Construction and Building Materials 166 (2018) 723–731

Contents lists available at ScienceDirect

Construction and Building Materials

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

Influence of superfine ettringite on the properties of sulphoaluminate cement-based grouting materials

Haiyan Li, Xuemao Guan, Xuyang Zhang, Peng Ge, Xingxing Hu, Dinghua Zou *

School of Material Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China

HIGHLIGHTS

- S-ettringite was prepared via SNAS method by introduction of citric acid.
- The 4-h compressive strength increased by 380% when adding 4 wt% S-ettringite.
- Decline of setting time of CBGM paste was shown by the addition of S-ettringite.
- Effect of S-ettringite on the hydration and microstructure of CBGM paste was studied.
- Due to crystallization inducting effect and seed effect S-ettringite changed the hydration of paste.

ARTICLE INFO

Article history:
Received 29 November 2017
Received in revised form 1 February 2018
Accepted 2 February 2018
Available online 22 February 2018

Keywords:
Superfine ettringite
Compressive strength
Setting time
Sulphoaluminate cement
Grouting materials

ABSTRACT

Superfine ettringite (S-ettringite) synthesized in this research presents same structure with the ettringite produced by the hydration of cement, which is expected to promote the hydration of sulphoaluminate cement-based materials. There are few literature reports on laboratory synthesis of superfine ettringite. In this paper, preparation of S-ettringite via separate nucleation and aging steps method by introduction of citric acid is presented. The effect of the S-ettringite on hydration, microstructure and properties of CSA cement-based grouting materials (CBGM) was experimentally investigated. Results show that specimens containing S-ettringite displayed a significant improved performance with regard to compressive strength at early and later ages and setting time. Compared to the control specimen, 4-h compressive strength increased by 380% and initial setting time shortened by 55.6% when 4 wt% S-ettringite was added, respectively. Due to the crystallization inducting effect and seed effect, the addition of S-ettringite changed the morphology of ettringite, and meanwhile promoted the hydration exothermic rate and increased the amount of hydration products, which thus generate higher compressive strength and shorter setting time.

1. Introduction

Grouting technology whose slurry with condensation and hardening property is widely employed in modern engineering field to strengthen the fracture which existing in the matrix and accomplish the goal of reinforcement [1,2]. Calcium sulphoaluminate (CSA) cement, owing to its micro-expansion, better corrosion resistance ability and high early compressive strength, is widely adopted in grouting engineering. The water to binder ratio (w/b), a crucial parameter in cement-based grouting material for repair and consolidation, is always in the scope of 0.5–1.5 [3] . In the case of high water to binder ratio (w/b $\geq$ 0.5), compressive strength and setting time of CSA cement-based grouting materials (CBGM), however, do not satisfy the demands of projects such as emergency repairs, large section coal seam roadway and so forth. Cement additives, for example the inorganic lithium-based [4] hardening accelerators, are widely used to speed up hardening and improve the early age compressive strength of CSA cement-based materials. However, disadvantages such as low compressive strength at later age and poor sulfate corrosion resistance [5] arise therefore.

Nowadays, the application of ultra-fine powder in cement-based materials has evolved voluminously. Owning to exceedingly small particle size, ultra-fine powder can fill the empty spaces, so giving rise to a higher packing density and producing a thicker binding matrix as well.

A lot of ultra-fine particles like nano-SiO_2 [6], grapheme oxide nanosheets [7], nano-TiO_2 [8], nano-Al_2O_3 [9], carbon nanotube [10] and nano-CuO [11] have been widely employed to improve the physical, mechanical and other properties of Portland cement

* Corresponding author.
E-mail address: zoudinghua@hpu.edu.cn (D. Zou).

https://doi.org/10.1016/j.conbuildmat.2018.02.013
0950-0618/

Table 1
Mineralogical composition of the CSA clinker/ %.wt.

$C_4A_3\bar{S}$	β-C_2S	C_4AF	f-SO_3	f-CaO	CaO.TiO_2
74.54	18.25	3.86	0.81	2.02	3.01

Table 2
Chemical composition of the CSA clinker/%.wt.

L.O.I	SiO_2	Fe_2O_3	TiO_2	Al_2O_3	CaO	MgO	SO_3	Alkali
0.17	6.36	1.27	1.77	38.27	40.23	1.15	8.88	0.15

L.O.I: loss on ignition.

Table 3
Chemical composition of the anhydrite/%.wt.

L.O.I	SiO_2	Fe_2O_3	MgO	Al_2O_3	CaO	SO_3	Alkali
6.14	1.04	0.18	2.64	0.23	38.63	50.11	0.12

L.O.I: loss on ignition.

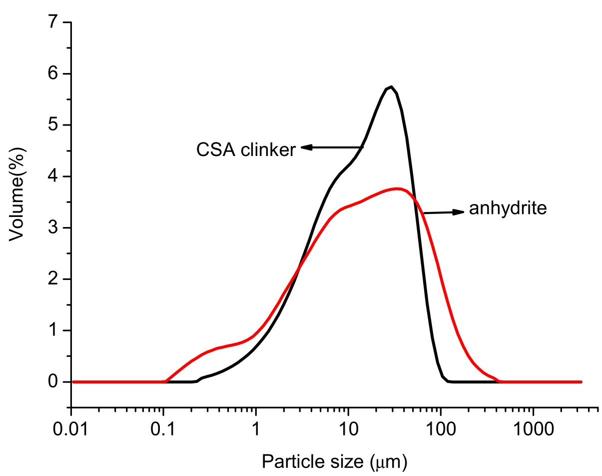

Fig. 1. Particle size distribution of CSA clinker and anhydrite used in all experiment.

and concrete. There are less researches on the effect of superfine material on the properties of CSA cement-based materials. Recent research has showed [12] that Nano-SiO_2 and Nano-TiO_2 prompted the hydration exothermic rate and improved the microstructure of CSA cement pastes.

Based the theory of crystal growth, the Gibbs free energy change of nucleus formation on the like substrate is smaller than that on the unlike substrate [13], meaning that superfine material with a similar structure to hydration products of cement paste may have better ability to improve physical and mechanical properties of cement-based materials.

Ettringite, calcium aluminate trisulfate hydrate ($Ca_6[Al(OH)_6]_2(SO_4)_3{\cdot}26H_2O$), is produced in the hydration of various kinds of inorganic binders and is labeled "cement bacillus" by Ref. [14]. The appearance of ettringite mineral often was related with poor concrete performance for the reason that the reformation of ettringite (delayed ettringite) in the hardened concrete leads to cracking and expansion [15]. In contrast, primary ettringite is not hazardous [16] and even large amounts of ettringite may cause only insignificant volume changes in some cementitious systems. It is also recognized that the formation of ettringite under controll can lead to particular hydraulic properties utilized for building chemistry aims: extremely high early strength, reducing plastic shrinkage, lower drying shrinkage and superior sulfate resistance [17]. As a crystal seed, the addition of AFm phase with nano structure can significantly accelerate the hydration exothermic rate of CSA cement paste [18]. Similarly, superfine ettringite may have the ability to promote the hydration of cement-based materials as ettringite is another kind of hydration product of CSA cement.

Ettringite is traditionally synthesized by co-precipitation reactions from $Al_2(SO_4)_3{\cdot}18H_2O$ aqueous solution and CaO suspensions [19]. Calcium sulfate ($CaSO_4{\cdot}2H_2O$ or $CaSO_4{\cdot}0.5H_2O$) reacts with $Ca_3Al_2O_6$ (C_3A) at room temperature) is another preparation method of ettringite [20]. However, the particle size of ettringite synthesized by above-mentioned two methods is under the scope of micron level (several to several ten microns). There are few literature reports of the laboratory superfine ettringite synthesis.

In this paper, we present a route to synthesize S-ettringite by a method involving separate nucleation and aging steps (SNAS), of which the major characteristics are an extremely fast mixing and nucleating procedure in a converted colloid mill followed by a separate aging process. The performance of the S-ettringite was assessed by examining the compressive strength and setting time of CBGM, and a possible origin of the improved performances observed is suggested based on the results of hydration heat, Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis and differential thermal analysis (TG-DTA), scanning electronic microscopy (SEM) and energy dispersive spectrometer (EDS).

Table 4
Component of CSA cement-based grouting material/%.wt.

Component	CSA clinker	Anhydrite	Quicklime	Na-bentonite	NW[a]	SG[b]
Slurry A	91.40	–	–	6.88	1.47	0.25
Slurry B	–	68.35	22.78	7.39	1.48	–

[a] Naphthalene Water reducer (NW).
[b] Sodium Gluconate (SG).