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Research paper

Transformations of calcium sulphates in solidified carbonated volatile fluidized ashes

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A B S T R A C T

Carbonation of volatile fluidized ashes with the use of carbon dioxide can be a means to their transformation into a product with a possible application as an additive to cement and concrete. Currently, due to its physical-chemical characteristics and particularly because of the high concentration of free calcium oxide, the possible applications of this product are highly limited, perhaps even none existent. A significant reduction or even the complete elimination of CaO can be achieved by its transformation into calcium carbonate. In carbonated volatile fluidized ashes, two components relevant to the binding time of mortar, as well as its durability, can be found: calcium carbonates and calcium sulphates.

During the investigation it was assumed that calcium carbonate, being poorly water-soluble, would not react with the remaining components of the porous water of the volatile fluidized ash. Crystalline phases of calcium sulphates, anhydrite, gypsum and bassanite occurring in bound volatile fluidized ashes after carbonation demonstrate the possibility of crystallization in the presence of calcium carbonate. In particular, a change in the concentration of bassanite indicates that this phase, as a precursor to the crystallization of gypsum, may play a significant role in the process of binding carbonated volatile ashes.

1. Introduction

The technique of combustion in a fluidized bed has a number of advantages, such as the non-complicated preparation of fuel, high efficiency and process capability and the significant reduction in the emission of sulphur compounds (desulphurisation), hydrocarbons and nitrogen oxides into the atmosphere (Marcisz, 2008). Fluidized-bed boilers are becoming more attractive as regards their use in combustion processes, particularly, of low-calorie or alternative fuels, biomass, and co-firing processes, as well as waste activated sludge (Koornneef, Junginger, & Faaij, 2007:; Marcisz, 2008). However, increasingly bigger boilers are being built with the prospect of the development of conventional energy and its new generation of combustion in oxygen to allow the future acquisition of carbon dioxide for the purpose of sequestration and its use as a chemical substrate in industrial processes (Zhu, 2013).

One of the largest units with a capacity of 460 MW operating on supercritical parameters has been in use in Poland since 2012 and the problem, as in other units of this type, is the management of volatility and bottom ashes. It is well known that usefulness for cement and concrete is very limited for the reason that they do not exhibit strong pozzolanic properties (Bapat, 2013). In addition to the above reason, the high content of free calcium oxide (CaO_W) which does not comply with standards and may adversely affect the properties of concrete (PN-EN, 2011; PN-EN, 2012; PN-EN, 2014). In addition, volatile fluidized ashes contain sulphates, which similarly to free calcium oxide, coexist different phases and by blocking the contact surface with the make-up water, slow the hydration process and consequently affect the properties of the cement slurry and ultimately the process of bonding cement components, combined with the role of phase AFm and AFt in concrete (Matschei, Lothenbach, & Glasser, 2007). It should be noted, however, that in a study conducted within the framework of project entitled: "Concrete based on cements with volatile ash from fluidized bed boilers" (2010), positive results of using volatile ash from fluidized brown and bituminous coals as additives in concrete were achieved.

In an attempt to adapt fluidized ashes to the requirements of their use in the building industry, studies of these ashes' carbonation by means of technical carbon dioxide were carried out, so that the free calcium content was reduced to below 1% (Łączny et al., 2015). Many studies indicate that calcium carbonate is an active

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Abbreviations

AFm	alumina, ferric oxide and mono-sulphate phase in cement (Al_2O_3-Fe_2O_3-mono)
Aft	alumina, ferric oxide and tri-sulphate phase in cement (Al_2O_3-Fe_2O_3-tri)
CaO_w	free calcium oxide
CVFA	Carbonation Volatile Fluidized Ash
CVFA-B	Bound Carbonation Volatile Fluidized Ash
VFA	Volatile Fluidized Ash
VFA-B	Bound Volatile Fluidized Ash
XRD	X-ray diffraction
XRF	X-ray fluorescence spectrometry

ingredient of cement slurry and there is an optimum ratio of the amount of sulphates to carbonates, at which concrete achieves its optimum strength (Kurdowski, 2010). Hence, it was assumed that in carbonized volatile fluidized ash, anhydrite phase transitions may be different from in those fluidized volatile ashes which contain free calcium oxide. Consequently, this may have an impact on their use as an additive to concrete.

In the case of volatile ash from fluidized bed boilers, what is important for their properties is the composition of the amorphous substance present in the waste and the variability of the mineral phases of ashes resulting from the diversity of the mineral matrix of the burnt hard coal (Bzowski & Michalik, 2009). This especially applies to the presence of sulphur and sulphides in the burnt coal or other fuels and waste. Sulphates in fluidized ashes occur mainly in the form of anhydrite ($CaSO_4$), as a result of the gaseous binding of SO_2 contained in the boiler exhaust. However, its formation passes through many stages, which has been described in detail by E.J. Anthony and D.J. Granatstein (Anthony & Granatstein, 2001).

The beneficial role of sulphates and carbonates occurring in carbonated fluidized ashes indicates the need for this study, the aim of which is to identify the course of change of calcium sulphate which is present in the ashes after mixing cement slurry with water and after the process of spontaneous binding in normal conditions, over a long period of time (28 days). The presented results of this study constitute a preliminary attempt to explain this phenomenon.

2. Materials and methods

The volatile fluidized ash (10 01 82), which was used in this study, was derived from the 460 MW unit operating in TAURON Wytwarzanie S.A. – Power Plant Branch Łagisza in Bedzin (Poland). The homogeneous ash sample, marked as VFA, was subjected to carbonation in a fluid reactor, by a procedure published in J. Łączny et al. (2015), and the resulting sample was marked CVFA. Then, cement slurry was made out of two samples through the addition of distilled water so that the ratio of water to VFA ash was 0.53 and for carbonated CVFA ash 0.43. The samples were marked VFA-B and CVFA-B and stabilisation for a period of 28 days under moist conditions.

Mineralogical studies were performed by means of the DSH power method, utilizing the geometry of Bragg-Brentano using a D8 Discover diffractometer by Bruker, in the Department of Environmental Monitoring of the Central Mining Institute in Katowice, CuKα radiation, an Ni filter and a LYNXEYE_XE detector. The mineral composition was determined and calculated on the basis of the licensed standards of ICDD (International Centre for Diffraction Data) and the following databases: ICSD (Inorganic Crystal Structure Database) and NIST (National Institute of Standard and Technology). For registration and diagnostic purposes, the DIFFRAC v.4.0. Bruker AXS program was used. The quantitative calculations of individual crystalline phases were made on the basis of the Rietveld methodology (Albinami & Willis, 1982; Bish & Post, 1993; Mahieux, Aubert, Cyr, Coutand, & Husson, 2010; Kowalska, 2013), using the Topas v.4.2. Bruker AXS programme. The content of amorphous substance in the tested samples was calculated using ZnO as an internal standard.

The basic chemical composition of the examined fluidized ashes was determined by fluorescence X-ray spectrometry with dispersive wavelength (XRF). XRF Primus 2 by the Rigaku Corporation, in the Department of Environmental Monitoring of the Central Mining Institute in Katowice, was used for the determinations.

The study was performed in the Department of Environmental Monitoring of the Central Mining Institute in Katowice with the certificate of accreditation No. AB 145 by the Polish Centre for Accreditation in Warsaw.

3. Results

The chemical analyses of volatile fluidized ash before (VFA) and after (CVFA) carbonation obtained after combustion at 815 °C showed no significant differences (Table 1), while differences in mineral composition were observed (Table 2).

The mineral composition of both examined fluidized volatile ashes had a heavy presence of amorphous substance and among the crystalline phases - anhydrite, quartz and feldspar. The differences in fluidized ashes before (VFA) and after (CVFA) carbonation are primarily the amount of free lime and calcite which was clearly documented in the resulting diffraction patterns (Fig. 1).

The muscovite, identified in the ashes, matches the pattern (PDF 00-046-0741) described as "potassium mica, dehydroxylated muscovite" of a synthetic structure. This pattern was obtained by heating muscovite 2M1 for 5 h at a temperature of 850 °C. Due to the lack of the precise structural characteristics of this pattern, quantitative calculations were performed based on the parameters of the reference standard for this type of substance (PDF 04-017-7272). Therefore, the quantitative calculation of muscovite after dehydroxylation should be treated as indicative.

Determined mineral phases in the sample of set cement mortar with fluidized volatile ash content (VFA-B) are presented in the diffraction pattern (Fig. 2) and the calculated content of these phases in Table 3. In contrast, the mineral phases identified in the sample of the set cement mortar involving carbonized fluidized volatile ash (CVFA-B) are presented in the diffraction pattern (Fig. 3) and the calculated content of these phases in Table 4.

Table 1
Chemical composition of volatile fluidized ashes before (VFA) and after (CVFA) carbonation.

Component	VFA	CVFA
	in %	
SiO_2	37.38	37.61
TiO_2	0.68	0.66
Al_2O_3	22.10	22.17
Fe_2O_3	6.50	6.43
CaO	19.39	19.06
MgO	2.14	2.05
Na_2O	0.74	0.70
K_2O	2.19	2.16
P_2O_5	0.33	0.32
SO_3	7.73	7.94
Sum	99.18	99.10

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