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Evaluation and optimization of Ultra-High Performance Concrete (UHPC) subjected to harsh ocean environment: Towards an application of Layered Double Hydroxides (LDHs)

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HIGHLIGHTS

- Chloride resistance of UHPC can be improved with addition of 1% C-LDHs.
- Chloride binding capacity of C-LDHs in cement paste is much higher than cement and SCMs.
- Proper amount of C-LDHs can optimize the pore structures of UHPC.
- Volume stability of UHPC cured in ocean environment is enhanced by C-LDHs.

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ABSTRACT

In this study, the feasibility of improving the durability of Ultra-High Performance Concrete (UHPC) by incorporating calcined Layered Double Hydroxides (C-LDHs) was investigated. The spread flow, air content, permeable porosity, compressive strength, and durability of the designed UHPC were evaluated. Furthermore, the influence of C-LDHs on cement hydration and microstructure of the designed UHPC were studied. Experimental results indicated the incorporation of 1% C-LDHs improved durability of UHPC in chloride and sulfate environment, with compressive strength enhanced simultaneously. The chloride binding capacity of C-LDHs is far better than that of cement, fly ash and silica fume, reaching a chloride absorbance of 3.28 mg/g. Therefore, C-LDHs is a functional anions absorbent materials in UHPC system, which is promising in the currently critical components of offshore buildings and structures.

1. Introduction

Recently, the rising threat of corrosion by seawater on the offshore structures has promoted fast development of construction materials, in order to enhance the resistance of key cement-based components of buildings and infrastructures against high concentration of saline water [1]. As one of the notable representatives, Ultra-High Performance Concrete (UHPC) which is characterized with remarkable strength and durability has now been widely investigated by researchers to solve these problems [2–5]. Differing from conventional concrete, UHPC is consist of high strength cement and variable fine supplementary cementitious materials (SCMs), such as silica fume (SF), fly ash (FA), blast-furnace slag (BFS) or even metakaolin (MK), with a small volume percentage of short steel fibers [6,7]. The outstanding mechanical properties make it an excellent construction material for bridge decks, storage halls, thin wall shell structures, and other infrastructures that need stronger protection and longer service life [8–10]. Although UHPC is of a tremendous potential to be applied in critical components of structures in harsh ocean environment, the evaluation of durability of UHPC still needs further investigations to ensure the safety of structures.

As is well known, one of the key factors that influence the durability of concrete are permeability and ions transportation. Despite the fact that UHPC is a relatively denser material compared to conventional concrete, the space among the particles of cement and SCMs is close to nano-scale [11], where the water molecules can penetrate through these nano-pores and thus bring anions like sulfate, chloride and carbonate (SO_4^{2-}, Cl^- and CO_3^{2-}) into the system and finally detriment the materials severely [8]. Therefore, significant research efforts have been focused on searching a suitable material to optimize the pore structure of concrete and thus reduce the capillary pores of the system and finally enhance the overall performance of UHPC.

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Furthermore, penetration of harmful anions, such as chloride and sulfate, endangers the life cycle of UHPC that served in harsh ocean environment [12]. Once the concentration of anions, for instance free chloride ions, in cement matrix reaches a threshold value and accommodates around steel fibers can corrosive reaction take place via electrochemical reactions [13]. Hence, decreasing the concentration of free adverse anions from UHPC pore solution is a highly efficient method to prevent degradation of UHPC-based components in harsh ocean environment.

For the sake of finding a material that suitable for the above two requirements, LDHs is found for providing its function to meet the needs of both permeability and anions absorption [14]. LDHs, also called layered double hydroxides, are extensively researched to decrease the concentrations of ions in several fields like water treatment and environmental protection [15–17]. Furthermore, few studies have researched the effect of LDHs for improvement of durability of plain cement-based concrete [18–21]. The formula of LDHs is represented by $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{-x/n}_{n}\cdot yH_2O$, in which M^{2+} and M^{3+} are divalent and trivalent metal cations, A^{n-} is the interlayer anions and x is $M^{3+}/(M^{2+}+M^{3+})$ molar ratio. LDHs obtains multi-layered microstructure and is constructed through the regular accumulation of electropositive (M^{2+}, M^{3+})$(OH)_6$ octahedral particles similar to brucite and electronegative interlamination, which consists of anions and water molecules [22].

Additionally, with the technical development of LDHs production, a newly preparation method has been developed for a quick and efficient yield of LDHs [14]. This kind of LDHs is mainly MgAl-CO_3 LDHs, which is the most ordinary type of LDHs in nature, also called hydrotalcite. The LDHs exhibits an anions preference as follows: $CO_3^{2-} > SO_4^{2-} > F^- > Cl^- > NO_3^-$ [23]. Hence, carbonate intercalated in the interlayer of MgAl-CO_3 LDHs need to be firstly released through calcination at 550 °C in order to immobilize less affinity and harmful anions in LDHs. Decomposition of original MgAl-CO_3 LDHs (O-LDHs) takes place at 500–550 °C and generates a magnesium–aluminum oxide solid solution. The anion adsorption of this solid solution is attributed to the reconstruction and rehydration from binding of anions in water to form original layered structures [20]. The schematic process of LDHs reconstruction is presented in Fig. 1. Therefore, calcined layered double hydroxide (C-LDHs) is a promising adsorbent in cement system due to the ability to remove chloride and sulfate ions through reconstruction [24–26]. Therefore, C-LDHs is a promising material in cement matrix for their anions immobilization to improve seawater resistance of UHPC.

Therefore, on the basis of these preconditions mentioned above, the goal of this research is to study the durability of pure UHPC cured in simulated sea environment and investigate the effect of C-LDHs on the overall performance of UHPC and evaluate its influence on the microstructure of UHPC. The mix design of UHPC is based on the goal of producing densely packed cementitious materials, via adopting the optimized Andersen and Andreasen packing model. Moreover, the interaction mechanism between C-LDHs and cement paste is investigated through advanced test technologies, including X-ray diffractometry, thermogravimetry and isothermal calorimetry. The results are expected to improve the durability of UHPC and build a defensive system against salts corrosion into critical components of concrete structures.

2. Experiment

2.1. Raw materials

The cementitious materials applied in this research were P·II 52.5 cement, fly ash (FA) and silica fume (SF), which were provided by Huaxin Cement Corporation (China). The chemical composition

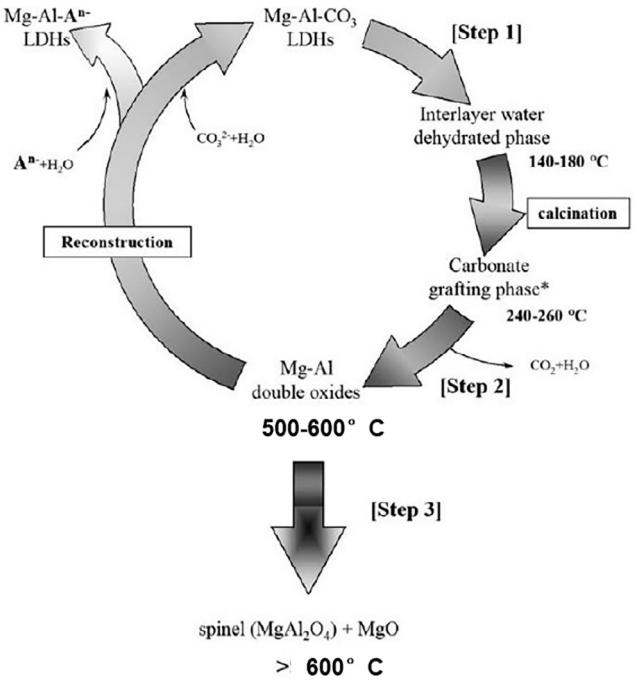

Fig. 1. Schematic process of C-LDHs adsorption through reconstruction.

of cement, FA and SF were analyzed by X-ray fluorescence (XRF), which are presented in Table 1. The XRD pattern of fly ash and silica fume are presented in Fig. 2. Two kinds of natural river sands were applied with the fraction of 0–0.6 mm and 0.6–1.25 mm, respectively. Short steel fibers with dimensions of 13 mm long and 0.2 mm diameter were used to enhance the mechanical properties of designed UHPC. A polycarboxylic ether based superplasticizer (SP) was adopted to modify the workability of designed UHPC.

LDHs was produced by Beijing University of Chemical Technology (BUCT) with a facile preparation method [14]. C-LDHs was prepared by heating O-LDHs from room temperature to 550 °C with a heating rate of 3°/min and then kept at 550 °C for another 5 h before cooled down to ambient temperature naturally. The chemical composition of O-LDHs and C-LDHs are also given in Table 1. The particle size distribution and X-ray diffraction pattern of O-LDHs and C-LDHs are presented in Fig. 3 and Fig. 4. Fig. 3 shows that the particle size of O-LDHs and C-LDHs are between 30 nm and 300 nm, with most LDHs situated at around 100 nm. In Fig. 4, the main characteristic peak of O-LDHs is clearly situated at $2\theta = 11.7°$, indicating a well-crystallized MgAl-CO_3 LDHs. However, the crystalline state of C-LDHs was changed to nearly non-crystalline phase after calcination at 550 °C. Only low intensity of magnesium oxides (MgO) can be detected in XRD. Rehydrated layered double hydroxides (R-LDHs) was generated after O-LDHs reconstructed its original double layers through rehydration, but with less degree of crystallinity than that of O-LDHs.

2.2. Methodology

2.2.1. Mix design of UHPC

Different mix design methods were adopted to better optimize recipes of concretes. According to the characteristics of multimodal and discretely sized particles, some researchers [27,28] proposed several methods to optimize mix design, including LPDM, SSM and CPM. Fennis [29] improved the methods above according to the assumption of [27,28]. Nevertheless, the approaches above were difficult to contain pretty small sized particles in these