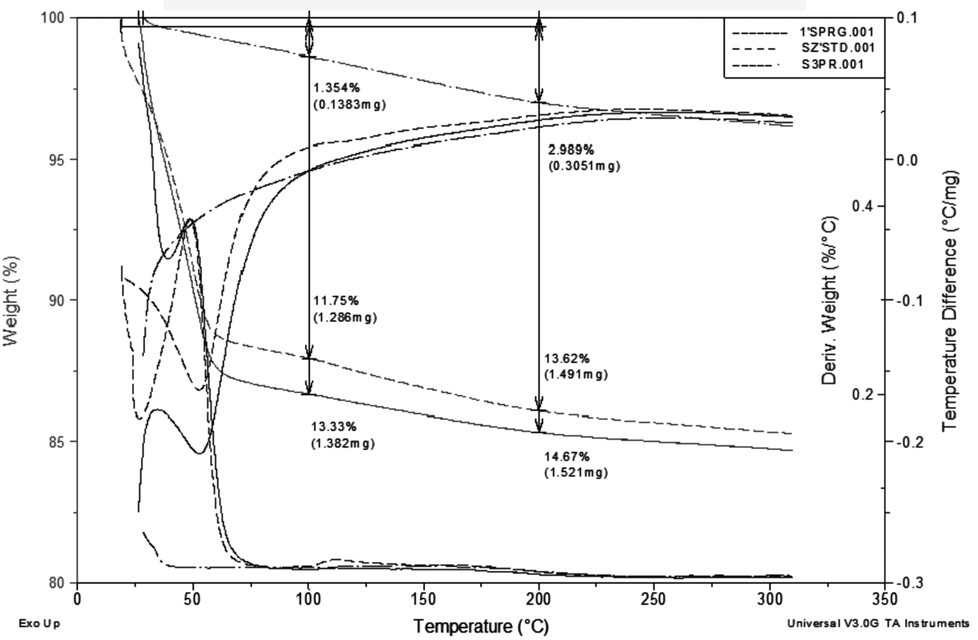

Fig. 5. Thermogram for sample S

Analyzes explicitly show that the sample marked 3 had been dried before testing. Samples D contain less free water up to 200 °C than samples G and S. In the tested temperature range no significant differences between the ABKS A ABKM were detected.

2.4. X-ray diffraction

To analyze the effect of adding calcium sulfite to AAC, the content of tobermorite-1.1nm was taken. Tobermorite is a crystal structure, with chemical formula Ca5Si6O16(OH)2•4(H2O), forming during the process of autoclaving AAC. The presence of tobermorite-1.1nm as a binding material provides a well-structured autoclaved aerated concrete (AAC) with good mechanical properties [4].

Averaged samples for analysis were prepared by taking the material in an amount of about 20g from five different locations of the particular concrete block and milled in an impact mill for 15 minutes. The obtained grist was subjected to diffractometric analysis. Nine measurements were performed for the selected angular range 28–31° for samples with the extension .PR or .PRG with the addition of calcium sulfite and extension .STD with the addition of calcium sulfate [5]. Table 1 summarizes all the results obtained during X-ray diffraction analysis.

Table 1

Specification of signals and their intensity

Sample	Intensity [cps] (Position °2Th0)		Average Intensity [cps](Position °2Th)	
	28.9	30	28.9	30
1’D PRG	732	255	690	259
1’G PRG	745	247		
1’S PRG	772	275		
G3 PR	543	202		
D3 PR	756	280		
S3 PR	591	145		
D2’ STD	436	219	670	362
G2’ STD	681	335		
S2’ STD	894	532		

Table 1 shows that the average signal intensity for tested samples, with the addition of calcium sulfite (.PR and .PRG) and with the addition of calcium sulfate, is very similar and their value adjustments are 689.8 and 670.3 cps for angle 28.9 °2Th. Differences in the intensity of the angle °2Th 30 position were observed. Respectively, for AACM average intensity amounts to 259 cps, whereas for AACS it’s 362 cps. Figure 6 shows results for 9 tested AAC samples.

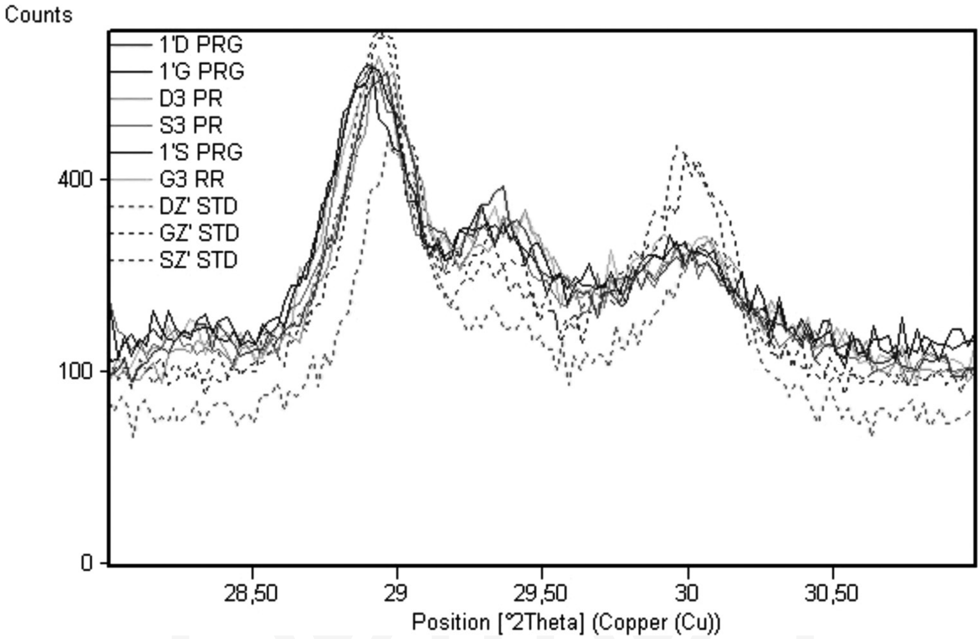

Fig. 6. Comparison of registered diffractograms

3. Results and discussion

Obtained thermograms show no significant differences in physicochemical transformations associated with heating of analyzed materials, especially in the area of temperature corresponding to rising and curing batched concrete mix before hydrothermal treatment in the process of autoclaving. Decomposition of sulphates occurs only at temperatures of about 1000°C, which is essential for safe functioning of autoclaves (especially the danger of corrosion due to sulfur dioxide desorption) and during exploitation AAC in the construction works. X-ray powder diffractometry analysis were performed to examine the differences in characteristic signal intensities of tobermorite 1.1 nm in the samples AACS and AACM. The obtained results show that the intensity of the signal for an angle 28.9° is similar for both, ABKS and ABKM, samples and amount to respectively 670 and 690 cps. In comparison, the intensity for an angle 30° differs significantly for the studied materials. For AACS it amounts to 362 cps, whereas for AACM it's 259 cps, what reflects lower content of the tobermorite-1.1 for modified concrete samples. This result may suggest that the addition of semi-dry FGD waste to the AAC has an impact on the formation of this compound in structure of concrete.

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