



Synthesis and characterization of modified hydrotalcites and their ion exchange characteristics in chloride-rich simulated concrete pore solution



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ABSTRACT

Two modified hydrotalcites (MHTs) intercalated with nitrate and aminobenzoate anions, (i.e., CaAl-MHT-NO₃ and CaAl-MHT-pAB) have been synthesized. The intercalation of CaAl-MHT-pAB was achieved by anion exchange of nitrate in the host material, CaAl-MHT-NO₃, which was prepared by a coprecipitation method. Materials characterization was conducted by means of X-ray diffraction (XRD), thermal analysis, IR-spectroscopy and environmental scanning electron microscope (ESEM). Element analysis further confirmed both nitrate and p-aminobenzoate anions were successfully intercalated into the interlayer space of MHTs with an intercalating ratio of 81.2% and 33.1% respectively. Volhard's titrimetric analysis demonstrated that ion exchange occurred between free chlorides in simulated concrete pore solution and anions intercalated in MHTs. The preliminary results reported in this paper shed light on the promising use of MHTs as a new type of additive for improved corrosion protection of reinforced concrete.

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1. Introduction

The use of reinforcing steel to improve the tensile properties of concrete has been an accepted practice for many years. The combination of steel and concrete is a composite which exhibits the best performance when the two materials are bonded together. The matrix material, concrete, however is porous and highly heterogeneous. Exposed to service environment, the durability of concrete can be compromised by the ingress of water with dissolved corrosive ions, chlorides, and other deleterious species which cause corrosion of the reinforcing steel. This occurs via deterioration of the passivation layer of the steel, present only at high pH values. Comparing to those factors which could potentially impose a serious threat on the durability and serviceability of reinforced concrete structures [1,2], chlorides penetration has been recognized as one of the critical processes [3,4]. Traditional standards oversimplify the complexity of the mechanisms involved and consequently, modern service life design approaches mainly aim at providing sufficient concrete cover depth to the reinforcing steel. New genera-

tion reinforcement such as stainless steel is much more expensive than ordinary reinforcing (carbon) steel [5,6]. Cathodic prevention or protection may be also effective; however both are a special niche expertise and are thus not applied on a wide scale [7]. Coatings on the concrete surface are not able to guarantee a long enough protection (10–20 years), which causes the need of a cycle of maintenance of its own [5]. The application of corrosion inhibitors has been proposed but they are generally not reliable in terms of long-term efficiency [5,8].

In the last two decades, more effort was focused on the development of new or modified compounds able to prevent or stop corrosion and other durability related issues [8–10]. The application of modified hydrotalcites (MHTs) may represent a promising strategy for use in concrete with the purpose to improve corrosion resistance. Hydrotalcite is one of the most representatives of a large mineral group of Layered Double Hydroxides (LDHs), which are also known as hydrotalcite-like materials. A key feature of hydrotalcite-like materials is their high anionic exchange capacity which makes exchange of the interlayer ion by a wide range of organic or inorganic anions versatile and easily achieved [11]. Generally, the naturally occurring hydrotalcite which has the chemical formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ is regarded as the parent material of LDHs group. The carbonate anion is tenaciously held in the interlayer space of the hydrotalcite, so ion-exchange reaction hardly occurs

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in carbonate form hydrotalcite [12]. However, such materials are believed to have a potential to be modified or tailor-made as an active component of concrete. For the envisaged use as an additive to concrete against chloride attack, certain inorganic or organic anions with known inhibitive properties could be intercalated in the structures of MHTs, which then can be slowly released, possibly 'automatic' upon arrival of chloride ions. Such inhibition would also increase the chloride threshold level for corrosion initiation and/or reduce the subsequent corrosion rate of steel reinforcement in concrete. Fig. 1 schematically shows a typical structure of MHTs and more detailed information related to MHTs' molecular structure and chemical composition can be found elsewhere [13]. Hydrotalcite or hydrotalcite-like phases have been found in hydrated slag cements, which are known to be able to bind more chloride ions than pure Portland cements [14–16]. More recently, Kayali et al. [17] demonstrated that hydrotalcite which comprises 53.94% of the crystalline phases in hardened ground granulated blast furnace slag (GGBFS) paste is the main hydration product responsible for the remarkable improvement in chloride binding by concrete containing GGBFS. The existence of hydrotalcite-like phases such as Friedl's salt (a chloride-bearing AFm phase) or its iron analog and/or Kuzel's salt (a chloride- and sulfate-bearing AFm phase) have been believed to contribute to chloride binding and thus enhance the corrosion resistance of reinforced concrete [18]. The beneficial effects of Friedl's salt on binding chloride in cement and Kayali's work [17] support the idea of using MHTs in concrete as an effective chloride scavenger and the increased binding would definitely slow down chloride transport through concrete matrix.

This paper reports on the synthesis of a calcium aluminate-based MHT as a model material and experiments designed to investigate the feasibility of MHTs with the selected intercalating inorganic or organic molecules of relevance to be able to act as a scavenger for chloride. The primary objective of the paper is therefore to provide preliminary information to explore the promising use of the other various MHTs compositions with selected intercalating inhibitive anions suitable for additives for concrete with a perspective view to reduce chloride-induced corrosion of reinforced concrete.

2. Experimental

2.1. Materials

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and Sodium nitrate (NaNO_3) were obtained from Merck KGaA. NaOH, p-aminobenzoic acid (pABA) and p-aminobenzoate sodium salt were obtained from

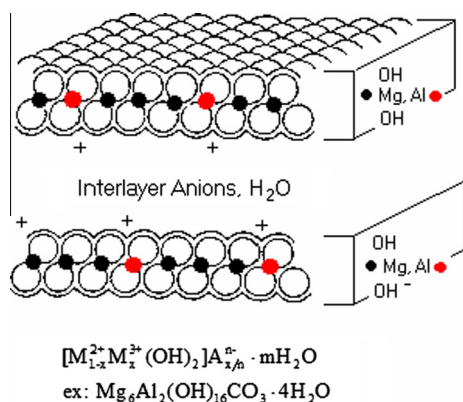


Fig. 1. Schematic diagram of a typical MHT structure.

Sigma-Aldrich. All reagents are ACS grade (>99% purity) and used as received without further purification. Boiled distilled water was used for the preparation of aqueous solution and filtration.

2.2. Synthesis

2.2.1. Preparation of CaAl-MHT- NO_3

The CaAl-MHT- NO_3 was synthesized by a pH-controlled coprecipitation synthetic method as described elsewhere [11,19]. Typically, 66.1 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 45 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed together in 320 ml of water and then the solution was added dropwise within 1.0 h to a solution of 24 g of NaOH and 34 g of NaNO_3 in 290 ml of water under vigorous stirring and N_2 atmosphere. Once addition was completed, the resulting suspension was maintained at 65 °C for 16–18 h under vigorous stirring, after which the solid precipitate was collected and washed thoroughly with boiled distilled water. The product was then dried for 16–18 h at 105 °C under vacuum.

2.2.2. Preparation of CaAl-MHT-pAB

The intercalation of p-aminobenzoate was carried out using anion exchange reactions as previously reported studies [10,19,20]. Typically, 5.0 g of the CaAl-MHT- NO_3 is dispersed in 500 ml 0.1 M aqueous solutions of 4-aminobenzoate sodium salt. The mixtures were allowed to react for 16 h under N_2 atmosphere and vigorous stirring at 65–70 °C. The organic derivatives were isolated by filtration. After being washed thoroughly with boiled distilled water, the solid product was then dried under vacuum for 4 h at 105 °C.

2.3. Characterization

X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were carried out to check the structural characteristics of MHTs. XRD was performed on a Bruker D5005 diffractometer equipped with Huber incident-beam monochromator and Braun PSD detector using $\text{Cu K}\alpha$ radiation in the 2θ region between 5° and 90°. FT-IR spectra were recorded using a Perkin-Elmer Spectrum 100 Series spectrometer equipped with universal Attenuated Total Reflexion (ATR) unit over the wavenumber range of 4000–600 cm^{-1} . The samples were scanned 32 times each time with 4 cm^{-1} resolution. To investigate the thermal stability of the MHTs and also for the compositional analysis purpose, thermal analyses on powder samples were carried out using a NETZSCH STA 449 F3 Jupiter® simultaneous thermal analyzer TG/DSC under flowing Argon (50 ml/min) at a heating rate of 10 K/min from 40 to 1100 °C.

The morphology of the synthetic products were examined by an Environmental scanning electron microscope (ESEM, Philips XL30 Series) equipped with an Energy Dispersive X-ray (EDX) element analyzing system. Shimadzu TOC-VCPH total organic carbon analyzer and a spectrophotometer (Spectroquant® Nova 60, Merck, Germany) were employed respectively to analyze the intercalation ratio of the corresponding organic anions and nitrate after dissolution of a known amount of intercalation compound in dilute HCl solution. Duplicate tests were conducted with the specimen involved.

2.4. Ion exchange of MHTs with chloride in simulated concrete pore solution

Ion exchange of MHTs with chloride was carried out in 0.1 M NaOH solution simulating the alkaline pore liquid of concrete [6,21]. Two different chloride concentrations (i.e., 0.1 M and 1.0 M NaCl solutions) were selected. The two selected chloride concentrations are to represent the practical experience: the first value

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