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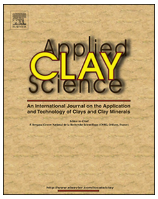

Research paper

Chloride removal and corrosion inhibitions of nitrate, nitrite-intercalated Mg—Al layered double hydroxides on steel in saturated calcium hydroxide solution

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ABSTRACT

The aim of this study is to evaluate the chloride removal and corrosion inhibitions of NO_3^-, NO_2^- intercalated Mg—Al layered double hydroxides (LDH) on steel in saturated calcium hydroxide solution by a comparative experiment. Mg-Al-LDH intercalated with NO_2^- was synthesized by anion exchange in the host material, Mg-Al-NO_3 LDH, which was prepared by a coprecipitation method. The chloride equilibrium isotherm, corrosion potential and polarization resistance of steel (decided by electrochemical impedance spectroscopy (EIS)) in the solution were measured. Besides, scanning electron microscopy (SEM), X-ray diffraction instrument (XRD) and infrared spectroscopy were applied to observe the morphologies and microstructures of LDH. The results indicate that the LDH intercalated with NO_3^-, NO_2^- have excellent chloride removal capacities. Compared to LDH-NO_3, the maximum chloride uptake amount for LDH-NO_2 is relatively lower. However, the corrosion of steel for LDH-NO_2 has a higher chloride threshold level. The dual effects, i.e., the uptake of chloride ion as an absorbent and the release of NO_2^- ions as an inhibitor, contribute to the better inhibition effect for LDH-NO_2.

1. Introduction

Chloride-induced corrosion of steel is a major cause of the durability of reinforced concrete structures exposed to chloride-laden environment, which leads to huge economical loss and maintenance cost. Chloride-induced corrosion of steel damages the reinforced concrete in two ways. First, steel corrosion can reduce the cross-sectional area of steel bars. Second, it produces corrosion products with a larger volume than that of the steel, which increases the tensile stress in the concrete. The tensile stress may result in cracking and eventual structural failure (Andrade et al., 2004; Xu et al., 2016).

For addressing this issue, the fabrication of concrete with high resistance to chloride ingress is generally accepted to be an effective basic strategy (Bharatkumar et al., 2001; Neville and Aitcin, 1998). One alternative route for such fabrication is to add some functional materials with good chloride binding capacity into concrete. The increase of chloride binding will delay the transport of chloride through concrete, and prolong the corrosion initiation of steel in concrete. In previous literatures (Duan et al., 2013; Yang et al., 2013a), Layered Double Hydroxide (LDH), also called as hydrotalcite-like material as an candidate of functional materials has been proposed. It can be represented by a general formula of $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}[A_{x/n}{}^{n-}\cdot H_2O]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, A^{n-} is the interlayer anion and x is $M^{3+}/(M^{2+}+M^{3+})$ molar ratio (Cavani et al., 1991). The layered structure of LDH is constituted by the periodical stacking of positively charged sheets (brucite-like layers) separated by interlayer spaces containing solvated anions. The anions in the interlayer are weakly bonded to the principal layers by hydrogen bonding, and hence the anions are liable to be exchanged by other kinds of anions that are more easily intercalated into the interlayer. Owing to high anion-exchange capacity, the LDH is promising for the application as an effective absorbent for chloride ions in cementitious materials. This ideal can be supported by the beneficial effects of hydrotalcite-like phases such as Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$) on binding the chloride ions in cement concrete.

Moreover, a double effect against chloride-induced corrosion of steel may be attained once the anions in the interlayer of LDH preserve inhibitive property. Apart from the uptake of chloride ion as the absorbent, the LDH intercalated with the inhibitive anions may release the inhibitive anions when it contacts with the chloride ions. The inhibitive anions can work as an efficient inhibitor to mitigate the corrosion of reinforcing steel. Based on this, it is highly desirable for the application

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of the LDH intercalated with inhibitive anions in the reinforced concrete to protect the steel from chloride-induced corrosion (Tatematsu and Sasaki, 2003; Yang et al., 2013b).

Prior to this investigation, we have reported the chloride removal of Mg-Al-LDH intercalated with NO_3^-, NO_2^- in aqueous solutions (Xu et al., 2017). The NO_2^- ions are chosen because the nitrite-based inhibitors have been proved to be highly effective. However, different behaviors of chloride removal and corrosion inhibition for the Mg-Al-LHDs can be anticipated in concrete due to its high alkalinity. To date, there is still lack of adequate knowledge on the inhibitive effects of LDH for the application in real concrete. In this article, the chloride removal and corrosion inhibitions of NO_3^-, NO_2^- intercalated Mg-Al-LDH on steel are evaluated in saturated calcium hydroxide solution by a comparative experiment. The saturated calcium hydroxide solution is applied to simulate the alkaline pore solution of concrete. Mg-Al-LDH intercalated with NO_2^- was synthesized by anion exchange in the host material, Mg-Al-NO_3 LDH, which was prepared by a coprecipitation method. The chloride equilibrium isotherm, corrosion potential and polarization resistance of steel (decided by electrochemical impedance spectroscopy (EIS)) in the solution were measured. Besides, scanning electron microscopy (SEM), X-ray diffraction instrument (XRD) and infrared spectroscopy were applied to observe the morphologies and microstructures of LDH.

2. Experiment

2.1. Preparation of Mg-Al-LDH

Mg-Al-NO_3 LDH was prepared by a co-precipitation method described elsewhere (Xu et al., 2017). Solution A containing Mg $(NO_3)_2{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ with Mg/Al molar ratio of 2.0 ($[Mg^{2+}] + [Al^{3+}] = 1.0$ mol/L) and solution B containing 1.75 mol/L NaOH and 0.75 mol/L $NaNO_3$ were simultaneously dripped into 50 ml deionized water in a 500 mL flask with vigorous stirring under N_2 atmosphere. The pH value of mixture was maintained at around 10.0. After this, the resulting suspension was aged at 65 °C for 18 h in a thermostatic bath. The final precipitate was filtered, washed thoroughly, and dried at 90 °C for 24 h.

Mg-Al-LDH intercalated with NO_2^- was synthesized by anion exchange in the host material, Mg-Al-NO_3 LDH. Firstly, 5 g Mg-Al-NO_3 LDH was dispersed into 500 mL aqueous solution containing 0.1 mol/L $NaNO_2$. Subsequently, the mixture was allowed to react for 16 h under N_2 atmosphere and vigorous stirring at 65 °C. The solid product was filtered, washed thoroughly, and dried at 90 °C for 24 h to obtain Mg-Al-LDH intercalated with NO_2^-. It should be pointed out that only 79% of NO_3^- in the Mg-Al-LDH was exchanged by NO_2^-, which was decided by the differences of major mass losses of the TG-DSC curves of prepared LDH-NO_2 and LDH-NO_3 in previous paper (Xu et al., 2017). Moreover, all the chemical reagents were analytically pure. Boiled deionized water was adopted to prepare various aqueous solutions.

2.2. Chloride equilibrium isotherm

Saturated $Ca(OH)_2$ solution was prepared by adding excessive amount of $Ca(OH)_2$ into water. Then, different levels of sodium chloride (2、5、10、20、40 and 80 mmol/L) were added in the prepared solutions. Subsequently, 1 g LDH intercalated with NO_3^- and NO_2^- were added into the solutions with constant 1:10 solid/solution ratio, respectively. The mixtures were vigorously stirred under N_2 atmosphere and maintained at the temperature of 25 °C for 48 h so that the chloride uptake equilibrium was attained. The filtrates were analyzed by means of potentiometric titration using 0.01 mol/L $AgNO_3$ to determine the chloride concentrations. The chloride loadings on the LDH were calculated from the following equation:

$$W = (C_0 - C)V/m \tag{1}$$

where W is the chloride uptake loading at the equilibrium (mmol/g), V the volume of solution (L), C_0 and C the initial chloride and equilibrium chloride concentration (mmol/L), respectively, and m is the mass of LDH (g).

2.3. Corrosion measurement

The steel specimen with a size of 5 mm × ∅ 10 mm was cut from a steel bar with a cylindrical surface. The chemical composition (in wt%) was 0.22% C, 0.30% Si, 0.65% Mn, 0.05% S, 0.045% P and the residual Fe. One end surface of each specimen was chosen to carry out the corrosion measurement and the remaining area was sealed by means of epoxy resin. Prior to application, the exposed surface was polished using a series of silicon carbide emery papers of grades 400, 800 and 1000, degreased in acetone and then washed in distilled water. For simulating the field condition, the steel specimens were firstly immersed into the saturated calcium hydroxide solution for 7 days to implement pre-passivation. Moreover, the as-prepared Mg—Al— NO_3 LDH and Mg—Al— NO_2 LDH were added into the saturated calcium hydroxide solutions with the contents of 1.0 wt% and 2.0 wt%, respectively. Subsequently, the steel specimens after the pre-passivation were transferred into the solutions to carry out the corrosion measurement. The aggressive chloride ions were added gradually in several steps. The intervals of the addition were 1d and each dosage was 0.01 mol/L.

Before each addition of chloride ions, open-circuit potential (E_{corr}) of the steel specimen was measured. Subsequent to the E_{corr} measurement, EIS scan was carried out by applying a sinusoidal potential perturbation of 10 mV in the frequency range from 10 mHz to 100 kHz. The obtained EIS spectra were analyzed with an equivalent-circuit to obtain the values of polarization resistance (R_p) by ZsimpWin software.

For the corrosion measurement, the Partstat 2273 Advanced Potentiostat/Galvanostat/FRA system was applied. The saturated calomel electrode and platinum electrode were connected to work as a reference and auxiliary electrode, respectively. For obtaining reproducible results, the corrosion measurements were repeated three to five times. All the potentials reported in this study are in the saturated calomel electrode scale. All measurements were carried out at ambient temperature. Considering the importance of pH value on the corrosion of steel, the pH values of solutions with the additions of nitrate, nitrite-intercalated Mg—Al LDH were measured by a pH meter.

2.4. Microstructure observation

The morphologies of LDH samples were observed by Hitachi-3400 N scanning electron microscopy (SEM) at an accelerating voltage of 15 kV. D8 ADVANCEX X-ray powder diffractometer was applied to characterize the phase compositions of LDH samples using a with Cu Kα radiation (40 kV and 30 mA) at a scanning rate of 10°/min. Fourier transform infrared (FT-IR) spectra in the range 4000–390 cm^{-1} of LDH samples as KBr pellets were recorded with a Nicolet IS10 spectrometer.

3. Results and discussion

3.1. Chloride uptake isotherms of NO_3^-, NO_2^- intercalated LDH

The equilibrium isotherms of chloride uptake on the LDH intercalated with NO_3^- and NO_2^- in the saturated calcium hydroxide solution are shown in Fig. 1. The chloride uptake loading and chloride concentration at the equilibrium state exhibit a distinct non-linear relationship. With the increase of chloride concentration, the chloride uptake loading is raised. For fitting the experimental data, two non-linear equations are used, as shown below:

Langmuir isotherm:

$$W = QbC/(1 + bC) \tag{2}$$