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

Citation for published version (APA):

Qu, Z., Yu, Q., & Brouwers, H. J. H. (2018). Relationship between the particle size and dosage of LDHs and concrete resistance against chloride ingress. *Cement and Concrete Research*, 105, 81-90.
<https://doi.org/10.1016/j.cemconres.2018.01.005>

Document license:
TAVERNE

DOI:
[10.1016/j.cemconres.2018.01.005](https://doi.org/10.1016/j.cemconres.2018.01.005)

Document status and date:
Published: 01/03/2018

Document Version:
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

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

ARTICLE INFO

Keywords:

Ca-Al-NO₃ layered double hydroxides
Tortuosity
Rapid chloride migration
Long-term chloride diffusion test
Transport property
Mechanical property

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).

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:

Table 1
Material types and densities.

Materials	Specific Density (kg/m ³)
CEM I 52.5 R	3150
Coarse Sand (0–2)	2640
Superplasticizer	1050

Fig. 1. Comparison of LDH-13 dispersion after 1 h: (a) mixing 10 mins by hand in water and (b) mixing 10 mins by hand in SP + water (70%).

cement: sand in the mortar mixture was selected as 0.45:1:2.75 by mass. LDHs synthesized under different pH values were added at the content of 0%, 0.5%, 1%, 1.5% and 2% by volume of mortar, respectively. All the mortars are prepared with a similar flowability as the reference sample with a flow table test result of diameter of 195 ± 5 mm that has been proven to provide a workable mixture in application. The densities of the raw materials are shown in Table 1. In order to disperse the Ca-Al-LDHs well, the synthetic LDHs were mixed in the SP-water solution (70% water) first for 10 min by hand and then added in the mixing process to prepare the mortars. The dispersing efficiency of the Ca-Al-LDHs in water and water mixed with SP after mixing 10 mins can be observed via visual inspection (Fig. 1.) which is also used in [15, 21]. It is shown that in water, sedimentation of LDH at the bottom of the bottle was noticed after 1 h while with the aid of SP, the LDHs are dispersed much better and no sedimentation occurs.

Fresh mortars were cast in cubes (150 mm in length) and prisms ($40 \times 40 \times 160$ mm³). One day after casting, the specimens were demolded and cured in water. The cylindrical samples for the RCM test and long-term diffusion test were extracted from the cubes by drilling and cutting at the age of 27 days. At the age of 28 days the RCM test [44] and long-term diffusion test [45] began. Mortar prisms were used for the determination of flexural and compressive strengths according to EN 196-1 [49], after 28 days of curing.

2.3. Water-permeable porosity

The water-permeable porosity of the designed mortar is measured applying the vacuum-saturation technique, which is referred to as the most efficient saturation method [41]. The saturation is carried out to at least 3 samples ($100 \times 100 \times 20$ mm³) for each mix, following the description given in NT Build 492 [44]. The water permeable porosity is calculated from Eq. (1):

$$\varphi = \frac{m_s - m_d}{m_s - m_w} \times 100 \quad (1)$$

where φ is the water permeable porosity (%), m_s is the mass of the saturated sample in surface-dry condition measured in air (g), m_w is the hydrostatic mass of water-saturated sample (g) and m_d is the mass of oven-dried sample (g).

2.4. RCM test

For each developed mixture, three cylinder cores (diameter of 100 mm, height of 150 mm) were extracted from the cast cubes. One specimen for the RCM test was retrieved from each core, giving in total 3 test specimens (cylinders with a diameter of 100 mm and height of 50 mm) for each mix. Then these specimens were tested at the age of 28 days. One day prior to the RCM test, the specimens were pre-conditioned (vacuum-saturation with limewater), following the same procedure as described for the measurements of water-permeable porosity in [44].

2.5. Chloride diffusion test

The chloride diffusion coefficient was determined by using the long-term bulk immersion tests (NT Build 443 [45]). The test was carried out on triplicate cylindrical specimens with the same size as the RCM test. At the age of 28 days, all faces of the cylinders except the one exposed to chloride solution were coated with an epoxy resin and then immersed in limewater until the mass of the samples stabilized. Subsequently, the saline solution was prepared, 165 g of NaCl per dm³, and the samples were exposed to this environment. The containers with the samples were shaken once every week. After each five weeks, the exposure liquid was replaced with a fresh solution. After the immersion period of 68 days, the specimens were removed from the solution. One specimen was split for the determination of the chloride penetration depth by spraying AgNO₃ solution. The chloride concentration profiles were measured to the two remaining specimens immediately after the exposure period, by grinding off material layers and determining their total chloride content. The powder collected from each layer was dried at 105 °C until a constant mass was reached. Subsequently, the total chloride concentration was determined by the potentiometric titration method. The diffusion coefficient was obtained by fitting the measured profile to the solution of the 2nd Fick's law, as described in NT Build 443 [45].

3. Results and discussion

3.1. Characterization of the synthesized Ca-Al-NO₃ LDHs

The XRD analysis clearly shows that the expected Ca₄Al₂(OH)₁₂(NO₃)₂·4H₂O LDHs can be obtained under a pH value from 11 to 13 (Fig. 2). The XRD patterns of the 3 samples exhibit the characteristic [0 0 2], [0 0 4], and [0 0 6] reflections of Ca-Al-LDHs with interlayer anions (Joint Committee on Powder Diffraction Standards (JCPDS) file No. 89-6723). The nitrate ion is known to bond with one of its C₂ axes parallel to the c-crystallographic axis of the LDH [50]. The first peak ($2\theta = 10.26^\circ$) in the pattern indicates that NO₃[−] is intercalated into the interlayer. In addition, the sharp and symmetric features of the diffraction peaks strongly suggest that the produced Ca-Al-NO₃ LDH was highly crystallized, having a three-dimensional order [33]. All the samples have the rhombohedral space group with lattice parameters of $a = 5.731 \text{ \AA}$ and $c = 48.32 \text{ \AA}$ and all the lines can be indexed according to the published structures of these LDHs [33, 50]. Trace of calcite is observed at the angle of 29.6° (2θ), indicating slight carbonation of the samples. All the phases of the synthesized LDHs are consistent with the previous research [33, 51], in which co-precipitation method was also applied.

Fig. 2. XRD pattern of the Ca-Al-NO₃ LDHs. Fig. 3. The 4000–400 cm^{−1} region of FTIR spectra of the synthetic Ca-Al-NO₃ LDHs.

The FTIR spectroscopy of Ca-Al-NO₃ LDHs prepared under different pH value is shown in Fig. 3. The synthetic LDHs present similar FTIR spectroscopy pattern confirming the XRD results. The overlapping bands at 3483 cm^{−1} and 3636 cm^{−1} are attributed to the stretching vibrations of lattice water and OH[−] associated to Ca²⁺ in Ca-Al-NO₃ LDHs, respectively [33, 52]. The peak at 1621 cm^{−1} shows the H-O-H bending vibration of the adsorbed water molecule. The peaks at 788 cm^{−1} and 528 cm^{−1} reflect the stretching and deformation vibrations of M-OH. The anti-symmetric stretching vibration of NO₃[−] source is reflected by the sharp split peaks at 1384 cm^{−1} and 1344 cm^{−1} [33, 50].

The particle size distributions and SEM images of the LDH nano-flakes are presented in Figs. 4 and 5, respectively. With the increase of the pH value, the particle size of the LDHs decreases respectively, as seen in Fig. 4. As the LDHs present flaky shapes which would result more errors with the laser light scattering technique, the size changes are further evaluated by the SEM pictures, as shown in Fig. 5. It is clear that LDH-11 exhibits the largest particle with an average diameter (D) of 9.5 μm and thickness (t) of 102 nm while LDH-13 exhibits the smallest one (D = 3.2 μm and t = 35 nm), while LDH-12 possesses a

Fig. 4. Particle size distribution of LDHs with different sizes by laser light scattering.

medium size (D = 6.3 μm and t = 66 nm). Under alkaline condition, all of the prepared LDHs present flake-like structure with similar high aspect ratios (i.e. 91–95), calculated by $\lambda = D/t$. The high aspect ratio indicates that the synthesized LDHs can be used as an efficient barrier to increase the tortuosity of the mortars [17, 18]. The differences in the particle sizes are obviously related to the crystallization pathway during the LDH formation.

Generally, LDHs are formed by co-precipitation reaction of trivalent and divalent

cations at high pH values (≥ 10) from aqueous solution. The pH value of the reaction solution has an important influence on the nucleation and precipitation processes and will influence the particle size of LDH [34]. During the Ca-Al-LDH formation and development reactions, precipitation of Al³⁺ and Ca²⁺ and dissociation of Al(OH)₃ and Ca(OH)₂ occur on the surface of the solid particles. Hence, the speed of nucleation plays a key role on determining the growth of LDH crystals. It has been reported that Al³⁺ is first precipitating as a hydroxide [30, 53]. Moreover, Ca²⁺ concentration will decrease as soon as there is no more aluminium in the solution. A higher pH value accelerates the growth of the LDH crystals, resulting in less time for crystallization and smaller particle sizes. When NO₃[−] is supersaturated, it will enter into the interlayer of LDH continuously to achieve the Ca-Al-NO₃ LDH. This is also supported by references [33, 35]. Consequently, the decrease of the particle sizes results in higher specific surface areas as shown in Table 2. The LDH-13 exhibits a specific surface area of 50.5 m²/g, which is higher than that of LDH-12 (40.3 m²/g) and LDH-11 (28.4 m²/g). The BET surface area of the particles does not show a reverse proportion relationship between the size (D and t), probably due to the internal pores of the particles [54] which is also supported by the pore volume data in Table 2. Thus, through the control of the nucleation process under different pH values, it is indeed possible to produce LDH nano-flakes with different sizes.

The external specific surface area of the particles can be calculated by:

$$S_s = \frac{A_p}{m_p} \quad (2)$$

where S_s is the specific surface area of the particle considering only the external surface, A_p is the external surface area of the particle and m_p is the mass of the powder. In the present study, the particles can be assumed as cylinders (See Fig. 5), therefore, A_p can be calculated by:

$$A_p = 2 \times \frac{\pi D^2}{4} + \pi D t \quad (3)$$

where the D is the diameter and t is the thickness of the particle. It should be mentioned that the assumed shape of the particle is close to reality. Next, m_p can be calculated by:

Fig. 5. SEM micrographs of LDHs prepared under different pH values (a) pH = 11 (b) pH = 12 (c) pH = 13.

Table 2

Physical property of the synthetic Ca-Al-NO₃ LDH.

LDH	Diameter D (μm)	Thickness t (nm)	Aspect ratio, λ ^a	Specific density ρ (g/cm ³)	BET surface area A (m ² /g)	Internal surface area (m ² /g)	External surface area (m ² /g)	BJH pore volume (cm ³ /g)
LDH-11	9.5	102	93	2.24 ± 0.2	28.4	19.5	8.9	0.116
LDH-12	6.3	66	95	2.26 ± 0.2	37.4	23.7	13.7	0.09
LDH-13	3.2	35	91	2.28 ± 0.1	62.2	36.6	25.6	0.185

^a Calculated by λ = D/t.

$$m_p = \rho V_p \quad (4)$$

The S_s of the LDH-11, LDH-12 and LDH-13 can be computed from Table 2, yielding 8.9 m²/g, 13.7 m²/g and 25.6 m²/g. These values are lower than the BET surface area, which includes the total surface area. This difference can be attributed to the internal pores of the LDH powders, as shown in Table 2. As the BET surface area comprises both the external area and internal area, the internal surface area of LDH-11, LDH-12 and LDH-13 amounts 15.69 m²/g, 23.71 m²/g and 36.59 m²/g, respectively (Table 2). It is interesting to observe that the calculated internal surface area is reversely proportional to the diameter of the three LDHs. The pores contained in the three synthesized LDHs include macro-, meso- and micro-pores, which further contribute to an enhanced chloride binding capacity. The largest pore volume of LDH-13 will possess the best chloride binding capacity [55, 56], which will be further discussed in Section 3.3.

3.2. Porosity and mechanical properties of the mortar

The water-permeable porosities of the mortars with different contents of the as-prepared LDH are shown in Fig. 6. It can be seen that the introduction of LDH nano-flakes into the cement matrix has very limited effect on the porosity. All the samples present similar porosities between 13.1% and 13.8%. This is accordance with the results in [15, 21] which reported that the nano-flakes refine the microstructure but do not change the total porosity. Nevertheless, the nanoscale thickness of LDH particles acts as nucleation sites for cement hydration products such as CSH gel and the hydration products fill in the water filled voids resulting in more uniform distribution, leading to a more refined microstructure (see Fig. 9a).

The compressive and flexural strength of the mortar with different contents of the as-prepared LDH are shown in Figs. 7 and 8, respectively. With the addition of LDH nano-flakes, a parabolic growth tendency of the flexural and compressive strength of the mortars can be

Fig. 6. Porosity of mortars at 28 days.

Fig. 7. Compressive strength of mortars at 28 days.

Fig. 8. Flexural strength of mortars at 28 days.

observed. The mechanical properties of all the designed mortars improve obviously compared to the reference and LDH-13 presented the highest strength increase than LDH-11 and LDH-12, which can be attributed to the strengthening effect of the LDH nano-flakes. Smaller nano-platelets play a role as micro filler (micro-sized aggregate) which can modify the microstructure of the cement paste [40, 41]. It was reported [54] that micro-filler under the size of 10 μm shows an efficient micro-filler effect. The thickness of the LDH is in nanoscale that can act as active sites for the hydration of the cement paste. For the mortars containing LDH-13, the compressive strength of the mortar is about 66.1 MPa, which gradually increases to about 68.2 MPa with 1% LDH addition, i.e. an improvement of 17% compared with the reference sample. Afterwards, this value slightly decreases to about 59.23 MPa when 2% LDH is added. From 0.5% to 1% addition of LDHs, the mortars with a smaller LDHs size present a higher compressive strength even though they present a slightly higher porosity. This can be attributed to the micro-filler effect of the LDH nano-flakes and the smaller particles perform better than the bigger ones to improve the microstructure of the mortar. However, with the increase of the LDHs addition content, the probability of agglomeration also increases as shown in Fig. 9b. It has been reported that the cluster of the nano-fillers will weaken the enhancement effect [15].

The flexural strength of the mortar has increased for all the samples containing LDH, as shown in Fig. 8. This is attributed to the distribution of the nano-platelets that play a role of micro beam and help to form a stronger and stiffer mortar matrix. For the LDH-13, a similar increase trend can be observed like the compressive strength. At 1% addition of LDH, the mortar exhibits the highest flexural strength with about 12.3 MPa and then this value decreases to about 11.4 and 11.1 MPa at 1.5% and 2% addition respectively. Hence, an optimal amount of LDH at which the highest compressive strength or flexural strength of the designed mortars are achieved is seen here. At 1% addition content, LDH-13 shows the highest increase for the flexural strength with 55% improvement comparing to the reference sample. This is due to the enhanced micro filler effect, resulting in a better interconnection of the CSH gel for the smaller size of the LDH-13. While with the increase of the addition content from 1%–2%, the increase of the flexural strength of all the samples becomes smaller which can be explained by the agglomeration of the nano-flakes, resulting in clusters as shown in Fig. 9b, which reduced the micro filler and strength increase effect. It is also widely accepted that with the decrease of the sizes of the micro or nano particle, agglomeration is easier to happen due to the higher specific surface area [53, 54].

The influence of the 2-D nano-fillers on the mechanical property of concrete is different from the reported research in [15, 21]. This may be explained by the different physical states of the LDHs and graphene nano-platelet (GNP). Graphite like materials will bend under external force and this unique property has been used to prepare wearable

Fig. 9. SEM image of fracture surface of cement mortar with the addition of Ca–Al–NO₃ LDHs LDH-13: (a) at 1%, (b) clustering at 2%.

electronic equipment and flexible screen. Different with the flexible GNP, LDH is a kind of stiff unit element [53] and will transfer the stress efficiently and which improves the mechanical properties. In [57], stiff 2-D nano-fillers have been suggested to be used in ultra-high performance concrete (UHPC) due to the excellent mechanical property enhancement effect. It should also be noticed that the agglomeration influences more in the decrease of compressive strength than the flexural strength. This can be attributed to the micro-beam effect of the LDH-nano flakes as proven in [57], 2D stiff filler is more effective to disperse the stress from the vertical direction.

3.3. Physical barrier effect of the LDHs

The chloride migration coefficients (D_{RCM}) of concrete containing various LDH contents are displayed in Table 3. The addition of LDH could reduce the chloride migration as the 2D nano-flakes increase the tortuosity of the mortar. As stated the in [15, 21], the apparent chloride diffusion coefficient D which can be expressed as:

$$D = \frac{D_0}{\tau^2} \quad (5)$$

where D is the apparent chloride diffusion coefficient for the mortars containing LDH and D_0 is the initial chloride diffusion coefficient for the reference sample, τ is the tortuosity factor [15, 21]. The tortuosity factor for the random distribution of nano-flakes can be expressed by [15]:

$$\tau = 1 + \frac{\lambda}{2} \phi \left(\frac{2S + 1}{3} \right) \quad (6)$$

where λ and ϕ are the aspect ratio and volume fraction of LDH in the matrix, respectively. S is the orientation factor and when the LDHs are randomly oriented, S takes the value of 0.

Eq. (5) has been applied to describe the relationship between the apparent chloride diffusion coefficient D and initial chloride diffusion D_0 while taking the tortuosity into account [15]. According to the Eq. (3), nano-flakes with same the λ would result in the same tortuosity increase and contribute equally to the decrease of the chloride diffusion coefficient. This phenomena has been widely reported in the hybrid composite materials such polymers [17, 18]. However, in the present research, although the LDHs nano-flakes possess almost the same aspect ratio, the smaller flakes result in a better chloride resistance due to the enhanced micro filler effect. Taking the mix 1% addition of LDH as an example, the τ should be 1.16 and the D should be decreased by 26% while it is 12.7%, 17.0 and 25%, for the mortars containing different sizes of LDH. This indicated an improved model is needed to describe the 2D nano flake effect on the transport property of cement-based system that will be investigated in the future research.

For the samples containing 0.5% and 1% hexagonal LDH nano-

flakes, LDH-13 presents the highest chloride resistance by 13% and 25% reduction, respectively. The addition of LDH can be considered as impermeable barriers inside the cement paste, which increases the tortuosity and decreases the pore connectivity for ingressive ions to penetrate through. From 0.5% to 1% addition content, smaller size fillers bring increased barrier properties that is in consistent with the mechanical properties improvement. This is due to the enhanced micro filler effect that refines the pore structure. With the addition content of 1.5%, the decrease of the chloride migration is 24%, 23% and 22%. Due to the agglomeration, LDH-13 does not perform the best regarding the migration coefficient decrease. This trend is also found in the 2% addition situation. The decrease is 24%, 23% and 21%, for LDH-11, LDH-12 and LDH-13, respectively. Although the addition of nano-flakes can increase the transport resistance, the poor dispersion at high dosage will decrease the barrier efficiency due to the clustering of the LDH which can be seen in Fig. 9b. It is concluded the addition of LDH-13 with 1% concrete presents the highest physical barrier effect.

3.4. Combined physical and chemical barrier effect of the LDHs

The transport of chloride into concrete in non-steady state conditions can be described by the following equation, taking into both chloride binding and diffusion account:

$$\frac{\partial c_t}{\partial t} = \frac{\partial c}{\partial t} + \frac{\partial c_b}{\partial t} = \frac{\partial c}{\partial t} \left(1 + \frac{\partial c_b}{\partial c} \right) = D_0 \frac{\partial^2 c}{\partial x^2} \quad (7)$$

or in the form of Fick's second law

$$\frac{\partial c}{\partial t} = \frac{D_0}{\left(1 + \frac{\partial c_b}{\partial c} \right)} \frac{\partial^2 c}{\partial x^2} = D_{app} \frac{\partial^2 c}{\partial x^2} \quad (8)$$

Solving Eq. (8) with the following initial and boundary conditions:

$$\begin{aligned} c(x > 0, t = 0) &= c_i \\ c(x = 0, t > 0) &= c_s \\ c(x = \infty, t > 0) &= c_i \end{aligned} \quad (9)$$

yields:

$$c(x, t) = c_s - (c_s - c_i) \cdot \operatorname{erf} \left(\frac{x}{\sqrt{4D_{app}t}} \right) \quad (10)$$

where c is the free chloride concentration, c_s is total chloride concentration in the surface layer, c_i is initial chloride concentration, and D_{app} is diffusion coefficient.

It should be noted that the chloride binding $\partial c_b / \partial c$ changes with the free chloride concentration (c), indicating the diffusion coefficient (D_{app}) should not be constant. A constant D_{app} is based on an over-simplification that also explains the large differences between the

Table 3

Results of chloride migration coefficient (D_{RCM}), surface chloride concentration (C_s) and diffusion coefficients (D_{app}).

Mix	$D_{RCM} (\times 10^{-12} \text{ m}^2/\text{s})$	$C_s (\text{g}_{\text{Cl}}/100\text{gmortar})$	$D_{app} (\times 10^{-12} \text{ m}^2/\text{s})$
Ref	13.53	4.38	11.72
LDH-11-0.5%	12.82	5.55	10.56
LDH-11-1.0%	11.81	5.27	9.69
LDH-11-1.5%	10.35	5.37	8.77
LDH-11-2.0%	10.28	5.58	10.60
LDH-12-0.5%	12.52	5.53	9.46
LDH-12-1.0%	11.23	5.52	8.25
LDH-12-1.5%	10.62	5.46	9.84
LDH-12-2.0%	10.15	5.59	10.02
LDH-13-0.5%	11.84	5.89	6.61
LDH-13-1.0%	10.15	5.85	5.53
LDH-13-1.5%	10.49	5.72	9.20
LDH-13-2.0%	10.76	5.65	10.31

Fig. 10. Measured chloride diffusion profiles and the fitting curves cement mortar with (a) LDH-11, (b) LDH-12 and (c) LDH-13.

diffusion coefficients reported in the literature [3, 8, 42]. The chloride content profiles of the concrete with LDH and the fitted curves and the parameters (D_{app}) for each mix are displayed in Fig. 10 and Table 3, respectively. Compared with the physical barrier effect, it is remarkable that the decrease of D_{app} is very significant. The reduction is 10%, 20% and 40% at 0.5% addition of LDH and 17%, 30% and 53% at 1% addition to LDH-11, LDH-12 and LDH-13, respectively. This can be explained by the combined effect of the physical barrier and chemical binding ability of the LDH. The chloride binding of LDH nano-flakes is investigated by XRD and the XRD patterns of LDH-13 after equilibrium with NaCl solution (0.02 M) are shown in Fig. 11. The crystal changes are in line with previous research [33]. When LDH mixed with 10% NaCl solution, chloride perfectly intercalates into the interlayer of Ca–Al–NO₃ LDHs that gives the Ca–Al–Cl LDHs. The d-spacing of the [0 0 2] crystal plane is reduced from 8.445 Å to 7.813 Å as a consequence

Fig. 11. XRD patterns of (top) synthetic LDH-13 and (bottom) LDH-13 immersed in 10% NaCl solution for 24 h.

of the substitution of NO₃[−] for Cl[−], which is in accordance with the smaller thermochemical radius of Cl[−] (0.168 nm) than NO₃[−] (0.200 nm) [33]. Smaller anion groups preferentially exchange with those of larger sizes, if they have the same charge density [53]. This indicates that, when chloride penetrates into the concrete, LDHs can immobilize the chloride ions to slow down the chloride penetration process [27, 51]. At a lower addition content, LDH-13 presents a reduced permeability that is likely due to the pore refinement and barrier effect. At higher addition contents, the dispersion of LDH-13 will be more difficult, resulting in clusters that form porous zones that reduces the barrier effect, which is in line with the mechanical properties and the chloride migration coefficients.

4. Conclusions

This research presents an investigation on the mechanical and transport properties of mortars incorporating LDH nano-flakes, prepared with a simple co-precipitation method. The influence of the synthesis environment on the properties of LDH and the effect of the size and dosage of nano-flake on the properties of the mortars were investigated. The synthesized LDHs were characterized by XRD, PSD, FT-IR and SEM. Based on the presented results, the following conclusions can be drawn:

1. Through the control of pH values employing a co-precipitation route, LDH nano-flakes with different sizes are prepared. With the increase of the pH value of the co-precipitation solution, the size of the synthesized LDHs decreases while the specific surface area increases. LDH-11 presents an average diameter (D) of 9.5 μm and thickness (t) of 102 nm while LDH-13 exhibits the smallest one ($D = 3.2$ μm and $t = 35$ nm) and LDH-12 possesses a medium size ($D = 6.3$ μm and $t = 66$ nm). All the LDHs exhibit similar high aspect ratio, between 91 and 95. The XRD and FTIR analyses confirm that the as-prepared LDHs possess the same crystalline phases and function groups.
2. The addition of LDH nano-flakes improves both the compressive and the flexural strength. The LDH prepared under pH = 13 with the smallest particle size presents the most efficient strength enhancement. This can be attributed to the increase of the stiffness of the samples through the addition of nano-flakes. Applying 1% (vol.) of LDH-13, the compressive and flexural strength of the designed mortars are increased by 17% and 55%, respectively.

3. The addition of LDH nano-flakes improves the physical barrier effect of the mortars owing to the increase of the tortuosity. 1% of LDH-13 is found to be the optimum content to improve the chloride transport resistance and the chloride migration coefficient (D_{RCM}) is reduced by 25%.
4. The mortars with the addition of LDHs perform excellent long-term transport property due to the chloride binding ability and physical barrier of the LDH nano-flakes. The chloride diffusion coefficient is reduced 53% at 1% LDH-13 addition.

Acknowledgements

The authors would like to acknowledge the financial support by STW-foundation (10979) and China Scholarship Council (201606950006). Dr. P. Speisz in ENCI/HeidelbergCement Benelux and Mr. Y. Chen are acknowledged for many fruitful discussions during this research. Furthermore, the authors wish to express their gratitude to the following sponsors of the Building Materials research group at TU Eindhoven: Rijkswaterstaat Grote Projecten en Onderhoud; Graniet-Import Benelux; Kijlstra Betonmortel; Struyk Verwo; Attero; Enci; Rijkswaterstaat Zee en Delta-District Noord; Van Gansewinkel Minerals; BTE; V.d. Bosch Beton; Selor; GMB; Icopal; BN International; Eltomation; KNAUF Gips; Hess AAC Systems; Kronos; Joma; CRH Europe Sustainable Concrete Centre; Cement & Beton Centrum; Heros; Inashco; Keim; Sirius International; Boskalis; NNERGY; Millvision; Sappi; Studio Roex and Van Berlo (in chronological order of joining).

References

- [1] P. Monteiro, *Concrete: Microstructure, Properties, and Materials*, McGraw-Hill Publishing, 2006.
- [2] C. Andrade, Calculation of chloride diffusion coefficients in concrete from ionic migration measurements, *Cem. Concr. Res.* 23 (1993) 724–742.
- [3] Q. Yuan, C. Shi, G. De Schutter, K. Audenaert, D. Deng, Chloride binding of cement-based materials subjected to external chloride environment—a review, *Constr. Build. Mater.* 23 (2009) 1–13.
- [4] Q. Yu, P. Spiesz, H. Brouwers, Ultra-lightweight concrete: conceptual design and performance evaluation, *Cem. Concr. Compos.* 61 (2015) 18–28.
- [5] R. Zhong, M. Xu, R.V. Netto, K. Wille, Influence of pore tortuosity on hydraulic conductivity of pervious concrete: characterization and modeling, *Constr. Build. Mater.* 125 (2016) 1158–1168.
- [6] Q. Yu, P. Spiesz, H. Brouwers, Development of cement-based lightweight composites—part 1: mix design methodology and hardened properties, *Cem. Concr. Compos.* 44 (2013) 17–29.
- [7] R.A. Patel, Q.T. Phung, S.C. Seetharam, J. Perko, D. Jacques, N. Maes, G. De Schutter, G. Ye, K. Van Breugel, Diffusivity of saturated ordinary Portland cement-based materials: a critical review of experimental and analytical modelling approaches, *Cem. Concr. Res.* 90 (2016) 52–72.
- [8] V. Elfmakova, P. Spiesz, H. Brouwers, Determination of the chloride diffusion coefficient in blended cement mortars, *Cem. Concr. Res.* 78 (2015) 190–199.
- [9] P. Spiesz, Q. Yu, H. Brouwers, Development of cement-based lightweight composites—part 2: durability-related properties, *Cem. Concr. Compos.* 44 (2013) 30–40.
- [10] Z. Wu, K.H. Khayat, C. Shi, Effect of nano-SiO₂ particles and curing time on development of fiber-matrix bond properties and microstructure of ultra-high strength concrete, *Cem. Concr. Res.* 95 (2017) 247–256.
- [11] C. Andrade, R. d'Andrea, N. Rebolledo, Chloride ion penetration in concrete: the reaction factor in the electrical resistivity model, *Cem. Concr. Compos.* 47 (2014) 41–46.
- [12] O.E. Gjorv, *Durability Design of Concrete Structures in Severe Environments*, CRC Press, 2014.
- [13] G. Quercia, P. Spiesz, G. Hüsken, H. Brouwers, SCC modification by use of amorphous nano-silica, *Cem. Concr. Compos.* 45 (2014) 69–81.
- [14] S. Ahmad, A.K. Azad, An exploratory study on correlating the permeability of concrete with its porosity and tortuosity, *Adv. Cem. Res.* 25 (2013) 288–294.
- [15] H. Du, H.J. Gao, S. Dai Pang, Improvement in concrete resistance against water and chloride ingress by adding graphene nanoplatelet, *Cem. Concr. Res.* 83 (2016) 114–123.
- [16] J.C. Maxwell, *A Treatise on Electricity and Magnetism*, Clarendon Press, 1881.
- [17] G. Moggridge, N.K. Lape, C. Yang, E. Cussler, Barrier films using flakes and reactive additives, *Prog. Org. Coat.* 46 (2003) 231–240.
- [18] J.P. DeRocher, B.T. Gettelfinger, J. Wang, E.E. Nuxoll, E. Cussler, Barrier membranes with different sizes of aligned flakes, *J. Membr. Sci.* 254 (2005) 21–30.
- [19] O.C. Compton, S. Kim, C. Pierre, J.M. Torkelson, S.T. Nguyen, Crumpled graphene nanosheets as highly effective barrier property enhancers, *Adv. Mater.* 22 (2010) 4759–4763.
- [20] R.K. Bharadwaj, Modeling the barrier properties of polymer-layered silicate nanocomposites, *Macromolecules* 34 (2001) 9189–9192.
- [21] H. Du, S. Dai Pang, Enhancement of barrier properties of cement mortar with graphene nanoplatelet, *Cem. Concr. Res.* 76 (2015) 10–19.
- [22] R. Yu, P. Spiesz, H. Brouwers, Effect of nano-silica on the hydration and microstructure development of ultra-high performance concrete (UHPC) with a low binder amount, *Constr. Build. Mater.* 65 (2014) 140–150.
- [23] P. Spiesz, S. Rouvas, H. Brouwers, Utilization of waste glass in translucent and photocatalytic concrete, *Constr. Build. Mater.* 128 (2016) 436–448.
- [24] L. Raki, J. Beaudoin, L. Mitchell, Layered double hydroxide-like materials: nanocomposites for use in concrete, *Cem. Concr. Res.* 34 (2004) 1717–1724.
- [25] S.W. Tang, Y. Yao, C. Andrade, Z. Li, Recent durability studies on concrete structure, *Cem. Concr. Res.* 78 (2015) 143–154.
- [26] P. Duan, W. Chen, J. Ma, Z. Shui, Influence of layered double hydroxides on microstructure and carbonation resistance of sulphoaluminate cement concrete, *Constr. Build. Mater.* 48 (2013) 601–609.
- [27] H. Pöllmann, J. Göske, Fixation of chromate in layered double hydroxides of the TCAH type and some complex application mixtures, *Minerals as Advanced Materials II*, Springer, 2011, pp. 103–114.
- [28] A. Alcantara, P. Aranda, M. Darder, E. Ruiz-Hitzky, Bionanocomposites based on alginate–zein/layered double hydroxide materials as drug delivery systems, *J. Mater. Chem.* 20 (2010) 9495–9504.
- [29] D. Yan, J. Lu, J. Ma, S. Qin, M. Wei, D.G. Evans, X. Duan, Layered host–guest materials with reversible piezochromic luminescence, *Angew. Chem. Int. Ed.* 50 (2011) 7037–7040.
- [30] J. Zhang, F. Zhang, L. Ren, D.G. Evans, X. Duan, Synthesis of layered double hydroxide anionic clays intercalated by carboxylate anions, *Mater. Chem. Phys.* 85 (2004) 207–214.
- [31] Y. Chen, Z. Shui, W. Chen, Q. Li, G. Chen, Effect of MgO content of synthetic slag on the formation of Mg–Al LDHs and sulfate resistance of slag-fly ash-clinker binder, *Constr. Build. Mater.* 125 (2016) 766–774.
- [32] O. Kayali, M. Khan, M.S. Ahmed, The role of hydrotalcite in chloride binding and corrosion protection in concretes with ground granulated blast furnace slag, *Cem. Concr. Compos.* 34 (2012) 936–945.
- [33] Y. Chen, Z. Shui, W. Chen, G. Chen, Chloride binding of synthetic Ca–Al–NO₃ LDHs in hardened cement paste, *Constr. Build. Mater.* 93 (2015) 1051–1058.
- [34] Z. Yang, H. Fischer, R. Polder, Synthesis and characterization of modified hydrotalcites and their ion exchange characteristics in chloride-rich simulated concrete pore solution, *Cem. Concr. Compos.* 47 (2014) 87–93.
- [35] A. Seron, F. Delorme, Synthesis of layered double hydroxides (LDHs) with varying pH: a valuable contribution to the study of Mg/Al LDH formation mechanism, *J. Phys. Chem. Solids* 69 (2008) 1088–1090.
- [36] Q. Wu, A.O. Sjöstad, Ø.B. Vistad, K.D. Knudsen, J. Roots, J.S. Pedersen, P. Norby, Characterization of exfoliated layered double hydroxide (LDH, Mg/Al = 3) nanosheets at high concentrations in formamide, *J. Mater. Chem.* 17 (2007) 965–971.
- [37] J. He, M. Wei, B. Li, Y. Kang, D. Evans, X. Duan, Preparation of Layered Double Hydroxides, *Layered Double Hydroxides*, (2006), pp. 89–119.
- [38] S. Ahmad, A. Azad, K. Loughlin, A Study of Permeability and Tortuosity of Concrete, in: 30th Conference on our World in Concrete and Structures, 2005, pp. 23–24.
- [39] A. Sharif, K. Loughlin, A.A.B. Nawaz, Determination of the effective chloride diffusion coefficient in concrete via a gas diffusion technique, *Concrete Durability and Repair Technology, Proceedings of the International Conference Held at the University of Dundee, Scotland, UK on 8–10 September 1999*, Thomas Telford, 1999, p. 185.
- [40] L.-Y. Li, J. Xia, S.-S. Lin, A multi-phase model for predicting the effective diffusion coefficient of chlorides in concrete, *Constr. Build. Mater.* 26 (2012) 295–301.
- [41] P. Spiesz, H. Brouwers, The apparent and effective chloride migration coefficients obtained in migration tests, *Cem. Concr. Res.* 48 (2013) 116–127.
- [42] L. Tang, Chloride Transport in Concrete—Measurement and Prediction, (1996).
- [43] H. Zibara, Binding of External Chlorides by Cement Pastes, National Library of Canada = Bibliothèque Nationale Du Canada, 2001.
- [44] N. Build, 492. Chloride Migration Coefficient From Non-steady-state Migration Experiments. Concrete, Mortar and Cement-based Repair Materials, Nordic Council of Ministers, 1999.
- [45] N. Build, 443. Concrete, Hardened: Accelerated Chloride Penetration, Nordtest Method, (1995).
- [46] H.-W. Olfs, L. Torres-Dorante, R. Eckelt, H. Kosslick, Comparison of different synthesis routes for Mg–Al layered double hydroxides (LDH): characterization of the structural phases and anion exchange properties, *Appl. Clay Sci.* 43 (2009) 459–464.
- [47] L.O. Torres-Dorante, J. Lammel, H. Kuhlmann, T. Witzke, H.W. Olfs, Capacity, selectivity, and reversibility for nitrate exchange of a layered double-hydroxide (LDH) mineral in simulated soil solutions and in soil, *J. Plant Nutr. Soil Sci.* 171 (2008) 777–784.
- [48] L.O. Torres-Dorante, J. Lammel, H. Kuhlmann, Use of a layered double hydroxide (LDH) to buffer nitrate in soil: long-term nitrate exchange properties under cropping and fallow conditions, *Plant Soil* 315 (2009) 257–272.
- [49] T. EN, 196-1. Methods of Testing Cement—Part 1: Determination of Strength, 26 European Committee for Standardization, 2005.
- [50] S. Zhonghe, M. Juntao, C. Wei, C. Xiaoxing, Chloride binding capacity of cement paste containing layered double hydroxide (LDH), *J. Test. Eval.* 40 (2012) 1–5.
- [51] Z. Yang, H. Fischer, J. Cerezo, J. Mol, R. Polder, Modified hydrotalcites for improved corrosion protection of reinforcing steel in concrete—preparation, characterization, and assessment in alkaline chloride solution, *Mater. Corros.* 67 (7) (2016) 721–738.
- [52] A. Radha, P.V. Kamath, C. Shivakumara, Mechanism of the anion exchange reactions of the layered double hydroxides (LDHs) of Ca and Mg with Al, *Solid State Sci.*

- 7 (2005) 1180–1187.
- [53] J. Plank, Z. Dai, P. Andres, Preparation and characterization of new Ca–Al–polycarboxylate layered double hydroxides, *Mater. Lett.* 60 (2006) 3614–3617.
- [54] G. Quercia, G. Hüsken, H. Brouwers, Water demand of amorphous nano silica and its impact on the workability of cement paste, *Cem. Concr. Res.* 42 (2012) 344–357.
- [55] C.-C. Yang, On the relationship between pore structure and chloride diffusivity from accelerated chloride migration test in cement-based materials, *Cem. Concr. Res.* 36 (2006) 1304–1311.
- [56] P. Li, D. Su, S. Wang, Z. Fan, Influence of binder composition and concrete pore structure on chloride diffusion coefficient in concrete, *J. Wuhan Univ. Technol. - Mater. Sci. Ed.* 26 (2011) 160–164.
- [57] D. Carnelli, R. Libanori, B. Feichtenschlager, L. Nicoleau, G. Albrecht, A.R. Studart, Cement-based composites reinforced with localized and magnetically oriented Al_2O_3 microplatelets, *Cem. Concr. Res.* 78 (2015) 245–251.