Construction and Building Materials 89 (2015) 13–24

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Influence of constant magnetic field on the properties of waste phosphogypsum and fly ash composites

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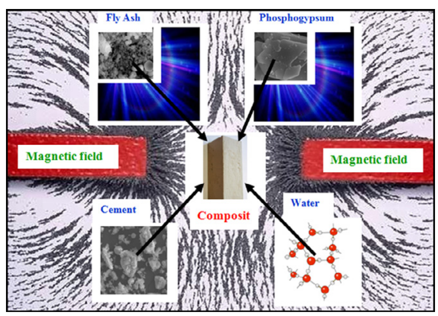
HIGHLIGHTS

- Constant magnetic field as an additional parameter in the creation of composites.
- Composites from waste.
- Thermal treatment of waste phosphogypsum.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 August 2013
Received in revised form 6 March 2015
Accepted 12 April 2015

Keywords:
Constant magnetic field
Building materials
Composites
Phosphogypsum
Fly ash

ABSTRACT

The paper presents a study of the effect of constant magnetic field on composites used in building industry. The effect of changes was obtained both by direct exposure of the samples to CMF and by using magnetically treated mixing water. Particularly good results were obtained in flexural strength test for (gypsum–phosphogypsum) composite, in which that parameter increased by 30% (from 2.35 to 3.07 MPa), as well as for (cement–fly ash–phosphogypsum) one, in which it increased by 150% (from 2.39 to 6.11 MPa). In compression strength test, that parameter for (cement–fly ash–phosphogypsum) composite improved by 110% (from 7.09 to 14.98 MPa).

1. Introduction

The aim of the paper was to present the potential applications of CMF (constant magnetic field) for improvement of the physical properties of some building materials and composites and to consider the possible mechanisms of the effect of CMF on materials. It was demonstrated by direct exposure of material samples to CMF in an electromagnet and by using magnetically treated water. Waste materials of phosphogypsum and fly ash type were the additional components of the composites besides the basic ones such as cement and gypsum. Phosphogypsum (PG) is one of the materials used in the presented study. It is a by-product of chemical industry, consisting mainly of calcium sulphate, formed in the process of phosphoric acid production [1]. PG waste may be applied as a mineralize in Portland cement clinker burning [2–7] and as an additive which, like natural gypsum, regulates the setting properties of cement [8–13]. The second material investigated in such studies are fly ashes (FA). They are obtained as waste in power plants where pulverised coal and brown coal is burnt. The researchers have been interested for a long time in the effect of magnetic fields on chemical processes. Although the energy of magnetic interactions is low, under specific conditions even weak magnetic fields may cause perceptible changes in the rate of chemical processes [14]. It was observed in the study that CMF affects stable rates of chemical reactions. CMF influences not only chemical and electrochemical

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http://dx.doi.org/10.1016/j.conbuildmat.2015.04.029
0950-0618/

reactions, but also the crystalline structure, physical and chemical properties of the final products [15–19]. A team of scientists headed by Gehr et al. [20], investigated SO_4^{2-} ions present in a solution, which was then placed in CMF of magnetic induction $B = 4.75$ T. The results indicated that CMF contributes to favourable gypsum properties with respect to its density and disintegration. The effect of CMF on atoms manifests itself as stresses in the crystalline network, whereas in a liquid magnetic fields acting both on electrons and on ionized atoms cause dynamic effects [21–23]. In the study by Mwaba et al. [24] the effect of magnetic field with 0.1 T induction on crystallization of $CaSO_4$ was investigated. The authors observed formation of crystals with larger surface area, acceleration of their formation, as well as one specific direction of growth of these crystals. Iwai et al. concluded in their study [25] that the magnetic field has a number of useful functions, such as, among others, the magnetic anisotropy phenomenon, or generation of Lorentz force. Beaugnon et al. [26] observed that the magnetic field, both homogeneous and inhomogeneous, exerts a certain force on the materials and can be used for modification of their physical properties. Water molecules present in the structure of building materials take various forms. Asymmetrical distribution of charges in the water molecule induces a large dipole moment of water. Free electron pairs generate electric forces, which attract the positively charged molecules present in the vicinity. Because of high electronegativity of oxygen, electrons agglomerate closer to the oxygen nuclei than to the hydrogen ones. Thus, the positive charge of hydrogen is emphasized. Protons attract negative charges, also the free pair of electrons of an appropriate another atom. Water contains H_3O^+ and OH^- ions, which are susceptible to the effects of both electric and magnetic field. The differences in the physical properties of water are manifested as the changes in the surface tension, viscosity, dielectric permittivity, electrical conductivity. This is the consequence of modification of water structure and molecular dynamics. The structure of water can be changed by electric field, magnetic field, pressure, content of other substances, or temperature. As stated in the paper by Coey and Cass [27], the changes caused by CMF in water persist for up to 200 h. Such changes are dependent on the magnitude of magnetic induction, as observed by Kobe et al. and Higashitani et al. in their studies [28,29]. They also depend, as stated by Backer and Judd, on the direction of magnetic field lines [30], as stated by Higashitani et al. and Tai et al., on the time of exposure to magnetic field [31,32] and, according to Alimi et al., on pH [33]. Higashitani and Oshitani [34] stated that CMF causes changes in the structure of water molecules and ions contained in water, as well as hydrated ions adsorbed on the surface of colloidal particles.

The study presented in this paper involved the development of cement-gypsum composites utilizing waste PG and FA. CMF was also used for magnetic processing of mixing water and initial seasoning of the produced samples (standardised trabecular samples). First, their properties such as radioactivity, humidity and chemical compositions were investigated. Then, the formulations of composites were designed so as to comply with the standards adopted for building materials. The properties of mixing water used for the composites such as density, viscosity, electric conductivity, chemical composition were also determined. Then the samples in the form of standardised trabecular samples were produced and subjected to tests for absorptive properties, frost resistance, mechanical strength when bent, compressed when crushed.

2. Materials and methods

2.1. Materials

Components of the composites were such materials as Portland cement (CEM I 42.5 R), manufactured by CEMMAC, 91442 Horne Srnie (Slovakia), compliant with the PN–EN 197–1 (EN 197–1:2000) standard; gypsum marked with symbol CE 06, manufactured by Dolina Nidy, compliant with EN 13279-1-B1/20/2; 1 mm (099) quartz sand of (0.1–1.2 mm) grain size range, supplied by Kreisel. The composites were obtained using waste materials such as raw PG from ''Police'' Chemical Plant in Police (Poland) and FA from the Heat and Power Plant in Lodz (EC-2) (Poland). Phosphate ore comes from Morocco. The mean humidity of raw PG obtained from five samples was 57.6%. The chemical composition of raw PG and FA was investigated according to standard analytical determination methods. The results have been presented in Tables 1 and 2.

The radioactivity of PG and FA were measured in the Intersector Institute of Applied Radiation Chemistry, Technical University of Lodz, Wroblewskiego 15, 90–924 Lodz (Poland). The measurements were performed using a HPGe Spectrometer cooled with liquid nitrogen with max. 30% efficiency for Pb-210. The samples were dried at 80 °C, then comminuted and weighed. Both sample types were normalised to two types of disc geometry – of 15 g and 50 g weight. The measurement time did not exceed 6 h. The measurement uncertainties were estimated on the basis of 1σ and for the selected measurement time. They usually do not exceed 10% of the measured radionuclide activity value. The efficiency curve was plotted using LABSOCS – Genie 2000 software, and calibration was verified against the IAEA 327 – Soil standard. The standard was measured on geometries of 15 and 50 g weight.

Two coefficients, f_1 and f_2, were used for assessment of the quality of building materials. Coefficient f_1 informs about body exposure to gamma radiation emitted by radionuclides of geological origin: potassium K-40, radium Ra-226 and thorium Th-228. It has a complex form, taking into account different weights of the particular radioisotopes:

$$f_1 = 0.000S_K + 0.0027S_{Ra} + 0.0043S_{Th} \leqslant 1 \quad (1)$$

where: S_K, S_{Ra}, S_{Th} – the respective concentrations of potassium K-40, radium Ra-226 and thorium Th-228 in Bq/kg.

Coefficient f_2 informs about the level of pulmonary epithelium exposure to alpha radiation of radon Rn-222, or its derivatives:

$$f_2 = S_{Ra} \leqslant 185 \text{ Bq/kg} \quad (2)$$

where: S_{Ra} – concentration of radium Ra-226 in Bq/kg.

The following activities (expressed as the means of two geometries) were measured for FA (Table 3).

As it follows from the calculations, coefficient f_1 for FA amounted to 0.9461, whereas coefficient f_2 was 103.2. Therefore, FA, even in its original form without any admixtures could be used. The following activities (means of two geometries) were measured for raw PG (Table 4).

As it follows from the calculations for raw PG, coefficient f_1 amounted to 2.483, whereas coefficient f_2 was 513.3. The above indicates that PG can be used only as an additive whose content will amount to ca. 1/3 of composite composition by weight. Then, f_1 will be equal to 0.8277 and f_2 will equal 171.1 [13].

2.2. Methods

2.2.1. Methods of thermal analysis (TG, DTG, DTA)

Thermogravimetry (TG), Derivative Thermogravimetry (DTG) and Differential Thermal Analysis (DTA) methods were used to investigate the polymorphic changes of the main component of PG in processing. A Thermogravimetric Analyser, with drying rate of 10 K/min., was used to obtain the respective derivatograms. Waste PG was processed by heating at 210–230 °C (483–503 K) in $t = 0.25$ h. On the basis of literature data [35] and own research, the progress of dehydration of $CaSO_4l2H_2O$, i.e., the main PG component in the process of heating was determined. The knowledge of processing-induced polymorphic changes of the main PG component is helpful for analysis of further investigation of composites. In theory, dehydration of gypsum dihydrate according to reaction (3):

$$CaSO_4 \cdot 2H_2O \rightarrow \alpha - CaSO_4 \cdot 1/2H_2O + 3/2H_2O \quad (3)$$

is possible from the point of view of thermodynamics from 107 °C (380 K) (Fig. 1).

Table 1
Chemical composition of PG.

Components of PG	Content (% by weight)
CaO	31.00
SO_3	42.83
P_2O_5	3.91
Fe_2O_3	0.50
SiO_2	0.13
F	0.26
Al_2O_3	0.77
H_2O crystall.	18.60
Rare-earth elements	0.60
Loss on ignition	1.40
Total	100.00
pH	2.4