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Relationship between the particle size and dosage of LDHs and concrete resistance against chloride ingress

Z.Y. Qu^{a,b}, Q.L. Yu^{b,*}, H.J.H. Brouwers^{a,b}^a State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, PR China^b Department of the Built Environment, Eindhoven University of Technology, P.O. Box 513, 5600, MB, Eindhoven, The Netherlands

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ABSTRACT

The present study investigates the transport properties of cement mortar with Ca-Al-NO₃ layered double hydroxides (LDHs). A co-precipitation method is applied to synthesize the Ca-Al-NO₃ LDHs and the effect of the synthesis environment on the size and particle shape is studied. The synthesized Ca-Al-NO₃ LDHs are analytically characterized by XRD, SEM and FTIR analyses. The relationships between the sizes and addition amount of Ca-Al-NO₃ LDHs and the mechanical and transport properties of mortars are investigated. Rapid chloride migration (RCM) tests are performed to the cement mortars with Ca-Al-NO₃ LDHs. The results show that permeability of the designed concrete decreased with the addition of Ca-Al-NO₃ layered double hydroxides (LDHs). The decrease of chloride migration coefficients can be attributed to the enhanced barrier effect because of the increase of tortuosity. In long-term natural diffusion tests, LDHs present significantly enhanced barrier effect due to the combined chloride binding ability and improved tortuosity.

1. Introduction

The durability of concrete in most cases is related to its permeability (or more precisely penetrability) to fluids [1–3]. The permeability is a resultant of many factors such as the permeable porosity of the hardened cement paste [4], tortuosity of the concrete matrix and aggregates [5] and the quality of aggregate/cement paste interface [6, 7]. At a high permeability, aggressive substances can easily penetrate into the concrete, facilitating its deterioration. Decreasing the porosity has been proven as an efficient way to improve the durability of concrete [8]. Nano-materials like nano-silica have been applied to increase the packing density of the concrete [9, 10], which however has certain limitation such as the limit of minimum porosity [11]. Another strategy to improve the durability performance is to reduce the permeability of the concrete by increasing its tortuosity.

Tortuosity is a parameter describing an average elongation of fluid streamlines in a porous medium as compared to a free flow. In cement-based materials, tortuosity is mainly related to its pore structure and the distribution of the impermeable aggregates. Marolf et al. concluded that the decrease of porosity would result in an increase of the tortuosity as the transport path in the pore structure is getting more tortuous [12]. Some other researchers found that concrete with a higher tortuosity presented a better durability performance compared with the reference samples with the same porosity [13–15]. According to the theoretical

work by Maxwell and Cussler [16, 17], an addition of only 1% of flake-shaped additives with a high aspect ratio by volume will obviously increase the physical barrier property of the hybrid matrix. The tortuosity of penetration path for diffusing molecules is principally influenced by the following factors: the volume fraction of the nano-flakes, their morphologies, dispersion (e.g. orientation perpendicular to the diffusion direction) and their aspect ratio [17]. DeRocher et al. found that particle size also plays an important role on determination of the barrier effect of the flakes in polymer matrix [18]. Compton et al. found that only 1% of crumpled graphene nano-sheets by volume can decrease the permeability of a polymer matrix up to 70% due to the high aspect ratio of the graphene [19]. Demonstrated improvements on the barrier properties of layered silicate hybrid polymer matrix with simultaneously improved mechanical properties were also reported by Bharadwaj [20]. However, up to date, research on using 2-D nano-particles to increase the tortuosity of cementitious composites is still limited. Recently, Du et al. reported the use of graphene nano-platelet (GNP) in cement mortar and concrete to study its barrier effect on the transport properties [15, 21]. The addition of the randomly distributed GNP can enhance the tortuosity and decrease the chloride transport by 50% in both concrete and mortar [15, 21]. However, due to the bending of the GNP, the mechanical properties of the hybrid mortar and concrete were not improved. Furthermore, the influence of the sizes of the nano-flakes on the transport property of concrete has not been

* Corresponding author.

E-mail address: q.yu@bwk.tue.nl (Q.L. Yu).<https://doi.org/10.1016/j.cemconres.2018.01.005>Received 9 May 2017; Received in revised form 6 October 2017; Accepted 8 January 2018
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investigated. Especially filler sizes (i.e. micro filler effect) strongly influence the concrete property [22, 23].

The addition of reactive species, which can destroy or bind the diffusing harmful species before they can transport through the matrix, has been proven as an effective method to minimize fluids transport within concrete [24]. For instance the incorporation of sufficient reactive siliceous granular skeleton, slag and silica fume has shown to be beneficial to limit chloride transport due to the chloride binding effect [25]. Among the reactive additives, layered double hydroxides (LDHs) have been intensively investigated for their potential to reduce the concentrations of aggressive anions in pore solution, consequently reducing the carbonation and chloride penetration rate of concrete [26]. LDHs are a class of synthetic anionic clays with a typical flake shape. As the anions in the interlayer are weakly bonded to the principal layers by hydrogen bonding, the anions can be exchanged with other kinds of anions that are more easily intercalated into the interlayer. Hence, LDHs with their anion exchange capability are considered as important adsorbents in chemical engineering [27–29]. In recent years, different kinds of LDHs have been investigated for immobilizing the CO_3^{2-} and Cl^- source, consequently reducing the carbonation and chloride penetration rate of concrete [30, 31]. Kayali et al. found that due to the function of hydrotalcite, hydrated slag cement is able to bind more chloride ions than Portland cement [32]. Chen et al. studied chloride-rich simulated concrete pore solution applying the synthesized LDHs, which showed ion exchange ability between chlorides and internal layer ions [33]. Yang et al. compared the influence of two different kinds of modified hydrotalcite on chloride transport in cement mortar and found that the internal layer ions have a big influence on their binding ability [34]. However, no research has been reported on the application of LDH nano-flakes to improve the tortuosity of cementitious composites.

Owing to the availability of facile synthetic methods as well as the structural characteristics, it is possible to prepare LDHs and LDH-based materials with various physical and chemical properties [34–36]. A simple and cost-effective route to prepare the LDH is co-precipitation method. In most of the studies, the synthesis of LDH compounds is realised at a high pH value (≥ 10) for the co-precipitation of trivalent and divalent cations [35]. Seron et al. investigated the formation mechanism of Mg-Al- NO_3 layered double hydroxides (LDHs) with varying pH [35]. The increase of the pH value (from 10 to 13.2) will accelerate the precipitate speed of the Al^{3+} and Mg^{2+} , which results in smaller particle sizes of LDH. Duan et al. prepared Mg-Al- NO_3 LDH through a facile co-precipitation method and found that both raw material ratio and pH value influence the final property of the LDH [37].

Several laboratory test methods such as gas diffusion test and pore structure analysis have been adopted to investigate the influence of tortuosity on the concrete durability [38–40]. As the chloride-induced corrosion of reinforcing steel is directly related to the shortened service of life of concrete structures, chloride diffusion coefficient is widely used to quantify the chloride ingress speed in concrete [41, 42]. In this study, the Rapid Chloride Migration (RCM) test is applied to investigate the physical barrier performance of the LDH nano-flakes hybrid mortars. As the AgNO_3 colourimetric indicator in RCM test allows reliable free-chloride penetration detection for the concrete or mortar, the output of the chloride diffusion coefficient (D_{RCM}) calculated based on the true free-chloride penetration front will not be affected by the binding ability of LDH. This is because that at the very low free-chloride concentration (i.e. the chloride penetration front) chloride binding is very limited during the migration tests, so the D_{RCM} remains unaffected by binding [41]. It has been reported that the binding equilibrium is achieved even up to two months of exposure [41, 42]. For the free diffusion tests, the assumption of equilibrium is acceptable since the chloride exposure period is sufficiently long (at least 8 weeks [43]). Therefore, RCM test is applied to investigate the physical barrier effect of the LDH and long-term chloride diffusion test was carried out according to the relevant test standards [44, 45] to investigate the

enhanced barrier effect with chloride binding ability in this study.

The present research aims at investigating the influence of nano-flakes sizes on the barrier effect of concrete. Both the physical barrier effect (enhanced tortuosity) and chemical barrier effect (chloride binding ability) of LDH nano-flakes against chloride transport are investigated. Through the control of the pH value of the precursor solution, Ca-Al- NO_3 LDH with different sizes are synthesized by using a co-precipitation method which has been reported to possess a higher ion exchange efficiency compared with Mg-Al type LDHs. The synthesized LDHs are characterized by X-ray diffractometry (XRD), particle size distribution (PSD), Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscope (SEM). The mechanical properties of the designed mortars incorporating the LDHs are measured and the effects of LDHs are evaluated. RCM and chloride diffusion tests were carried out to investigate the physical barrier effect and the enhanced barrier effect due to chloride binding capacity. This work can shed light on the application of LDH nano-flakes as a highly effective barrier to enhance the durability properties of cementitious materials.

2. Experiment

2.1. Preparation and characterization of the Ca-Al- NO_3 -LDHs

Ca-Al- NO_3 LDHs is synthesized by using a co-precipitation method because of its facile and low cost features. In order to promote the real scale engineering application, LDHs are prepared under ambient conditions [33, 46–48]. However, in the present study, the pH value of the solution is changed to prepare LDH nano-platelets with different sizes. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) are dissolved in 200 ml deionized water with a stoichiometric ratio of 2:1 (4/3 M and 2/3 M) to give a 2 M solution. This solution is added into 200 ml sodium nitrate (NaNO_3) with a concentration of 2 M. The mixed solution is stirred vigorously with a magnetic stirrer for 2 h at room temperature ($20 \pm 1^\circ\text{C}$). The pH of the solution is adjusted to 11, 12 and 13 (monitored by a pH-meter) by adding sodium hydroxide (NaOH) solution (1 M). The precipitate is then filtered in a vacuum enhanced process and the obtained filter cake is washed with deionized water until the filtrate is free of soluble nitrates. The solid is then dried at 100°C in an oven for 12 h.

Laser light scattering (LLS) technique was employed to determine the PSDs of LDH nano-flakes, and a Malvern Mastersizer 2000 particle size distribution analyzer was used for the measurement. The specific density was obtained by using a gas pycnometer (AccuPyc II 1340). The AccuPyc works by measuring the amount of displaced gas (helium).

The X-ray diffractometric (XRD) analysis was performed by using a Cu tube (40 kV, 30 mA) with a scanning range from 5° to $65^\circ 2\theta$, applying a step 0.02 and 5 s/step measuring time. The qualitative analysis was carried out by using the Diffracplus Software (Bruker AXS) and the PDF database of ICDD. The FT-IR spectra of the reaction products were collected using a PerkinElmer FrontierTM MIR/FIR Spectrometer using the attenuated total reflection (ATR) method (GladiATR). All spectra were scanned 48 times from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} .

The morphological features of the Ca-Al- NO_3 LDHs and the morphology of the Ca-Al- NO_3 LDHs contained mortars were observed with a FE-SEM (JOEL JSM-5600). The obtained SEM image was also used to calculate the sizes and thickness of the LDHs based on the line intercept technique [33].

2.2. Preparation of the mortars

The cement used in this study is Portland Cement CEM I 52.5 R, provided by ENCI (the Netherlands). Normal sand with the fraction 0–2 mm is used as aggregates (Graniet-Import Benelux, the Netherlands). A polycarboxylic ether based superplasticizer (SP) is used to adjust the workability of mortar. The mix proportion of water:

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