Mater. Res. Soc. Symp. Proc. Vol. 1611 © 2014 Materials Research Society
DOI: 10.1557/opl.2014.766

Autoclaved Composites with Nanostructured Silica Additive

Victoria Nelubova[1], Valeria Strokova[1], Alla Cherevatova[1], Nataliya Altynnik[1] and
Konstantin Sobolev[2]
[1]The Belgorod State Technological University named after V.G. Shoukhov, Belgorod, Russia
[2]Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee,
Milwaukee, USA

ABSTRACT

This article deals with the development of autoclaved composites (AC) with nanostructured additive (NSA) and reports on the beneficial effects of NSA in autoclaved lime-silica mixtures.

Based on the results of X-ray diffraction and electron microscopy investigation, the effects of hydrothermal conditions on the mechanisms of lime-silica interaction are revealed. It is demonstrated that the addition of NSA intensifies the formation of the C-S-H phase, reduces the quantities of amorphous phases and enables the formation of low-base calcium hydrosilicates (11Å-tobermorite and xonotlite).

The physical and mechanical properties of autoclaved composites with NSA are investigated and optimized. The reported research demonstrates the feasibility of NSA application to improve the performance of autoclaved materials.

INTRODUCTION

Lime-silicate based autoclaved materials are among the most common masonry materials in Europe and Russia [1]. However, these materials are often characterized by reduced durability [2]. The development of low-cost autoclaved materials with improved quality based on local raw materials is an important task. High-quality building materials can be developed by the formation of an optimal structure controlled at the micro- and nano- scales. The application of nanomaterials and nanotechnology for the development of new types of construction materials can greatly enhance the materials performance including strength, durability, thermal- and chemical-resistance [3, 4]. The use of a nanostructured additive (NSA) can improve the performance of lime-silicate autoclaved materials [5–7].

Nanostructured silica (NSS) can be used as a binder in construction materials. The NSS system includes about 10% of nanoscale particles which are formed by mechano-chemical activation of raw materials and complex modification, for details see references [8, 9].

The developed NSS system can be applied not only as a binder, but also as an active component, e.g., as a nanostructured additive (NSA) [9]. Based on the composition and properties of NSS/NSA, it can be used as an active component of autoclaved silicate materials with improved strength, moisture- and frost- resistance.

EXPERIMENTAL PROCEDURE

In this research program, the main raw materials for manufacturing of silicate autoclaved materials were quartz sand (from Razumensky field, Belgorod), slaked lime Grade I (from public corporation "Building Materials," Belgorod) and tap water. For production of NSA the same quartz sand was used. The reference specimens were obtained using the following method. First, lime and siliceous components were milled in a vibratory mill to a specific surface of 300–350

m^2/kg. Then, the lime-silica binder was obtained by intergrinding the components at lime : sand ratio of 3:1 (by weight). The resulting lime-silica binder (LSB) was mixed with sand (used as an aggregate) at sand-to-LSB ratio of 6.4 and water to maintain the water-to-LSB ratio of 1.13 (by weight). The same LSB was used for NSA-modified mixtures. The nanostructured modifier was added by replacing the sand aggregates at a dosage of 5, 10, and 15% of LSB-sand mixture.

Upon mixing, wet composition was cast into sealed containers for initial heat release (during 30 minutes). The 50-mm cylinder specimens were subsequently die cast using a pressure of 20 MPa. The autoclaving of the specimens was realized at 180 ^{o}C under the pressure of 1 MPa using the following regime: increasing temperature and pressure for 2 hours; constant exposure at 180 ^{o}C and 1 MPa for 6 hours; decreasing the temperature and pressure (to lab conditions) for 2 hours. The autoclaving was performed using a hydrothermal synthesis unit cooperatively developed with the Institute of Experimental Mineralogy RAS (Chernogolovka, Russia) [10].

Four compositions were produced and tested for major performance characteristics such as density, compressive strength, and water absorption according to relevant State Standards. The porosity of LSB and LSB+NSA was tested by water absorption. The 28-day compressive strength was tested using a portion of the beam with area of 50 x 40 mm using a hydraulic testing machine PGM 100, at an average loading rate of 0.5 MPa/s. The reported values are the average results of three specimens.

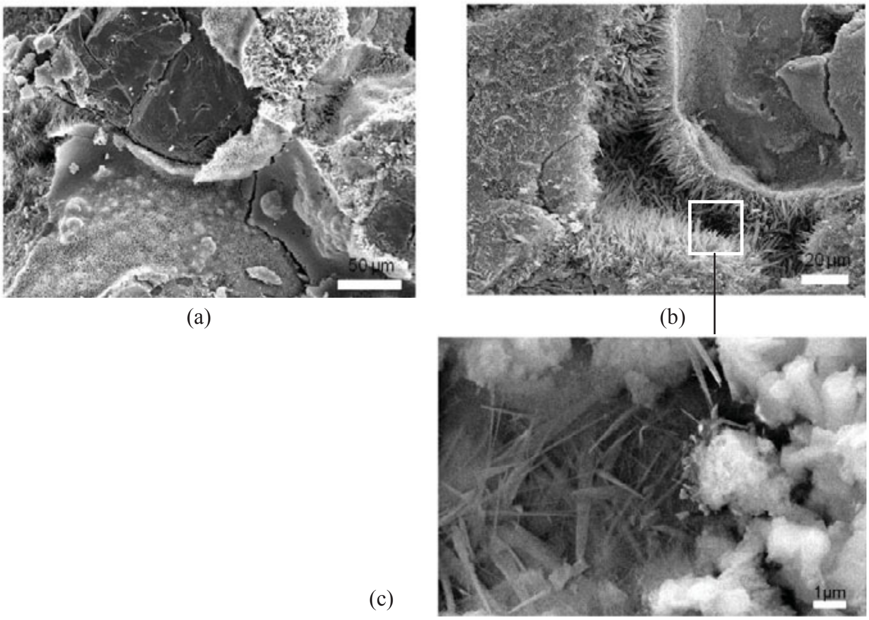
EXPERIMENTAL RESULTS

The performance of investigated composites is reported in Table 1. The research results demonstrate that the optimal dosage of the NSA in the composite mixture is 10% (by weight). The use of NSA enables almost two fold increase of strength vs. reference. In autoclaved materials even small decrease in the water absorption can improve the resistance to freeze-thaw. Further increase of NSA dosage leads to the reduction of strength (Table 1).

Table 1. The properties of developed autoclaved materials with NSA

Type	Density, kg/m^3	Compressive Strength, MPa	Water Absorption, %
Reference	1878	16.0	13.6
5 NSA	1890	21.0	13.0
10 NSA	1900	31.7	12.3
15 NSA	1910	18.0	12.4

The strength improvement in LSB+NSA composites can be explained by the densification of the structure of lime-silicate autoclave materials. Improved structure is obtained due to the presence of polydisperse particles including nanosized SiO_2 which complement finely ground quartz sand used in LSB. The microstructural analysis using SEM reveals the densification of the specimens with NSA (Fig.1). Large volumes of very fine (less than 100 nm in diameter) needle-like crystals of xonotlite (high temperature polymorph of 11Ǻ-tobermorite) can be observed on the surface of finely-milled silica grains and within the contact zone between the particles (Fig.1c). The presence of xonotlite phase can explain the improved strength performance of LSB-NSA specimens.



(a)

(b)

(c)

Figure 1. The microstructure of autoclaved silicate specimens a) reference specimen, (b) specimen with NSA, (c) the phase with needle morphology observed in 10 NSA material

The effect of NSA on structure of autoclaved LSB materials was investigated using quantitative XRD Rietveld phase quantification method comparing the reference specimens and specimens with NSA. In order to obtain the specimens with complete hydration and to identify the "ultimate" mineralogical composition, the increase of autoclave exposure to 24 hours was necessary. Upon autoclaving, the reference system was mainly represented by portlandite and quartz phases (Fig. 2, Table 2). In LSB-NSA systems, the XRD analysis reveals the reduction of portlandite phase with the increase in autoclaving time, indicating the complete transition of portlandite into C-S-H-phases during 24-hour treatment (Fig. 2, Table 2).

The hydrosilicate phases in autoclaved LSB+NSA system are mostly represented by xonotlite chain silicate (also observed in Fig.1c), which is the product of the high temperature transformation of 11Å-tobermorite. Consequently, a significant strength improvement in autoclaved silicate materials were observed due to the presence of nanostructured SiO_2 modifier that accelerates the formation of hydrate phases in the $CaO-SiO_2-H_2O$ system and promotes direct synthesis of low-base calcium hydrosilicates such as xonotlite and 11Å -tobermorite, which are the main contributors to improved strength in autoclaved LSB-NSA composites.

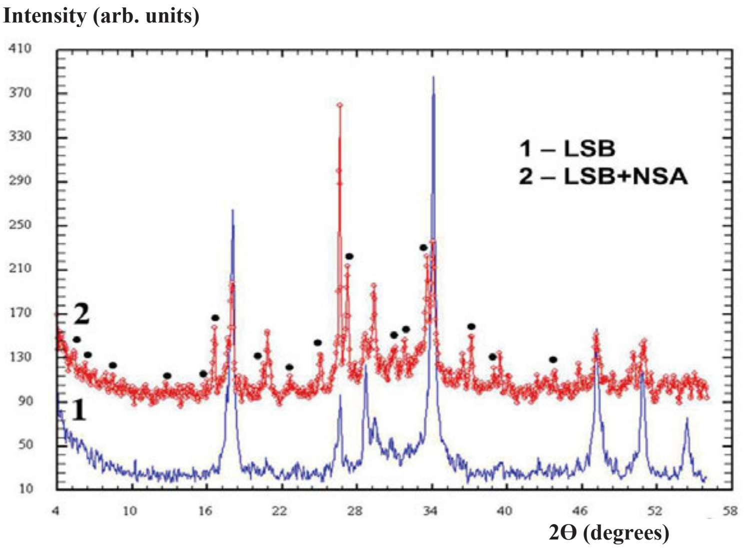


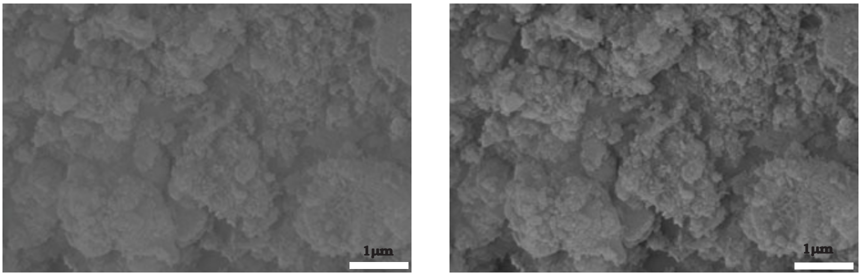
Figure 2. The phase formation in LSB and LSB-NSA specimens after 24 hours of hydrothermal treatment in an autoclave

Table 2. The effect of NSA on mineral composition of autoclaved LSB specimens

Type	**Mineral Composition, % (by weight)**					
	Quartz	Portlandite	Calcite	Xonotlite	Jennite	11Å-tobermorite
6 hours of autoclaving						
LSB	1	96	3	–	–	–
10NSA	15	80	5	–	–	–
24 hours of autoclaving						
LSB	1	94	1	2	1	1
10NSA	6	40	2	43	6	8

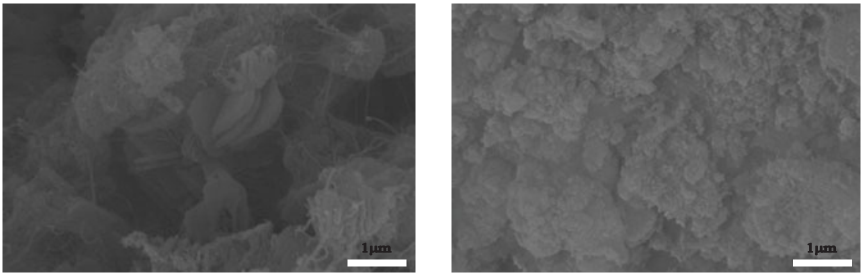
The structure of the reference specimens is mostly presented by flake globular formations, with well-defined formations of quartz (Fig. 3a). The distribution of the globular aggregates is also uneven. The addition of NSA leads to the acceleration of lime hydration and formation of uniform distribution of the hydrates (Fig. 3b). Increasing the duration of autoclaving to 24 hours brings considerable extension of the crystal phases formed in the system (Table 2). The reference specimens (Fig. 3c) contain isometric tabular-like formations with the size of less than 1 μm, represented by portlandite. This demonstrates an incomplete hydration of lime that might be related to reduction of hydration rates and inhomogeneity of a raw mixture.

The addition of NSA results in the formation of uniform composite structure (Fig. 3d) with evenly distributed globular phases densifying the material. The use of smaller particle sizes results in the formation of composites with uniform microstructure and enhanced strength and water absorption.



a b

6 hours



c d

24 hours

Figure 3. The microstructure of silicate specimens at different duration of autoclaving: (a, c) LSB; (b, d) LSB+NSA

CONCLUSIONS

The feasibility of nanostructured additive (NSA) application in lime-silica autoclave materials was evaluated. It was determined that the optimal content of NSA in the system is 10% by the weight of the LSB-sand composite. It was demonstrated that the use of NSA provides a significant, up to 100% improvement of compressive strength in autoclaved LSB composites.

It was determined that the use of NSA intensifies the formation of the C-S-H and assists the synthesis of low base calcium hydro-silicates such as xonotlite and 11A-tobermorite, which are the main carriers of strength. The increase of compressive strength and reduction of water absorption was achieved due to incorporation of ultra-fine and nanosized SiO_2 particles of NSA, synthesis of low-base hydrates and improvement of the packing density of LSB composite.

ACKNOWLEDGMENT

Authors would like to acknowledge the financial support from the Ministry of Education and Science of the Russian Federation.

REFERENCES

1. V.V. Nelubova, *Constr. Mater*. **9**, 2–5 (2008), *in Russian*
2. P. I. Bozhenov, *Technology of Autoclave Materials*, (Stroiizdat, Leningrad, 1978), pp. 368, *in Russian*
3. K. Sobolev, M. Ferrada-Gutiérrez, How Nanotechnology Can Change the Concrete World: Part 1. *American Ceramic Society Bulletin* **10**, 14–17, (2005).
4. I. Flores, K. Sobolev, L.M. Torres, P.L. Valdez, E. Zarazua, and E.L. Cuellar, *Transportation Research Record: Journal of the Transportation Research Board* **1** (2141), 10–14 (2010).
5. A. Cherevatova, V. Strokova, I. Zhernovsky, N. Pavlenko, V. Nelubova, K. Sobolev, The development of nanostrured SiO_2 binders for application in cellular concrete, NICOM 4: *4th International Symposium on Nanotechnology in Construction*, Greece, 2012.
6. I.V. Zhernovsky,V. Nelyubova, A.V. Cherevatova, V.V. Strokova, *Constr. Mater.* **11**, 100–103 (2009), *in Russian*
7. I. Zhernovsky, V. Strokova, N. Koshukhova, K. Sobolev, The use of mechano-activation for nanostructuring of quartz materials, NICOM 4: 4th International Symposium on Nanotechnology in Construction, Greece (2012).
8. A.V. Cherevatova, I. Zhernovsky, V.V. Nelyubova, *Refractories and Industrial Ceramics* **51** (4), 310–311 (2009), *in Russian*
9. V.V. Nelubova, V.V. Strokova, N.V. Pavlenko, I. Zhernovsky, *Constr. Mater.***2**, 11–15 (2013), *in Russian*
10. E.V. Fomina, V.V. Nelyubova, V.V. Strokova, N.I. Altynnik, *Constr. Mater*. **3**, 18–19 (2012), *in Russian*