Mater. Res. Soc. Symp. Proc. Vol. 1611 © 2014 Materials Research Society
DOI: 10.1557/opl.2014.774

The Application of Nano-Structured Silica Based Admixture in Gypsum Binders

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ABSTRACT

This article reports on a new composite gypsum binder (CGB) with nanostructured silica-based admixture (NSS). NSS is obtained by a wet ultrafine milling of quartz sand resulting in the formation of an inorganic polydisperse binding system, which has a high concentration of active nanoscale phase (about 10%). Developed CGB contains hemihydrate gypsum and nano-component based on quartz sand. It is observed that the addition of 15–20 % of NSS improves the rheological properties of gypsum systems through the formation of solvate shells hindering the access of water to gypsum particles; this process also retards the setting of binder.

The experimental program used infrared IR spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) to reveal the contribution of NSS. The porosity of CGB is analyzed by the kinetics of water adsorption and BET. The XRD and IR investigations determined the formation of a new sulfosilicate phase, hydroxyellestadite during the hydration of CGB. With the addition of NSS an overall reduction in pore volume, as well as the shifts in macro-, meso- and nano- porosity values are observed.

Analysis of CGB microstructure reveals that in the presence of the NSS the size and morphology of crystals are changed contributing to the formation of dense fine-grained structure. Experimental studies have demonstrated that the composite gypsum binders with NSS are characterized by reduced water absorption and increased density, as well as improved mechanical performance especially, higher compressive strength.

INTRODUCTION

Commercial grade gypsum-based materials have a low water resistance, which limits their application [1]. The gypsum compositions with improved performance (e.g. gypsum-pozzolanic binders) have been proposed [1, 2]. The addition of mineral components in gypsum binders can affect the setting time, the flow properties and improve the strength. The main objective of this study is to investigate the feasibility of zero-cement composite gypsum binders with nanostructured silica component (NSS) [3].

EXPERIMENTAL PROGRAM

The research program uses the hemihydrate gypsum as a binder and nanostructured silica (NSS) as silica component. NSS is an inorganic polydisperse mineral system with a high concentration of solid phase containing nanosized component in an amount of 5–10%. The NSS binder is obtained by wet milling of quartz sand in a ball mill [4, 5]. The NSS is manufactured as mineral slurry with a moisture content of 14–20%.

The ARL X'tra (Thermo Scientifie) diffractometer with Co–radiation is used for XRD analysis. Quantitative full-profile XRD Rietveld analysis is performed using the DDM v. 1.95a software [6]. IR study is conducted using VERTEX 70/70v IR-Fourier spectrometer. The measurement of the BET specific surface is made on the SoftSorbi-II N_2 analyzer. High

resolution scanning electron microscope (SEM) Supra 50 VP (LEO, Germany) is used in microstructural investigation.

The flow of the binder is reported of spread of the paste flowing from the 50x100mm cylinder. The compressive and flexural strength tests are carried out using a hydraulic testing machine PGM 100, at an average loading rate of 1 MPa/s. The reported strength values are the average results based on testing of six specimens.

The composite gypsum binders with 10 to 30% (by weight) of NSS are tested (Table 1). The water-gypsum ratio for all the mixtures is 0.5 (with corresponding adjustment for moisture content in NSS). The most efficient way to produce CGB consists of mixing the NSS with water to form slurry, further addition of gypsum and subsequent mixing. This method allows obtaining a homogeneous mixture with gypsum within 30 s of mixing. Fresh CGB mix is poured into the molds with dimensions of 160×40×40 mm. Hardening is done in molds in natural lab conditions at a temperature of 22 ± 2 °C for 2 hours and subsequent drying at 35 °C for 24 hours. Cube specimens with a size of 70×70×70 mm cured for 28 days are used for the water absorption and BET study. The specimens are dried to a constant weight and kept in water until complete saturation (to reach a constant weight, approximately for 4 hours). The hydrostatic weight of samples is recorded and water absorption and the total porosity of the samples are determined.

RESULTS AND DISCUSSION

Physical and Mechanical Properties of CGB

The effect of NSS addition on the flow of experimental compositions is evaluated. The results of CGB investigation are summarized in Table 1. The use of up to 20% of NSS has some fluidifying effect; however, the increase of the NSS dosage to 30% reduces the flow of the binder due to a large content of ultra-fine particles.

Table 1. The Characteristics of Composite Gypsum Binder

№	Composition of Binder, %		Flow, mm	Density, kg/m^3	24-hour Flexural Strength, MPa	24-hour Compressive Strength, MPa
	NSS	Gypsum				
1	-	100	18.0	1201	3.7±0.1	10.2±0.5
2	10	90	18.2	1263	4.0±0.1	11.9±0.3
3	15	85	18.6	1285	5.1±0.3	14.1±0.4
4	20	80	19.2	1308	5.0±0.2	14.0±0.6
5	25	75	18.3	1319	4.3±0.2	11.6±0.6
6	30	70	17.8	1330	3.5±0.1	9.5±0.2

The introduction of NSS into the gypsum binder results in an improvement of the 24-hour strength of the experimental samples. Upon the 24-hour thermal treatment at 35^{o}C the compressive strength of composites with 15 to 20% of NSS is increased by up to 40% (Table 1). The 4-hour water absorption of experimental samples with NSS is reduced due to densification of CGB matrix as characterized by a lower porosity of 32 and 42% for 15 and 20% NSS addition, respectively (Table 2). This experiment demonstrates that the optimal dosage of NSS in CGB is at 15–20% (by weight).

The Phase Composition of CGB

The interaction of NSS and gypsum binder is investigated. The formation of a new component in this system, hydroxyellestadite, acting as a structural buffer between the gypsum and quartz is detected by X-ray diffraction, XRD (Fig. 1). In the system CaO-SO_4-SiO_2-H_2O the buffer function is performed by the hydrated calcium sulfosilicate, particularly, hydroxyellestadite $Ca_5(SiO_4)_3(SO_4)_3(OH)_2$ [7].

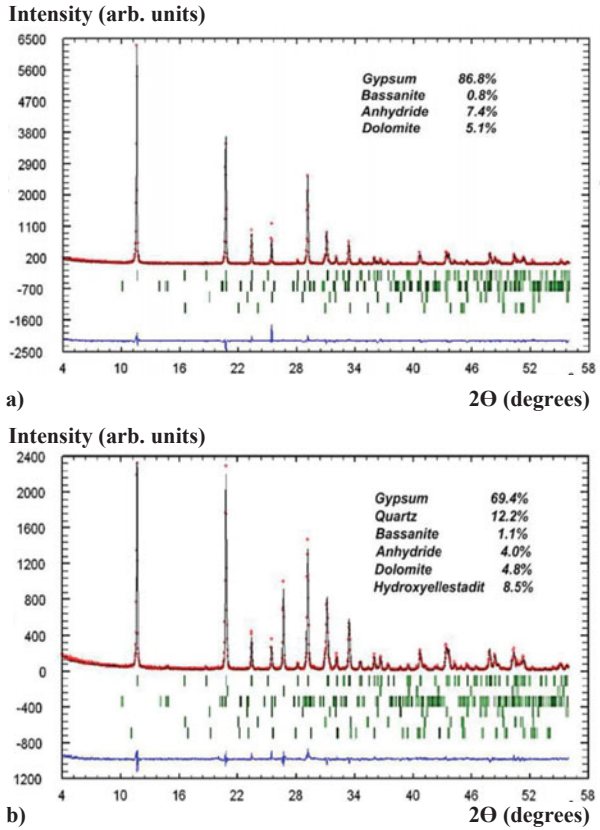


Figure 1: Rietveld's diagrams of (a) reference specimen and (b) CGB material

To verify this hypothesis, the obtained compositions are investigated using a full-profile quantitative XRD. The following mineral components are used for the quantitative XRD as structural models: gypsum ($CaSO_4 \cdot 2H_2O$; 2057-ICSD); bassanite ($CaSO_4 \cdot 0.5H_2O$; 79528-ICSD); α-quartz (SiO_2; 27745-ICSD); anhydrite ($CaSO_4$; 28546-ICSD); dolomite ($CaMg(CO_3)_2$; 52149-ICSD) and hydroxyellestadite [6, 7]. The results of the analysis of the reference specimen and

CGB with 15% of NSS are listed in Fig. 1a and 1b, respectively. In Fig 1, dots denote the experimental diffraction curves; the solid line corresponds to the reconstructed structure. The difference curve of the experimental and calculated diffraction spectra are indicated in the lower part. Strokes are the Bragg's reflection markers for all phases.

IR spectroscopy is used to confirm the presence of structural fragments specific to hydroxyellestadite in CGB. The comparative IR spectra of the NSS, gypsum and CGB are given in Fig. 2. The experimental IR spectra profiles represent the superposition of the elementary profiles of the absorption bands of the vibrational modes of various molecular groups in mineral components. The interpretation of CGB spectra is performed by deconvolution, using the fourth order derivative of spectral curves targeting the characteristic absorption bands of hydroxyellestadite. Fig. 3 shows the results of the deconvolution of spectral profiles in the long wave IR spectra of CGB. According to [9], the main absorption bands in the IR spectra of hydroxyellestadite are 514, 618, 644, 928.1049 and 1144 cm^{-1} and these are present in the CGB spectra (Fig 2, line 3 and Fig. 3, dotted line). Thus the obtained results based on the X-ray diffraction and IR spectroscopy prove the formation of the sulfosilicate phase of hydroxyellestadite in hydrated CGB. It should be noted that the formation of a stronger hydroxyellestadite phase (with a Mohs hardness of 4.5–5), can contribute to the improvement of the strength of CGB.

Analysis of CGB Structure

The porosity of the developed CGB is analyzed by measuring the kinetics of water saturation and Nitrogen absorption (BET analysis) as reported in Table 2. The use of NSS in gypsum binder results in a substantial decrease in the total porosity as compared with the reference sample. The use of NSS refines the porosity shifting the voids towards smaller size band (less than 95 nm).

Table 2. The porosity of CGB with addition of NSS

Mix ID	Composition of Binder, %		Total Porosity, ml/g	Volume of nano-voids (less than 95 nm), ml/g*
	NSS	Gypsum		
1	-	100	0.31±0.019	0.02
2	15	85	0.21±0.025	0.04
3	20	80	0.18±0.017	0.04

* The coefficient of correlation for the volume of voids data is R – 0.98

The morphology of reference and CGB based specimens are investigated by SEM (Fig. 4). It can be observed that the structure of reference material is represented by larger crystals, with fusion contacts. Commonly, such structure with large crystals has a larger number of defects and larger pores resulting in a higher total porosity and lower strength (Fig. 4a). The addition of NSS contributes to the formation of fine-grained structure characterized by higher contact area (Fig. 4b).

CONCLUSIONS

The effect of the NSS addition on the properties of the composite gypsum binders is investigated. The experimental results confirmed that the optimal content of NSS in gypsum system is 15-20%. The developed CGBs has a strength of up to 40% higher as compared to the reference gypsum binders.

The addition of NSS results in the formation of a new sulfosilicate phase of hydroxyellestadite, which contributes to the formation of a beneficial structure with lower total porosity and improved strength. In this case, the beneficial role of NSS component is defined and confirmed by the results of microstructural investigation.

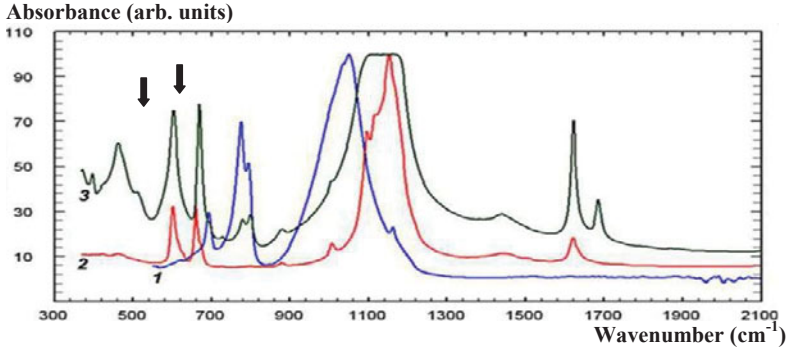


Figure 2: Normalized IR spectra of NSS (line 1), gypsum (line 2) and CGB (line 3).

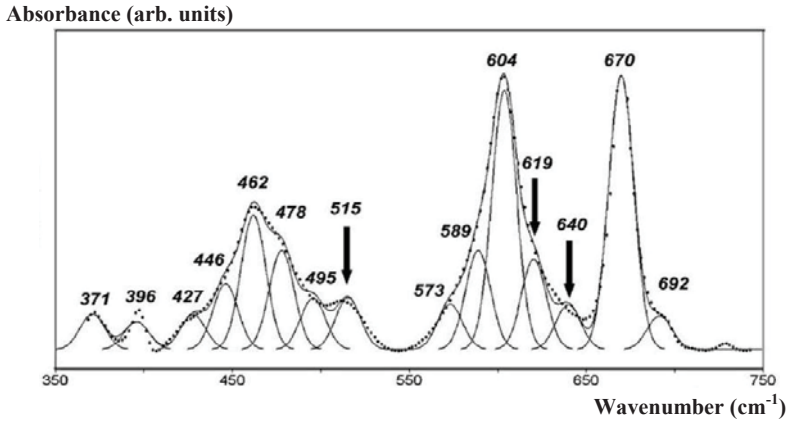
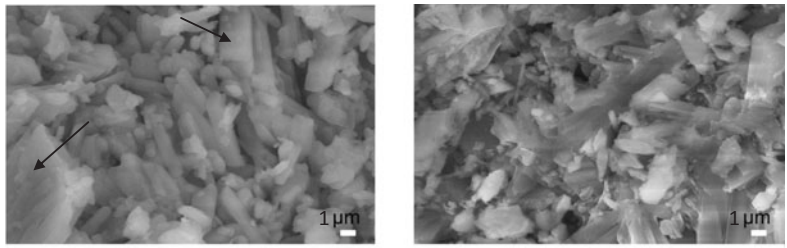


Figure 3: The deconvolution of the long wavelength IR spectra of CGB



(a) (b)

Figure 4: The microstructure of gypsum binders (a) reference sample (b) CGB with 15 % NSS.

ACKNOWLEDGMENTS

The reported work is supported by the Ministry of Education and Science of the Russian Federation, in the frame of the Program of Strategic Development of BSTU named after V.G. Shoukhov.

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