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Influence of LiAl-layered double hydroxides with 3D micro-nano structures on the properties of calcium sulphoaluminate cement clinker

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ABSTRACT

The effect of LiAl-layered double hydroxides (LiAl-LDHs) with 3D micro-nano structures on the early properties and hydration process of calcium sulphoaluminate cement (CSAC) clinker was investigated. Three Li–Al layered double hydroxides (LiAl-LDHs) with different particle size were prepared through a facile solvothermal method. CSAC clinker incorporating LiAl-LDHs with constant water to cement radio were made and tested. The results indicate that a higher content of LiAl-LDHs resulted in a faster hydration rate, a shorter setting time and a higher early compressive strength. Besides, with the decrease of the particle size of LiAl-LDHs, the hydration rate was accelerated with corresponding increase in compressive strength. However, the influence of particle size of LiAl-LDHs on the setting time of CSAC clinker is not significant. Moreover, the addition of LiAl-LDHs did not result in a new phase formed, but increased the quantity of hydration products providing higher compressive strength and shorter setting time.

1. Introduction

Grouting with cement based suspensions is widely used in tunneling and underground coal mine engineering for repair and consolidation and the suspension is composed of cement, water and, possibly, admixture.Calcium sulphoaluminate cement (CSAC) is widely used in grouting engineering and its main properties include impermeability, low alkalinity, high early compressive strength, micro-expansion, low temperature performance and better corrosion resistance capacity [1–3]. The water to cement ratio (w/c) is an important parameter in cement based grout and is directly related with the pumpability and penetration of voids. Cement grout for repair and consolidation have w/c in the range 0.5–1.5 [4]. However, for high water cement ratio (w/c $\geq$ 0.5) the compressive strength and setting time of CSAC often do not meet the requirements of special projects, including those that need short setting times of less than 10 min.

In recent years, the application of nanotechnology in cement-based materials has developed enormously. Due to its extremely small sized particles, nanomaterial can fill the voids, thus leading to a higher packing level ("filler" effect) and generating a denser binding matrix ("crystal nucleus" effect) as well. In this field, the utilization of nanomaterial as an additive is highly effective. Some researchers have employed nanoparticles in cementitious materials so as to modify mechanical strength and other properties. Various nanomaterials such as nano-SiO_2 [5], nano-TiO_2 [6], nano-Fe_2O_3 [7], nano-$CaCO_3$ [8] carbon nano-tubes and nano-clay [9]have recently been used in Portland cement or concrete to improve their mechanical, physical, durability and several other novel properties [10]. Chen et al. [11] investigated the effect of nano-TiO_2 on the hydration and workability of Portland cement pastes. Cement was partially replaced with nano-TiO_2 at level of 0%, 5% and 10% by weight. The results showed the addition of nano-TiO_2 significantly accelerated the hydration rate, shortened the setting time and increased the early compressive strength of CSAC clinker paste. The optimum content of nano-TiO_2 at 10% gave the highest strength and shortest setting time.

Besides the kinds of nanometer materials, the size of nanoparticles also has paramount influence on working performance. Quercia et al. [12] examed the morphological and textual characteristics of seven different amorphous silica used in Portland cement concrete, and found that the main parameters influencing the final mechanical properties of cement mortars were specific

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surface area, micropore volume and average size of the primary particles of the silica. Haruehansapong et al. [13] presented the compressive strength of Portland cement mortars containing silica fume (SF) and nanosilica (NS) with sizes of 12 nm, 20 nm and 40 nm. Results show that NS greatly enhanced the compressive strength of cement mortars, besides, cement mortar containing NS 40 nm gave higher compressive strength than those with NS 12 and 20 nm.

Recent research by Xu, Chen [14] has revealed that CaAl-layered double hydroxides (CaAl-LDHs) as a hardening accelerator in Portland cement enhanced the value of early compressive strength by 61%. However, the preparation of pure CaAl-LDHs is not easy and the effects of LDHs on the morphology, structure and hydration heat of cement have not been investigated. Until now, the effect of nanomaterials on the properties of CSAC clinker has seldom been reported in the literature.

Naturally occurring hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$, and synthetic hydrotalcite-like compounds, also called layered double hydroxides (LDHs), have been investigated for many years [15,16]. The formula of the LDH can be generalized to $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[(A^{n-})_{x/n}.mH_2O]^{x-}$ where M^{z+} can be Ni^{2+}, Zn^{2+}, Mn^{2+}, Ca^{2+}, etc.; M^{3+}: Al^{3+},Ga^{3+}, Fe^{3+}, Cr^{3+}, etc.; and A^{n-}: NO_3^-, Cl^-, CO_3^{2-},SO_4^{2-}, etc. $LiAl_2(OH)_6^+A^-$ is also an example of a layered double hydroxide, and its properties have been extensively investigated for many years. It is composed of sheets of lithium and aluminum atoms octahedrally surrounded by hydroxyl groups [17]. Their layered structure, nano-sized interlayer space and adjustable particle size are significant factors that should be considered when being used in many industries as high-performance catalytic materials, adsorbents, separation materials, additives in plastics and as biological and pharmaceutical materials [18–21].

The aim of this work was to investigate the content and particle sizes of LiAl-LDHs on the setting time and the early strength of CSAC clinker at high water cement ratio. For this purpose, three Li–Al layered double hydroxide (LiAl-LDHs) with 3D micro–nano structures were prepared through a facile solvothermal method, and then the effect of LiAl-LDHs on chemical and mechanical properties of CSAC clinker paste was examined.

2. Experiment

2.1. Materials

In this study, sulphoaluminate cement clinker was taken as binder material. Its chemical composition (by weight) is given in Table 1. The chemical reagents such as $LiNO_3$, $Al(NO_3)_3{\cdot}9H_2O$,$CO(NH_2)_2$, Na_2CO_3 and NaOH were of analytical purity.

2.2. Synthesis of LiAl-LDHs

Highly dispersed LiAl-LDHs were prepared by a solvothermal method [22]. In a typical procedure, a solution of 0.015 mol $LiNO_3$,0.005 mol $Al(NO_3)_3{\cdot}9H_2O$ and 0.065 mol of urea were dissolved respectively in mixtures containing different water alcohol ratios (75 ml H_2O/25 mlC_2H_5OH; 50 ml H_2O/50 mlC_2H_5OH; 25 ml H_2O/75 mlC_2H_5OH) in total volume of 100 ml. The solution was magnetically stirred for 20 min at 25 °C, then transferred to a polytetrafluoroethylene vessel. The container was sealed and placed in an oven to maintain at 393 K for 24 h. The solid was collected by filtration, then washed with deionized water until the washings reached a pH of 7.0, and subsequently dried at 373 K for 24 h. The samples prepared at different solvent ratio (75:25; 50:50; 25:75) are denoted by LDH-1, LDH-2 and LDH-3, respectively.

Table 1
Chemical composition of calcium sulfoaluminate cement clinker (% by weight).

	CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	SO_3	Loss	The sum
% (by weight)	40.96	34.46	9.63	2.21	0.87	8.67	0.52	97.32

2.3. Characterization of LiAl-LDHs

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-Ray diffractometer with Cu Kα radiation (λ = 0.154 nm) in the 2θ range from 3° to 70°. Scanning electron microscopy (SEM) images were taken by a JSM-6390LV scanning electron microscope (Japan) operated at 15 kV. Elemental analyses for Li and Al were performed by inductively coupled plasma (ICP) using a PerkinElmer Optima 7000DV (PerkinElmer, MA, USA). The particle size distribution was determined using a Malvern Mastersizer 3000 laser particle size analyzer.

2.4. Test methods

2.4.1. Setting time

The setting time test on the calcium sulfoaluminate clinker with and without LiAl-LDHs was measured in accordance with the Chinese National Standard GB/T1346. The water cement ratio was 0.34. The clinker was replaced by LiAl-LDHs at level of 0%, 0.5%, 0.75%, 1.0%, 1.25%, 1.5%, 2.0%, 2.25% and 3.0%, respectively.

2.4.2. Compressive strength

The compressive strength of CSAC clinker with and without LiAl-LDHs was tested in line with Chinese National Standards GB/T 7897-2008. CSAC clinker was mixed at water to cement ratio (w/c) of 0.6 and then the paste was put into the 2 × 2 × 2 cm^3 molds for vibrating. Subsequently, those specimens were cured in moist air at (20 ± 1) °C with more than 90% relative humidity for several hours, followed by demoulding. After that, the specimens were cured in water till the age required. Nine cubic specimens were prepared for each mixture, each three of which were cured until 1, 3,7 and 28 days respectively.

2.4.3. Hydration heat

The CSAC clinkers at water to cement ratio (w/c) of 0.6 with and without LiAl-LDHs were prepared to observe the hydration flow evolution. A TAM air isothermal calorimeter (TAM air, TA, American) was employed to measure the hydration exothermic rate within 70 h at 20 °C. The clinker was replaced by LiAl-LDHs at 0%, 1% and 3%.

2.4.4. XRD, FT-IR, SEM and TG-DSC

The specimens were collected from the crushed part of the compressive strength test specimen. The hydration of these specimens was terminated by using absolute alcohol, followed by being dried in a vacuum desiccator and analyzed by XRD, FT-IR, SEM and TG-DSC. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-Ray diffractometer with Cu Kα radiation (λ = 0.154 nm) in the 2θ range from 5° to 45°. Scanning electron microscopy (SEM) images were taken with a JSM-6390LV scanning electron microscope (Japan) operated at 15 kV. The IR spectral analysis was recorded from KBr disks using Bruke V70 IR spectrometer in the range from 400 up to 4000 cm^{-1}. The samples were prepared by using KBr pressed disk technique which can give a further reduction in scattering. Thermogravimetric analysis was carried out under Ar atmosphere using a Setaram Evolution TG/DSC instrument at 10 °C/min up to 900 °C.