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Compatibility between a polycarboxylate superplasticizer and the belite-rich sulfoaluminate cement: Setting time and the hydration properties

Bing Ma, Ming Ma, Xiaodong Shen *, Xuerun Li, Xiaodong Wu

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Material Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China

HIGHLIGHTS

- Polycarboxylate superplasticizer (PCS) was introduced to adjust the setting time of belite-rich sulfoaluminate cement.
- Setting time was greatly relevanted to the amount of polycarboxylate superplasticizer.
- PCS decreased the compressive strength at 1 day meanwhile increased the compressive strength at 28 days.
- PCS makes the morphology of pores in the cement pastes transformed from macropores to micropores at 28 days remarkably.

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ABSTRACT

Belite-rich sulfoaluminate cement, a novel type of cement, has been synthesized via a calcined process. This paper presents an experimental study on the effects of polycarboxylate superplasticizer on the setting time and the mechanical performance of this type cement to solve the problems of quick set at an early stage. The results indicate that the setting time depends upon the amount of the superplasticizer, especially for the initial setting time. The presence of the superplasticizer can delay the initial setting time remarkably when the dosage reaches 0.075%. The influence of the superplasticizer on the strength development at different hydration stages presented different results, observed by a decreased strength at an early stage and an increased strength at 28 days. X-ray diffraction (XRD) analysis, mercury intrusion porosimetry (MIP) characteristics and scanning electron microscope (SEM) images of the pastes were also studied to investigate the mechanism of compatibility between the superplasticizer and the cement.

1. Introduction

With the development of the global economy, there have been a number of efforts aimed at energy conservation and the reduction of emissions. Cement manufacturing is an industry that consumes a large amount of energy and emits a great deal of CO_2. For every ton of ordinary Portland cement (OPC) produced, 0.54 tons of CO_2 are released into the atmosphere because of the decomposition of calcite in the kilns. On average, 0.34 and 0.09 tons of CO_2 are also emitted due to fuel and electricity consumption, respectively [1,2]. Some studies have estimated that the cement industry contributes as much as 5% of the global anthropogenic CO_2 emissions [3,4].

Belite-rich sulfoaluminate cements (BRSCs) have been proposed as an alternative binder to reduce the CO_2 emission in cement clinker production because these materials require a lower utilization of limestone and a lower operating temperature, and they are easily ground [5]. Therefore, up to a 35% reduction in CO_2 emissions can be reached when comparing cement production of BRSC with OPC [6,7]. Hereafter, the cement nomenclature will be used: C=CaO, S=SiO_2, A=Al_2O_3, F=Fe_2O_3, \$=SO_3 and H=H_2O. BRSC are cements that mainly comprise belite (C_2S); ye'elimite ($C_4A_3\$$), which is also called Klein's salt or tetracalcium trialuminate sulfate; tricalcium aluminate (C_3A); and ferrite (C_4AF) [8,9]. It is widely recognized that BRSC pastes generally possess high mechanical strength at early ages through the formation of an initial ettringite (AFt) network and the subsequent infilling by mixtures of ettringite, calcium monosulfoaluminate (AFm) hydrate, alumina and ferrite gels [10,11]. BRSC pastes also have a high degree of impermeability and a high resistance to frost and corrosion, which is much better than the corresponding properties of OPC [12,13]. BRSC is, however, not perfect. There are major problems with BRSC, including the production of a fast hardening performance, a variation of the initial slump and a large slump loss of concrete. The setting time is especially unable to be controlled efficiently. Thus, an increasing amount of scientific and technical

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* Corresponding author. Tel.: +86 025 83587234; fax: +86 25 83221690.
E-mail address: xdshen@njut.edu.cn (X. Shen).

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research has focused on the use of cement admixture in recent years, with the aim of improving the technical characteristics (workability) of the final product and/or addressing the environmental issues [14–16].

Superplasticizers are recognized as important admixtures for their applications in cement and concrete technology. Their main function is to reduce the water-to-cement ratio and control the setting time without losing the fluidity of the cement pastes, which results in higher strengths in the curing ages and better durability of the concrete [17–19]. However, these changes in the strength and durability are contingent upon the compatibility between the chosen superplasticizers and the cement used. The compatibility of the mineral additions with, as well as their affinity for, a given admixture must therefore be determined [20–22]. The presence of mineral additions, such as limestone, fly ash and blast furnace slag, may affect the interaction between the superplasticizer and the cement. The performance of the additions could also be influenced by the admixtures. Conventional superplasticizers, such as naphthalene, melamine and lignosulfonate, disperse the particles due to an electro-steric mechanism. Since the 1980s, the application of the third generation of polycarboxylate acid-based superplasticizers (PCS) has been investigated. These superplasticizers possess an excellent fluidity at low water-to-cement ratios and provide slump retention over a prolonged period [23]. As soon as the superplasticizer molecules enter into contact with the cement particles, some of them are adsorbed onto the cement particles, creating negatively charged particles that repulse each other and produce space-steric effects so that they increase the dispersion of cement, which results in the cement particles being unable to flocculate further [24–30].

Despite polycarboxylate superplasticizers possessing good dispersion and retention properties, there has been very little investigation in the literature into the interaction and compatibility between this type of admixture and the BRSC. Thus, the purpose of the present study is to investigate the compatibility of the polycarboxylate superplasticizer with the BRSC, especially as to how the superplasticizer fulfills the criteria as both a setting and a hardening accelerator. In this respect, the choice of a polycarboxylate presenting a developed spatial molecular structure, such as a methacrylic acid ester-based polycarboxylate, seems to be appropriate to verify the previously indicated criteria.

2. Experimental

2.1. Raw materials

Alumina-rich fly ash (FA), desulfurization gypsum (FGD) and limestone were obtained from a plant in Zhejiang. PCS was obtained from Jiangsu Sobute (the solid content is 42.83%). The main oxide compositions of the raw materials, as determined by chemical analysis, are shown in Table 1.

2.2. Synthesis of BRSC

The BRSC clinker was prepared by mixing the limestone (60.58%), FA (31.21%) and FGD (8.21%). The mixture was mixed with water and pressed with a pressure of 15 MPa into a disk mold with a dimension of 40 mm × 25 mm. The disks were dried in the oven and then calcined in a Si-Mo rod resistance furnace at 1320 °C for 60 min. The sintered clinker was then immediately removed from the furnace and cooled rapidly by forced air. The clinker samples were all ground to be able to pass through an 80 μm sieve. The BRSC was prepared by mixing the clinker and the gypsum in the following proportion: clinker/gypsum = 90/10.

Table 1
Chemical composition of raw materials (wt.%).

Material	Limestone	FA	FGD
CaO	54.85	6.33	34.01
SiO_2	0.82	47.83	0.02
Al_2O_3	0.24	33.71	0.92
Fe_2O_3	0.54	5.13	0.19
SO_3	0.07	3.01	39.96
MgO	0.38	1.87	0.13
LOI[a]	42.12	1.23	24.94

[a] LOI: loss on ignition at 950 °C.

2.3. Preparation of hydration samples

All the tests were conducted using BRSC (mass ratio of clinker to gypsum was 90/10). The tests were conducted with two different matrices, with one matrix as a control to determine the effect of the presence of PCS. The first matrix (blank) consisted solely of BRSC without the PCS. In the second matrix (reference), varying concentrations of PCS were added, with the mass ratio from 0.025% to 0.25%. All of the pastes were mixed with water at a water/solid ratio (w/s) of 0.26. The hydration of the solid phase at different curing ages was stopped by submerging a part of the crushed pastes into ethanol for 2 days, and the stopped hydration samples were dried and placed into desiccator for further study. Herein, it is worth noting that the w/s ratios as well as the curing conditions, the type of binder, and the use of mineral and chemical admixtures have significant effects on the value of the total porosity and the pore size distribution [31].

2.4. Compressive strength tests

The composition of the standard mortars was as follows: BRSC/sand/water = 1/3/0.5. Prismatic samples (40 × 40 × 160 mm) were cured at 20 ± 1 °C and 95% relative humidity (RH). Then, the samples were removed from the mould after 1 d and immersed in water at 20 °C until they were utilized for compressive strength testing. Before the compressive strength tests, the prismatic samples were first subjected to a flexural test. After the specimens were cured for 1, 3 and 28 days, the compressive strengths were tested using the unconfined compression machine with a maximum load of 200 kN. The loading rate of the machine is 5 mm/min. Each compressive strength value represents the average of the results from 6 specimens tested.

2.5. Measurement of the absorbance

Admixture adsorption isotherms were determined for BRSC. A water solution was used to prepare the PCS suspensions. PCS was dissolved in water, and 50 g of each solution were mixed with 10 g of cement. The dosage ranged from 0 to 50 mg of PCS/g of cement. The suspensions were stirred magnetically for 30 min at 25 °C and subsequently centrifuged for 3 min to separate the supernatant from the solid. The amount of PCS present in the supernatant was determined with a SHIMADZU TOC-VCPH total organic carbon (TOC) analyzer. The amount of the admixture consumed in the process was defined as the difference between the amount initially added and the quantity remaining in the supernatant.

2.6. LOI tests of hydration specimens

After stopping hydration, a part of the sample was ground by agate mortar below 0.08 mm to determine the amounts of hydrates that were formed by the samples that were cured at different ages. LOI analysis was conducted in an atmosphere of air utilizing approximately 1 g of sample in a muffle instrument at 10 °C/min for a temperature up to 150 °C. Chemically bound water of ettringite was determined as the weight loss at 100–150 °C. The amount of ettringite in the hydrated pastes was determined by the process described by Lothenbach and Wieland [32], assuming that the weight loss between 50 °C and 120 °C corresponds to 32 molecules of crystal water per molecule of ettringite.

2.7. Materials characterization

In this study, all samples were finely ground to perform the X-ray powder diffraction (XRPD) measurements. XRPD patterns were recorded on an X'ARL with Cu Kα radiation (λ = 0.154 nm). The X-ray tube was operated at 40 kV and 40 mA. The optics configuration is a fixed divergence slit (1/2°) and a fixed incident anti-scatter slit (1°). Measurements were made in a θ–θ reflection configuration. Data were collected from 10° to 70° (2θ) with a step size of 0.02° for the clinker and for a degree range of 5–65° over 30 min for the hydration products. The samples were fixed during the measurement.

The hydration heat release of the different cements (blank and reference matrix) was determined by a conduction calorimeter. The calorimetry tests were conducted in an eight-channel Thermometric TAM Air instrument using plastic ampoules, and the heat flow was collected for time periods up to 75 h at a temperature of 20 °C and an atmosphere of air. The cement pastes (water/cement ratio of 0.5) were mixed before testing (4 ± 0.01 g sample mass).

The setting time test on the cement pastes was performed by utilizing a Vicat apparatus and following the Chinese National Standard (GB/T1346-2001) [33].

Porosity and pore size distribution were measured on fragments of the specimens by a mercury intrusion porosimetry (MIP) test. The specimens were first dried in a dryer at 25 °C for 7 days until their weight loss stabilized. The pressure applied