Use of Modified Hydrotalcites (MHTs) as a New Type of Smart Additive of Reinforced Concrete for Improved Corrosion Protection
- An Electrochemistry Performance Assessment in Simulated Concrete Pore Solution

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Abstract
Chloride-induced corrosion of the reinforcing steel in concrete is a major threat to the durability and serviceability of concrete structures. Modified hydrotalcites (MHTs) are promising materials to increase threshold values (or critical chloride content) of chloride content at which initiation of pitting corrosion takes place and/or to slow down or even stop corrosion propagation when corrosion has initiated in concrete. The main objective of my thesis is to evaluate the inhibition effect of MHTs (MHT-p, MHT-N) in simulated concrete pore solution compared to that of pure inhibitors (pAB, NaNO₂) with electrochemical methods.

Potentiodynamic polarization (PDP) was used to obtain information about corrosion mechanisms, corrosion current density and susceptibility of specific materials with anodic scans. Electrochemical impedance spectroscopy (EIS) was used to qualify the details of localized corrosion such as corrosion rates and initiation of pitting corrosion by simulating proper elements in equivalent circuit. Optical microscopy was used to confirm the results from the electrochemical tests by observing the corrosion spots on the steel surface at proper time.

From the interpretation of my test results, MHTs indeed improved inhibition effect of steel electrodes in simulated concrete pore solutions compared to that of pure inhibitors, especially for MHT-p. Due to the high anion exchange capacity in MHT-p, its critical chloride content shifted to a higher level when compared to the pure inhibitor (pAB). The improvement of MHTs is probably from their dual role against chloride induced corrosion: releasing inhibitive anions and capturing chloride anions at the same time to prevent the steel from corrosion initiation.

Keywords: Modified hydrotalcites, MHTs, corrosion, Smart additives, simulated concrete pore solution.
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Scientific paper
The key findings of my thesis have been summarized in the form of a scientific paper. This paper is presented on the next 16 pages.
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Abstract

Modified hydrotalcites (MHTs) are promising materials to increase threshold chloride concentration of corrosion initiation and/or slow down or even stop corrosion propagation when corrosion has initiated in simulated concrete pore solution. The anticorrosion behavior of MHTs was evaluated based on open circuit potential (OCP), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) accompanying with optical microscopic images. The results reported in this paper demonstrate that MHTs indeed improved inhibition effect in simulated concrete pore solution compared to pure inhibitors evidenced by shifting chloride content of corrosion initiation to higher level.

1. Introduction

It is well known that chloride-induced corrosion of the reinforcing steel is a major threat to the durability and serviceability of concrete structures. Corrosion-related issues accounts for great amount of unplanned repairs, significant economic loss, out of service time and waste of materials and energy [1-3].

Studies have showed that once the chloride-induced corrosion initiates, three main consequences occur [4]: (1) local pitting corrosion of the reinforcement; (2) cracking and spalling of the concrete cover due to the build-up of voluminous corrosion products; (3) decrease of ductility and reduction of cross section of the reinforcing steel. Therefore, designing concrete which can sustain environmental aggressiveness especially chloride intrusion is extremely important. Traditionally, nitrite containing compounds is widely used in concrete as an efficient commercial anti-corrosion inhibitor [5]. However, the use of this inhibitor was prohibited in some countries because of its toxicity; organic inhibitors have been proposed as one of the alternatives. However, the anti-corrosion effectiveness of most pure organic inhibitors is debatable especially when comparing to the nitrites based inhibitors. Thus, it is essentially important to find more effective measures to improve the corrosion resistance of reinforced concrete.

In the last two decades, a lot of work has been focused on developing new or modified materials which are able to prevent corrosion initiation and/or slow down or even stop corrosion propagation when corrosion has initiated. Accordingly, research has also been carried out to understand the fundamental working mechanism of these new materials [6-8]. A promising strategy to accomplish these tasks for use in concrete is modified hydrotalcites (MHTs) which are also known as layered double hydroxides or hydrotalcites like compounds. Deriving from their parent compound, i.e., the naturally occurring hydrotalcites, [Mg₆Al₂(OH)₁₆]CO₃·4H₂O, MHTs are a group of anion-exchangeable compounds consisting of stacks of positively charged mixed-metal hydroxide layers between which negatively charged anionic species and water molecules are intercalated [9]. The MHTs’ structure can be represented by a general formula:

$$\left[M_{1-x}^{+}M_{x}^{+} (OH)_{2}\right]^{x+} \left[A_{x/n}^{n-}\right]^{y-} \cdot mH_2O,$$
in which \( M^{II} \) and \( M^{III} \) are di- and trivalent metals respectively, \( (M^{II}: Mg^{2+}, Ca^{2+}, Zn^{2+}, Ni^{2+}, etc.; M^{III}: Al^{3+}, Fe^{3+}, Ga^{3+}, Co^{3+}, etc.) \) and \( A^{n-} \) are exchangeable interlayer anion species that could be inorganic or organic. The \( x \) value is in the range of 0.22–0.33. The most important key feature of MHTs is their high anionic exchange capacity (2–5 milliequivalents/g) which makes exchange of the interlayer ion by a wide range of both organic and inorganic anions possible and easily achieved.

A typical crystal structure of MHT is presented schematically in Fig.1.

![Fig.1 A typical representation of the crystal structure of hydrotalcite-like compounds [10].](image)

The hydrotalcite-like compounds in corrosion science have been applied in different aspects. In some research, hydrotalcites are produced on the top of metal surface as protective layer [11-18] which consequently provide corrosion protection. A different point of view of using hydrotalcite like compounds is working as a smart container for corrosion inhibitors for corrosion protection purpose [10, 17]. Hydrotalcite or hydrotalcite-like compounds have been found in hydrated slag cements, which are known to be able to bind more chloride ions than pure Portland cements. In this paper, we will focus on the later perspective used in simulated concrete pore solution. The existence of hydrotalcite like phases such as Friedl's salt (a chloride-bearing AFm phase) or its iron analogue and/or Kuzel's salt (a chloride- and sulfate-bearing AFm phase) have been reported to contribute greatly to chloride binding and thus to enhance the corrosion resistance of reinforced concrete [18]. The beneficial effects of Friedl's salt on binding chloride in cement support the idea of using MHTs in concrete as an effective chloride scavenger and the increased chloride-binding would definitely slow down chloride transport through concrete matrix. For the envisioned function as an additive to concrete against chloride-induced corrosion, certain inorganic or organic inhibitive anions with known effective inhibition properties could be intercalated into the structures of MHTs, which then can be slowly released, possibly 'automatic' upon arrival of chlorides ions. As expected, such behavior will increase chloride threshold concentration at which corrosion could initiate and subsequently depress corrosion degradation rate once the corrosion initiated on the steel surface in concrete. Different from other single-function protective inhibitors in concrete, MHTs play a dual role against chloride-induced corrosion: not only release the species that impart active inhibitive properties but also capture the corrosive agents (Cl-) in this case simultaneously [19]. Fig.2 presents the working mechanism of MHT as an additive in reinforced concrete. Both organic and inorganic inhibitive anions could be intercalated into MHT structure. Due to the nature of different anions, the improvement in terms of corrosion inhibition provided by could be different compared to the pure inhibitors. In this work, two synthesized MHTs, Mg(2)Al-pAB and Mg(2)Al-NO₂ were tested by electrochemical methods to investigate the improvement of MHTs compared to pure inhibitors (pAB and NaNO₂). The primary objective of the paper is therefore to explore how much enhancement the MHTs can account for with different intercalated organic or inorganic inhibitive species as a new type of smart additive for reinforced concrete to reduce chloride-induced corrosion.

![Fig.2 Ion exchange mechanism of MHTs in reinforced concrete exposed to chlorides [10].](image)
2. Experimental

2.1 Materials and solution preparation

Low-carbon steel (St 37) coupons with an exposed surface area of 3.14 cm$^2$ were used as working electrode. All steel coupons were ground with Nos. 320–2400 emery papers in water and further cleaned with acetone under ultrasonication aiming to obtain an equal steel surface roughness. A common three-electrode system cell, with carbon steel as working electrode, a saturated calomel electrode (SCE) as a reference electrode, Pt as a counter electrode was employed in electrochemical tests.

0.1M NaOH solution was used as the model alkaline solution to simulate the high alkalinity of the concrete pore liquid. Five solutions were prepared for the test: (1) 0.1M NaOH (Ref); (2) 0.1M NaOH+0.1M pAB; (3) 0.1M NaOH+0.1M Mg(2)Al-pAB (MHT-p); (4) 0.1M NaOH+0.1M NaNO$_3$; (5) 0.1M NaOH+0.1M Mg(2)Al-NO$_3$ (MHT-N).

For convenience, the abbreviations, Ref, pAB, MHT-p, NaNO$_3$ and MHT-N are used to represent these five alkaline solutions in this paper. According to the reference [20] it takes 2 days exposure in alkaline solution to reach a good passive state of carbon steel. It is widely accepted that the steel surface is considered passive if OCP is equal or more anodic than $-270$ mV [21-25]. After 2-day immersion in test solutions when the OCP of steel electrodes was higher than $-270$ mV, 0.1M NaCl was added to the test solutions and the solution were kept for five days during electrochemical tests. Electrochemical impedance spectroscopy (EIS) measurements were performed at 1h, 1d, 3d, and 5d after NaCl was added. Potentiodynamic polarization (PDP) tests were performed at 1d and 5d after the addition of NaCl. The concentration of NaCl was increased to 0.2M, 0.3M, and 0.4M until corrosion was detected. A new passivated steel electrode was used in a new prepared test solution for each NaCl concentration level. Every test was conducted for three times to check the reproducibility of results.

2.2 Test methods

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) were performed using Solartron 1286 potentiostat. All the measurements were done after the OCP values stabilized for 5 mins. All potential values were reported vs. saturated calomel electrode (SCE).

EIS is one of the most high-frequently employed techniques for the corrosion research in simulated concrete pore solution. EIS measurements in my research were done at the open circuit potential (OCP), the amplitude of the sine wave perturbation was 10 mV in frequency range: 0.01 Hz to 10 kHz. The Zview software was used to plot and fit the EIS data.

PDP test is often used for laboratory corrosion test. It can provide significant useful information regarding corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. The PDP measurement in my research was performed in the range of $-0.15$ to $+1.0$ V vs OCP at scan rate 0.5 mV/s. The Zview software was employed to plot the PDP curves and calculate the corrosion current density.

Olympus BX60M optical microscope was employed for the surface observation. Pictures were taken at several time nodes to compare the surface morphology change and to verify the corrosion spots.

3. Results and discussions:

3.1 Anticorrosion evaluation by OCP

In general, the evaluation of the open circuit potential (OCP) determines the time to corrosion initiation. In alkaline chloride-containing medium, the corrosion, in particular localized corrosion, results from the disruption of the passive layer on the steel surface. For steel in simulated concrete pore solution, it is widely accepted that if an OCP value is equal or more anodic than $-270$ mV [21-25] the steel surface is considered in passivation state. Fig.3 shows the most representative optical microscopic views of surface of steel. As can be observed, the steel surface became more smooth after five days immersion in alkaline solution (Fig.3(b)) than those just after gridding(Fig.3(a)).
Fig. 3 Microscopy images with x20 magnification of steel electrode surface after gridding (a) and 5-day passivation in concrete simulation solution (b).

Fig. 4 Optical microscopic images with x20 magnification of uncorroded steel electrode surface in the solutions at low chloride concentration levels. 0.1M NaOH+0.1M NaNO₂+0.2M NaCl.

Fig. 5 OCP evolution (a) in alkaline solution without NaCl; (b) reference group in 0.1M NaCl and other four inhibitor groups in 0.2M NaCl; (c) 0.3M NaCl; (d) in 0.4M NaCl.
0.4M NaCl (different concentrations of sodium chloride were added at 48h)

Fig. 5 depicts OCP evaluation of all series under different concentrations of NaCl at different time intervals in which OCPs have been averaged from three replicate tests per condition. Different concentrations of sodium chloride were added after 48h passivation in alkaline solutions. As can be seen from Fig. 5 (a) that for all the solutions where no chloride was added, the OCP values were all higher than -270mV (SCE) after two-day immersion indicating that steel electrodes were in passive states. This is also illustrated by microscopic images (Fig.3 (b)). It is worth noting that in the following 5 days after passivation the OCP of MHT-p and MHT-N did not significantly change compared to that of reference solutions. However various effects occurred when chloride was added to the test solutions. As can be observed in Fig.5 (b), the addition of 0.1M NaCl caused an immediate drop of the OCP of Ref indicating the corrosion initiated on the steel surface (Fig.6 (a)). It is interesting to note that the OCP values of other four series with inhibitors behaved similarly to the Ref at chloride concentration up to 0.2M, suggesting that no active corrosion occurred at this chloride concentration. Fig.4 shows the representative steel surface with low concentration of chloride addition in alkaline solution with inhibitors. As can be observed, the steel surface was still protected by the passive layer in alkaline solution with low concentration of chloride addition. When 0.3M NaCl were added, the OCP of pAB solution dropped immediately from 1h indicating active corrosion occurred. The corresponding pitting spot can be found in Fig.6 (b). Three other series’ OCP values were still more anodic than -270mV which means 0.3M chloride could not break down the passive layer on the steel surface during 5-day measurements. However, when chloride concentration was increased to 0.4M, the rest series’ OCP values dropped to more cathodic values than -400mV during 5 days (Fig.5 (d)) which are also confirmed by their corresponding optical microscopic images (Fig.6 (c), (d), and (e)). There was a more anodic value for MHT-N compared with NaNO₂ but only at early stage (2d and 3d) which is likely due to the positive effect of MHT structure on the corrosion initiation.
Fig. 6 Optical microscopic images of corroded steel electrode surface in the solutions at different chloride concentration levels (a) in 0.1M NaOH+0.1M NaCl, (b) in 0.1M NaOH+0.1M pAB+0.3M NaCl, (c) in 0.1M NaOH+0.1M NaNO$_2$+0.4M NaCl, (d) in 0.1M NaOH+0.1M MHT-p+0.4M NaCl, and (e) in 0.1M NaOH+0.1M MHT-N+0.4M NaCl.

Nevertheless, the results shown herein clearly revealed that the chlorides have been exchanged with both intercalated pAB anions and NO$_2^-$ anions. MHT-p subsequently showed some stronger improving inhibiting effect than MHT-N which is indicated by shifting of corrosion initiation of chloride concentration to a higher level when compared to their pure inhibitors. This probably can be explained by the difference of anion-exchange capacity between MHT-p and MHT-N which was carried out by Zhengxian’s unpublished work (Fig. 7). Taking account of 0.1M pAB intercalated in the MHT, the maximum amount of pAB that could be released is calculated to be 0.092M which is shown in Fig. 7(a), and at the same time the chloride that can be accommodated in hydrotalcite host structures can be as high as 0.076M alkaline solution with MHT-p. On the other hand, the maximum released inhibitive anion (NO$_2^-$) for 0.1M MHT-N was about 0.078M (Fig. 7(b)) and the maximum accommodated chloride concentration in hydrotalcite host structures was only about 0.065M.

Fig. 7 Ion exchange ratio of chloride and inhibitive anions in MHTs containing solution

As previously mentioned, it is worth noting that MHTs play a dual role against chloride-induced corrosion: capturing chloride anions and releasing inhibitive anions at the same time to prevent the steel from corrosion initiation. Therefore, the MHTs can be envisioned as both containers of corrosion inhibitors and traps of chlorides. Specifically, we can attribute the high threshold chloride concentration (0.4M) of corrosion initiation of MHT-p to the dual role function of MHT comparing to its pure inhibitor (pAB). The increased 0.1M of threshold chloride concentration of corrosion initiation is resulted from the ion exchange between chloride and pAB anions in the host hydrotalcite structure. When 0.4M NaCl were added to the solution, nearly 0.076M chloride was captured in the hydrotalcite structure accompanying with about 0.092M intercalated pAB has been exchanged.
In MHT-p solution that 0.4M chloride exchanged 0.092M pAB almost gave the same effect as the 0.3M chloride attacked to pure pAB solution which is in accordance with MHTs’ dual roles.

3.2 PDP evaluation of anticorrosion performance of MHTs

For chloride free solutions, the potentiodynamic polarization (PDP) tests were conducted after 2-day immersion in alkaline solutions. For solutions with chloride addition, PDP tests were conducted at 1d and 5d after chloride addition with two separate samples for each case. The most representative curves of potentiodynamic polarization were depicted in Figs 8, 9, and 10 for each case.

Fig. 8 (a) presents the PDP curves for steels electrodes after 2 days exposure in alkaline solutions without chloride addition. As can be seen, all the electrodes exhibited that corrosion potentials were more anodic than -270mV vs SCE and on the other hand the corrosion current density was in the range of 0.022-0.063μA/cm² (Fig.8(c)), indicating that all the specimens were in passive state. It is worthy to note that the two MHTs (MHT-p and MHT-N) attained lower corrosion current density than pure inhibitors which indicated their enhanced inhibition effect compared to pure inhibitors. As OCP values were almost identical for all the solutions except for Ref solution in 0.1M chloride condition (Fig.5(b)), PDP test just started from 0.2M NaCl for all series with pure inhibitors and MHTs. As expected the behaviors of all series with both pure inhibitors and MHTs under 0.2M chloride contamination for 5 days had similar behaviors compared to their counter solution without chloride addition which means the steel electrodes were in passive state. Whereas, the 0.2M NaCl addition to Ref solution severely damaged the passive layer on the steel electrode surface evidenced by very cathodic corrosion potential and large corrosion current density compared to solutions with inhibitors. The MHTs still gave positive effect on the inhibition effect, evidenced by lower anodic current density in passive region (Fig.8(b)) and lower corrosion current density (Fig.8(c)) compared to pAB and NaNO₂.

When the chloride concentration increased up to 0.3M, significant different behaviors were observed from MHT-p and pAB group. For both 1d and 5d, pAB group exhibited high corrosion current density (in the range of 0.7-1.4μA/cm²) and low corrosion potential suggesting that the steel in pAB solution with 0.3M chloride has been seriously corroded. On the other hand, MHT-p solution showed lower corrosion...
current density and higher corrosion potential as well as in NaNO₂ and MHT-N specimens (Fig.9 (a)). This proved again that the MHTs’ dual role significantly improved the steel inhibition effect especially from MHT-p solution. In other words, capturing chloride anions and releasing pAB inhibitive anions in MHT-p improved the chloride corrosion initiation concentration.

When 0.4M chlorides were added to the solutions for 1d, the MHT-p, NaNO₂ and MHT-N solutions gave similar trend in PDP curve (Fig.10 (a)). Further, the positive effect of MHT was well pronounced by the lower anodic current density. Within prolonged test duration to 5 days, all steel specimens were found corroded evidenced by dramatically increased corrosion current density and decreased corrosion potential (Fig.10). However, for MHT-N specimen, the corrosion current density remained slightly lower and corrosion potential remained slightly more anodic than NaNO₂ series.

Fig.10 PDP curves for solutions with 0.4M chloride addition at 1d and 5d (a) with their corresponding corrosion current density (b).

Fig.11 Summary of derived corrosion current density with increasing chloride concentration at 5 days (from 0.2M to 0.4M)

Fig.11 depicts a summary of derived corrosion current density with increased chloride concentrations at 5 days (from 0.2M to 0.4M), only in case of 0.4M NaCl for MHT-p, NaNO₂ and MHT-N. All four solutions with pure inhibitors and MHTs are in passive region with 0.1M and 0.2MNaCl addition at 5 days. There was high corrosion rate on steel surface in pAB solution.
with 0.3M NaCl addition at 5 days; on the other hand, the steel electrodes in the rest three solutions were still in passive state. With 0.4M NaCl addition, the steel electrode corroded in the rest three solutions (MHT-p, NaNO₂, and MHT-N). As can be observed in Fig.11, the corrosion current density remained very low if the added chloride concentration was below the threshold chloride concentration of corrosion initiation for all four solutions with inhibitors indicating that in this situation the inhibitors could protect the steel in alkaline solution. As previously discussed, the threshold chloride concentration of corrosion initiation of MHT-p is 0.4M which is 0.1M higher compared to its pure inhibitor, pAB. The abnormal low corrosion current density of MHT-p compared to NaNO₂ and MHT-N in 0.4M chloride containing solution at 5 days might result from the insoluble MHT-p inhibitors on the corrosion spots which impeded the development of localized corrosion.

### 3.3 EIS evaluation of anticorrosion performance of MHTs

In electrochemical impedance spectroscopy the most representative impedance plot curves were used. The fitted parameters (Table.1) are presented with normalized values (Ω or kΩ per cm²) corresponding to the impedance plots (Figs.13, 14, 16). As the EIS responses for 2-day and 5-day passivation for solution without chloride addition were almost identical (Fig.13) just depicts EIS responses of the steel electrodes after 5-day passivation in alkaline solution without chloride addition. As obtained from OPC evolutions, EIS responses are almost identical for solutions with pure inhibitors and MHTs under low concentration of chloride. EIS test results were thereby shown from 0.3M chloride. Fig.14 presents the EIS responses as an overlay of 1h, 1d, 3d and 5d for 4 kinds of alkaline solutions (pAB, MHT-p, NaNO₂, and MHT-N) under 0.3M chloride contamination; Since pAB presented serious corrosion at 0.3M chloride, test at 0.4M NaCl was not conducted. Fig.16 depicts the EIS response for 3 kinds of solutions (MHT-p, NaNO₂, and MHT-N) at 1h, 1d, 3d and 5d when chloride concentration was increased to 0.4M.

The equivalent circuit depicted in the Fig.12 was used to interpret the experimental responses of EIS results. In this circuit, there are five elements: \( R_i \) is the solution resistance, \( CPE_i \) is the constant phase element for passive film, \( R_f \) is the film resistance, \( R_{ct} \) is the charge transfer resistance and \( CPE_{di} \) is constant phase element for metal/solution double layer for steel in concrete simulation pore solutions with or without inhibitors.

![Fig.12 Equivalent circuit for analysis of impedance spectra.](image)

Therefore the equivalent circuit, containing two time constants in series with the solution resistance is considered to be sufficiently describing the response of the steel electrode in alkaline model solution. Selected summarized values of each element in the equivalent circuit for each series and time interval are given in Table.1. The physical meanings of each element in equivalent circuit are defined here to have better interpretation. \( R_i \) is the solution resistance. As seen from Table.1, \( R_i \) varies due to different inhibitors and \( R_e \) decreased when higher concentration of chloride was added to the solution. The first time constant \( (CPE_p, R_p) \) is associated with the whole surface charge transfer resistance and pseudodouble layer capacitance respectively [26]. The second time constant \( (CPE_{di}, R_{di}) \) describes the redox transformations, mainly Fe\(^{2+}/Fe^{3+}\), in the product layer. The use of constant phase element \( CPE \), further presented as \( Q \) instead of pure capacitance \( C \) is highly accepted in this kind research being attributed to in-homogeneities at different levels [27-30]. This replacement mainly concerns the heterogeneity of corrosion products formed on the surface when corrosion initiates and the participation of inhibitors in the product layer formation. The constant phase element is an empirical mathematical description of the measured impedance response and is defined as [31]: \( Z = \frac{(iw)^n}{Y_0} \), where \( Y_0 \) is a parameter with unit \( \Omega s^n \) and \( 0<n<1 \). When \( n=1 \), a CPE will be simplified as a pure capacitor; while on the other hand, when \( n=0 \) CPE simplifies an ideal resistor. The calculated global polarization resistance \( (R_p) \) values relating to product layer transformation including oxidation and reduction derived from EIS basing on a well-known, simplified calculation of \( R_{eq} = R_p + R_{di} \) are presented in Table.1[32].
<table>
<thead>
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<th>Table 4.1 Fitted parameters from EIS results in alkaline solutions</th>
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<tr>
<td><strong>Time interval</strong></td>
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<tr>
<td>Ref passive (0.4M NaCl)</td>
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<td>0.4M NaCl</td>
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<td>pAB passive (0.4M NaCl)</td>
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<td>1d</td>
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<td>3d</td>
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<td>5d</td>
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<tr>
<td>MHT-p passive (0.4M NaCl)</td>
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<td>1d</td>
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<td>0.4M NaCl</td>
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<tr>
<td>NaNO₂ passive (0.4M NaCl)</td>
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<td>0.4M NaCl</td>
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<td>1d</td>
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<td>MHT-N passive (0.4M NaCl)</td>
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<td>0.4M NaCl</td>
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MHTs improved corrosion resistance of steel in alkaline solutions.

Fig. 13 EIS response in Nyquist (a) and Bode (b) format for passive steel electrodes in alkaline solutions.

As can be seen from Fig. 13, the shapes of all experimental curves are reflecting similar electrochemical behaviors showing that all steel electrodes were in passive states evidenced by high phase angle (84-85°) and very high impedance values at low frequency. The EIS results confirmed that steel electrodes were well in passive states after 2-day immersion in alkaline solutions. As can be observed in Table.1 the values of all elements for all series tend to give similar electrochemical behaviors from EIS responses. Nevertheless, it is worthy to notice that MHTs (MHT-p and MHT-N) presented higher $n_1$ than the pure inhibitor indicating that the MHTs gave a thicker and more uniform passive layer [33,34]. On the other hand, the magnitude of $R_p$ and the phase angle for the steel electrodes exposed to MHTs (MHT-p and MHT-N) solutions (Fig. 13) were higher than those in pure inhibitors (pAB and NaNO₂) which mean...
resistive behavior. On the other hand, steel electrode in MHT-p solution was still in the passive state evidenced by the close to the capacitive behavior at low frequencies (indicating situation of passivity). Both high phase angle and high impedance value indicate that there was still a homogeneous protective layer on the steel surface impeding the corrosion initiation.

However, when 0.4M chloride were added to MHT-p, NaNO2 and MHT-N series, the EIS responses clearly shown that all series were corroded during 5 days. Fig.15 represents the evolution of corrosion as a function of time for all three series with 0.4M chloride addition in corresponding figures. As can be observed, NaNO2 and MHT-N (Fig.15 (a), (b)) exhibited similar EIS responses during the 5-day immersion in 0.4M chloride showing a gradual reduction of impedance with time evolution. In Nyquist plot, the curves of both NaNO2 and MHT-N became lower and shorter during 5-day immersion at 0.4M chloride accompanying by smaller diameters. As can be seen in the Fig.15 (a) and (b), for NaNO2 and MHT-N in the initial period (1h and 1d) after adding 0.4M chloride the steel were still protected evidenced by high phase angle in low frequency and high impedance value. While, the impedance values of these two solutions experienced a dramatic decrease in 3d after adding 0.4M chloride accompanying by drop of phase angle. These phenomenon suggests that steel lost its protective layers and corrosion initiated on the surface. In the following days, the pits kept growing and propagating which is shown by continuous decrease of impedance values and phase angle. Nevertheless, the MHT-N solution still gave better inhibition effect than the pure NaNO2 solution evidenced by larger diameter of semi-circle and higher impedance values. This is probably due to the dual roles of MHTs in alkaline solutions. Fig.15 (c) and (d) present the EIS responses in MHT-p solution with 0.4M NaCl addition. As can be observed, MHT-p was almost as effective as NaNO2 and MHT-N. The impedance and phase angle were still high at 1d after adding 0.4M chloride indicating that there might still be thick and homogeneous protective layer on the steel surface. In the 3d just as NaNO2 and MHT-N solutions the protective layer broke which is shown by the appearance of small semi-circle in Nyquist plot and dramatic phase angle drop at low frequency in Bode plot. It is noteworthy that the impedance value and phase angle at 5d did not decrease so much when compared to that at 3d indicating that the pitting corrosion did not propagate so much between 3d and 5d.
Fig. 15 EIS response in Nyquist and Bode format for alkaline solutions with 0.4M NaCl addition at different time intervals. NaNO$_2$ and MHT-N in Nyquist (a) and in Bode (b) format; MHT-p in Nyquist (c) and in Bode (d) format.

Fig. 16 $Y_{0}$ (a) and $R_p$ (b) evolution for pAB and MHT-p with 0.3M NaCl addition during 5d.

Fig. 16 (a) depicts a comparison of capacitance values ($Y_{0}$ and $Y_{0d}$) for both pAB and MHT-p series under 0.3M chloride attack for 5-day evolution. As can be observed, the values of $Y_{0}$ and $Y_{0d}$ for pAB series experienced an obvious increase associated with the decrease in the exponent ($n_1$) from 0.99 to 0.88 for Q$_f$ and ($n_2$) 0.75 to about 0.45 for Q$_{0d}$. The gradual increase of $Y_{0}$ of pAB suggested that the passive film was becoming thinner and less homogeneous because of the attack of chloride ions. The dramatic increase of $Y_{0d}$ of pAB solution after 1d indicated that a significant corrosion initiated on the steel surface which dramatically increased the capacitance of the double layer on the corrosion spots. In the following test day, the capacitance of double layer continued growing indicating that the corrosion spots expanded to larger area. In contrast, for specimen MHT-p, as observed both $Y_{0}$ and $Y_{0d}$ remained lower values compared to those for pAB specimen without big fluctuation accounting for homogeneous protective film under this chloride concentration. Fig. 16 (b) depicted $R_p$ evolution of pAB and MHT-p solutions with 0.3M NaCl for 5d. As can be observed the polarization resistance of pAB solution decreased of more than 2 orders of magnitude during 5d immersion suggesting the corrosion initiation and dramatic propagation. Although there was a) fluctuation on the evolution of $R_p$ of MHT-p specimen during 5d, $R_p$ remained high values indicating a solid protective layer on the steel surface during 5d. The recorded values of polarization resistance correspond very well to the capacitance values ($Y_{0}$ and $Y_{0d}$) for both pAB and MHT-p series under 0.3M chloride attack for 5d evolution.

Fig. 17 $Y_{0}$ (a) and $R_p$ (b) evolution for MHT-p, NaNO$_2$ and MHT-N with 0.4M NaCl addition for 5d.
The EIS responses of all inhibitors solutions showed inhibition performance blow critical chloride concentration. Pure pAB inhibitor showed corroded EIS performance with 0.3M chloride addition; nevertheless, the EIS response of MHT-p inhibitor with 0.3M chloride addition indicated the steel was well protected. 0.4M chloride could induce the breakdown of passive film in the steel surface in all other three solutions (MHT-p, NaNO₂, and MHT-N). Some improvement of MHT-N can still be observed through the equivalent circuit parameters compared to pure NaNO₂ inhibitor.

The microscope images confirmed the occurring of pitting corrosion on the steel surface by showing big pitting spot when high concentration of chloride was added to the test solution.
Reference


corrosion of steel in concrete. *Cement and concrete research*, 23(6), 1418-1430.


1. Introduction

It is well known that chloride-induced corrosion of the reinforcing steel is a major threat to the durability and serviceability of concrete structures. Corrosion-related issues accounts for great amount of unplanned repairs, significant economic loss, out of service time and waste of materials and energy [1-3]. The worldwide cost to treat these problems runs into billions of Euros every year. As known, steel in concrete is protected from corrosion by a passive film of cubic oxide (γ-Fe₂O₃ iron oxides) [4] which is formed in alkaline pore solution and serves as a barrier to metal dissolution. In other word, this kind of protection results from the ability of the hydroxyl ion from the concrete pore solution to prohibit steel corrosion process. When there is chloride attacking the steel in concrete the passive layer may not be effective and the steel may start corroding at a significant rate. Studies have showed that once the chloride-induced corrosion initiates, three main consequences occur [5]: (1) local pitting corrosion of the reinforcement; (2) cracking and spalling of the concrete cover due to the build-up of voluminous corrosion products; (3) decrease of ductility and reduction of cross section of the reinforcing steel. Therefore, designing concrete which can sustain environmental aggressiveness especially chloride intrusion is extremely important. Traditionally, nitrite containing compounds is widely used in concrete as an efficient commercial anti-corrosion inhibitor [6]. However, the use of this inhibitor was prohibited in some countries because of its toxicity. Organic inhibitors have been proposed as one of the alternatives. From the practical point of view, the anti-corrosion effectiveness of most pure organic inhibitors is debatable especially when compared to the nitrites based inhibitors. Thus, it is essentially important to find more effective measures to improve the corrosion resistance of reinforced concrete.

In the last two decades, a lot of work has been focused on developing new or modified materials which are able to prevent corrosion initiation and/or slow down or even stop corrosion propagation when corrosion has initiated. Accordingly, research has also been carried out to understand the fundamental working mechanism of these new materials [7-9]. A promising strategy to accomplish these tasks for use in concrete is modified hydrotalcites (MHTs) which are also known as layered double hydroxides or hydrotalcites like compounds. They are composed of cationic hydroxide layers with a structure similar to that of brucite with intercalated anions and water molecules between layers. Different kinds of anions, both organic and inorganic, of various sizes and orientations can be intercalated in the space between the hydroxide layers. The inserted anionic inhibitors can be released and replaced by other anions, preferably chloride ions, from the environment. The mechanism of MHTs’ reaction and effectiveness are from the adsorption, anion exchange capacity and mobility of the anions between the hydroxide layers [10]. MHTs are thought to play a dual role against chloride-induced corrosion: capturing aggressive chlorides and simultaneously releasing inhibitive anions to protect the reinforcing steel from corrosion.
This thesis evaluated the inhibition effect of MHTs (MHT-p, MHT-N) compared to their pure inhibitors (pAB, NaNO₂) against chloride induced corrosion in simulated concrete pore solution. There are 5 chapters in my thesis. In chapter 2, some background information of concrete pore solution, chloride induced pitting corrosion, the uses of inhibitors and investigation methods were given. Chapter 3 explained the experimental aspects such as the employed techniques, samples and procedure, etc. The results and discussion part were shown in Chapter 4. Conclusions and recommendations were given in Chapter 5 to support the related researches in the future.
2. Background

2.1 Concrete pore solution

Concrete is a composite material that essentially consists of a binding medium in which particles or fragments of aggregate are embedded (Fig2.1). Cement (main phases: $\text{C}_3\text{S}(3\text{CaO} \cdot \text{SiO}_2)$, $\text{C}_2\text{S}(2\text{CaO} \cdot \text{SiO}_2)$, $\text{C}_3\text{A}(3\text{CaO} \cdot \text{Al}_2\text{O}_3)$ and $\text{C}_4\text{AF}(4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3)$) is a fine, pulverized, dry, material that by itself is not a binder but develops the binding property as a result of hydration; aggregate is the granular material, such as sand, gravel, crushed stone, crushed blast-furnace slag, or construction and demolition waste that is used with a cementing medium to produce either concrete or mortar; water is responsible for the hydration of cement; admixtures are materials other than aggregates, cement, and water, that are added to the concrete batch immediately before or during mixing to improve or modify the properties of concrete. When water is added to cement, the hydration reactions happen which are mostly exothermic. The cement hydration process is shown in Fig2.2.

Fig2.1 Components of concrete((a) cement, (b) aggregate, (c) water, (d) admixture)
Fig 2.2 Process of cement hydration

Table 2.1 Portland cement compound hydration reaction (oxide notation)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Product</th>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (3CaO·SiO₂) Tricalcium silicate</td>
<td>+11 H₂O</td>
<td>= 3CaO·2SiO₂·8H₂O Calcium silicate hydrate (C-S-H)</td>
<td>+3 (CaO·H₂O) Calcium hydroxide</td>
<td></td>
</tr>
<tr>
<td>2 (2CaO·SiO₂) Dicalcium silicate</td>
<td>+9 H₂O</td>
<td>= 3CaO·2SiO₂·8H₂O Calcium silicate hydrate (C-S-H)</td>
<td>+CaO·H₂O Calcium hydroxide</td>
<td></td>
</tr>
<tr>
<td>3CaO·Al₂O₃ Tricalcium aluminato</td>
<td>+3 (CaO·SO₃·2H₂O) Gypsum</td>
<td>+26 H₂O Water</td>
<td>=6CaO·Al₂O₃·3SO₃·32H₂O Etrigite</td>
<td></td>
</tr>
<tr>
<td>2(3CaO·Al₂O₃) Tricalcium aluminato</td>
<td>+6CaO·Al₂O₃·3SO₃·32H₂ O Etrigite</td>
<td>+4 H₂O Water</td>
<td>=3(4CaO·Al₂O₃·SO₃·12H₂O) Calcium monosulfoaluminate</td>
<td></td>
</tr>
<tr>
<td>3CaO·Al₂O₃ Tricalcium aluminato</td>
<td>+ CaO·H₂O Calcium hydroxide</td>
<td>+12 H₂O Water</td>
<td>=4CaO·Al₂O₃·13H₂O Tetracalcium aluminato hydrate</td>
<td></td>
</tr>
<tr>
<td>4CaO·Al₂O₃·Fe₂O₃ Tetracalcium aluminoferrite</td>
<td>+10 H₂O Water</td>
<td>+ 2(CaO·H₂O) Calcium hydroxide</td>
<td>=6CaO·Al₂O₃·Fe₂O₃·12H₂O Calcium aluminoferrite hydrate</td>
<td></td>
</tr>
</tbody>
</table>
As shown in Table 2.1, the products of hydration make the cement mortar high alkalinity whose pH of the pore solution is 12.7-13.5 (except for low pH cement-based materials) [11, 12]. As a result, steel in uncontaminated concrete is usually in the passive state due to the high alkalinity of the pore solution, which enable the formation of a protective iron oxide layer. The thermodynamic domains of immunity, passivity and corrosion of iron and iron oxides in solution are depicted in Pourbaix diagrams (Fig 2.3) (Pourbaix 1963). In this high pH solution a very thin (1-5 nm) passive film composed of γ-Fe₂O₃ is stabilized on the steel surface to prohibit the metal solution and the initiation of corrosion, as proposed by Alekseev (1993) and Küter (2009). The exact composition and microstructure of the passive layer formed in concrete might differ from that formed in simulated concrete pore solution because of concrete’s complex chemical composition.

Fig 2.3 Simplified Pourbaix diagram for iron in water at 25°C (ion concentration 10⁻⁶ mol/l) (adapted from Angst 2011)
2.2 Chloride induced pitting corrosion

When the chloride ions penetrate into the pore solution and reach the steel surface, chloride ions react with the hydrated passive film (FeOOH) and form a soluble complex which dissolves in the surrounding solution breaking down the protective film on the interface between steel and concrete pore solution. The corrosion process is shown schematically in Fig2.4. The chloride ion will decompose the passive layer. The chemical reaction is shown in eq.2.1 and 2.2.

\[
FeOOH + Cl^- \rightarrow FeOCl^- + OH^- \quad \text{eq. 2.1}
\]
\[
FeOCl + H_2O \rightarrow Fe^{3+} + Cl^- + 2OH^- \quad \text{eq. 2.2}
\]

![Figure 2.4](image)

Fig2.4 Schmatic represatation of initiation of pitting corrosion on passive steel surface when chloride introduced [39]
Without passive layers’ protection, there will be a pit and iron dissolution according to eq.2.3 (oxidation reaction), meanwhile the electrons are transferred from anode to the cathode, where oxygen reduction takes place, according to eq.2.4. Fig 2.5 represents the propagation of chloride induced corrosion.

\[
Fe \rightarrow Fe^{2+} + 2e^- \quad \text{eq. 2.3}
\]

\[
\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad \text{eq. 2.4}
\]

This corrosion phenomenon is of an electrochemical nature which means that two electrode reactions are needed to occur, the oxidation and reduction reaction. Oxidation is a losing electron process, the metal releasing electrons. The oxidation step is also called corrosion reaction and takes place at the anodic site. The chemical reaction is presented in eq.2.3Electrons produced from metal oxidation are consumed by the reduction reaction at the cathodic site at the steel surface as shown in Fig2.5. The chemical reaction is shown in eq. 2.4.

Once the corrosion initiated, a very aggressive environment will be produced inside pits. To balance the electron current flew from the anodic areas inside the pits to surrounding cathodic areas, anions such as chloride ions flow to the anodic area which resulted in the hydrolysis of corrosion products inside the pits as shown in eq. 2.5,

\[
Fe^{2+} + 2H_2O + 2Cl^- \rightarrow Fe(OH)_2 + 2HCl \quad \text{eq. 2.5}
\]
As corrosion propagates, the corrosion products are formed precipitating on the steel surface by a series of reactions (eq. 2.6 - 2.8). The produced rust (unhydrated ferric oxide, Fe$_2$O$_3$) has much larger volume than that of the original steel which is shown in Fig 2.6. The resulted expansive stresses in concrete can cause cracking, spalling, or delamination which is shown schematically in Fig 2.7. Secondly, the progress of corrosion decrease the effective cross-sectional area of the reinforcing steel leading to a significant reduction in load-carrying capacity of the system.

\[
Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad \text{eq. 2.6}
\]

\[
Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad \text{eq.2.7}
\]

\[
2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot H_2O + 2H_2O \quad \text{eq. 2.8}
\]

Fig 2.6 Relative volumes of iron (oxy) hydroxides
There are several sources of chloride in concrete. Firstly, chloride can be contained at the time of mixing, through adding contaminated aggregates, seawater; secondly, there will be chloride in the admixtures; thirdly, the diffusion of chlorides from the environment due to direct exposure with marine environment and uses of deicing salts and chemicals. To confine the chloride content from these sources, there are standards to control the limit amount of chloride in concrete mixtures. For example, ACT 201.2R (2001) limits the total chloride ion content in an exposed reinforced concrete member to 0.1% of the weight of concrete.

2.3 Inhibitors

2.3.1 Application of corrosion protection inhibitors of steel in concrete
Corrosion of the reinforcing steel in concrete represents the most widespread deterioration of civil construction which leads to dramatic cost for repair and replacement all over the world. Although there is huge demand either to prohibit corrosion initiation or reduce the corrosion rate, the commercial market still lacks a simple, cheap and reliable technique to accomplish this task. Corrosion protection inhibitors were introduced to prevent the steel from corrosion and/or to restore the protective character of the cover concrete against chloride contaminated concrete. A consensus has been reached on the definition and requirement of corrosion inhibitive admixtures or repair systems for concrete, which is based on ISO definition [14] of a corrosion inhibitor and
is that:” Corrosion inhibitors are chemical compounds that, when added in adequate (preferably small) amount to concrete, can prevent or retard corrosion of steel in concrete, but do not show adverse effects on the concrete properties (e.g. compressive strength) or adversely affect the nature and microstructure of the hydration products”. In the early stage just as Nathan’s book [15] mentioned in the chapter “Inhibitors for use on reinforcing steel in concrete”, only a small a group of inhibitors had been seriously studied and much additional work would be required before inhibition of reinforcing steel corrosion can be considered practical. Since then increasing numbers of researches had been performed on concrete inhibitors’ studies. In the first period, researchers put more effort on inorganic inhibitors, such as calcium nitrite, sodium nitrite, stannous chloride, sodium benzoate and some other sodium and potassium salts (e.g. chromates), that prevented chloride induced corrosion initiation as anodic corrosion inhibitors. An ‘anodic inhibitor’ is one which retards the anodic process of metal dissolution, shifting the corrosion potential to more noble or anodic direction, whereas a ‘cathodic inhibitor’ retards mainly the cathodic process (usually oxygen reduction or hydrogen discharge) and induces a negative shift in the corrosion potential. Up to the mid-1970s, numerous corrosion protection inhibitors had been tested, none of them presented satisfactory inhibition effect, at the same time, giving rise to negative effect on strength development of the concrete. Among them sodium nitrite seemed to be the most effective inhibitors. Nevertheless, the added sodium nitrite in concrete induced substantial strength loss [16] and increased the risk of alkalisilica reaction (ASR) problems [17].

When time reached late-1970s, the application of calcium nitrite as commercial corrosion inhibitors made an important advance. Calcium nitrite not only provided the similar efficiency to sodium nitrite as inhibitors but also caused no known detrimental effects on the mechanical behaviors of concrete or its susceptibility to ASR [18]. Up to now calcium nitrite is the most widely studied corrosion protection inhibitor in concrete. In the USA, it has been widely used since 1978 with successful performance, in different kinds of concrete constructions such as parking, marine and highway structures. Unfortunately, many of these kinds of inorganic corrosion inhibitors are health hazards for the inhibition of corrosion in aqueous media [19, 20].

In the following period, interests in organic inhibitors for steel in concrete had risen because of their environmentally friendly reasons. Alkanolamines and Amines compounds are widely used in this field. Nevertheless, the effectiveness of organic corrosion inhibitors was debatable especially when compared to inorganic ones, such as nitrite compounds. Thus, continuing researches in the domain of materials science is essentially needed in searching for more effective measures to improve the corrosion resistance of reinforced steel in concrete. More recently, more research interest has been attracted in developing new or modified materials which are able to prevent corrosion initiation and/or slow down or even stop corrosion propagation, as well as in understanding the underlying working mechanism [21-23]. A promising strategy to accomplish these tasks for use in concrete is modified hydrotalcites (MHTs) which are also known as layered double hydroxides or hydrotalcites like compounds.

2.3.2 Working mechanism of different inhibitors

As known, the steel in uncontamintated concrete are always in a inhibitive state, being protected by a thin film of oxy-hydroxides dormed spontaneously in the alkaline pore solution. But when ingressed chloride ions content are high enough to destroy the passive film, dissolving the γ-
Fe₂O₃ layer in some specific place, pitting corrosion initiation happens there. The mechanistic action of corrosion inhibitors are thus not uniform corrosion like the successful use of corrosion inhibitors in the oil field, gas or petroleum industry [24,25] but localised or pitting corrosion of a passive metal arising from the presence of chloride ions. According to reference D. W. DeBerry [26], the studies of inhibitors for pitting corrosion especially the typical situation for steel in concrete are not sufficient. Chloride ions are responsible for pitting corrosion. Inhibitors for pitting corrosion can act [1]

- By a competitive surface absorption process of inhibitors and chloride ions (reducing the effective chloride content on the passive surface)
- By increasing or buffering of the pH in the local (pit) environment
- By competitive migration of inhibitors and chloride ions into the pit so that the high chloride contents necessary to sustain pit growth cannot develop

Moreover, some of the inhibitors especially commercial inhibitors are blends of several compounds, which means that more than one mechanism will be involved to explain the inhibition effect.

### 2.3.2.1 Nitrite

Nitrite compounds inhibitors have been deeply studied. The first recorded study about nitrite as inhibitors for use in concrete dates back to the late 1950s. Soviet Union’s scientists studied mixtures of NO₂⁻, NO₃⁻ and CaCl₂ as ‘antifreeze’ admixtures. Since then, a mass of researches have been focused on inhibitive effect of sodium or calcium nitrite by using different experimental techniques in solutions, in mortat and in concrete. As mentioned, the passive films on the steel surface in concrete stabelized at alkaline environment can be destroyed by the presence of enough content of chloride ions. In the dissolution process ferrous ions, Fe(II), are formed. Nitrite act a role as a passivator due to its oxidising properties and stabilises the passive film according to the following reactions[27-29]

\[
2\text{Fe}^{2+} + 2\text{OH}^- + 2\text{NO}_2^- \rightarrow 2\text{NO} + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}
\]  
**eq. 2.9**

\[
\text{Fe}^{2+} + \text{OH}^- + \text{NO}_2^- \rightarrow \text{NO} + \gamma \text{FeOOH}
\]  
**eq. 2.10**

The enhanced inhibition performance from nitrite compounds is related to its ability to oxidize ferrous ions to ferric ions which are insoluble in aqueous alkaline solution blocking the ferrous ions into the electrolyte. Researches have shown that nitrite is not incorporated into passive film, but react with anodic corrosion products in an early stage competing with chloride ions evidenced [30] by similar passive film composition from the XPS surface analytical test with or without nitrite inhibitors with Fe(III) in the passive film and no incorporated nitrogen. In the presence of chloride ions, it is suggested that the [NO₂⁻]/[Cl⁻] concentration ratio must be higher than a threshold value to maintain the steel in passive state. Although different researches gave minor inconsistent threshold ratio values, ranging from 0.5 to more than 1.0 [31-33], the risk of intensified pitting with ingressed chloride ions may rely on multiple factors such as the initial...
surface condition of the steel, the quality of the concrete and the source of the chloride. From all the above it can be concluded that

- Sufficient nitrite concentration is needed to confront ingressed chloride ions
- The passivation reaction consumed some nitrite

2.3.2.2 Organic inhibitors

Although nitrite-based admixture presented effective corrosion inhibitive performance worldwide especially in the USA with relatively long record of good performance, European countries such as Switzerland and Germany forbade the wide use of nitrite compounds as additions to concrete because of their toxicity to human health by environmental regulations [34]. Great effort has been given to identify an alternative corrosion inhibitors in concrete since 1990s, numerous organic inhibitors have been studied including various amines, alkanolamines, their salts with organic and inorganic acids and emulsified mixtures of esters, alcohols and amines [34]. Nevertheless, the information about the detailed compositions of organic inhibitors is so limited that it is rather hard to confirm the supposed mechanism of organic inhibitors’ action and effectiveness against corrosion in concrete. Even for many pure organic compounds as inhibitors against corrosion in simple aqueous media the mechanic features still remain imperfectly understood [35]. In some researches organic inhibitors are said to act by adsorption on the metal surface through a polar group, then forming an organic layer, then may retarding either anodic or cathodic process. While, some organic corrosion inhibitors are supposed to act as chelating agents which can form five- or six-membered chelate groups of inhibitor (such as –NH₂, -OH, -SH, -COOH and –SO₃H) [36] and metal cation. Amines and alkanolamines are widely used as commercial corrosion inhibitors for use in concrete because of their excellent water solubility and the negligible influence on concrete’s properties. The lone pair of the nitrogen atom in the functional group of amines and alkanolamines is thought to be absorbed on the steel surface donating electrons to iron ions on steel surface which act as a Lewis acid. The electronic properties of the functional group which containing the nitrogen atoms will influence amines adsorption as well.

2.3.2.3 MHTs inhibitors

Although organic inhibitors are environmentally friendly as an alternative inhibitors in concrete, the anti-corrosion effectiveness of most pure organic inhibitors is debatable especially when comparing to the nitrates based inhibitors. Therefore, the continuous design of corrosion protection inhibitors for steel in concrete is an issue of prime importance for a wide range of industrial applications against chloride induced corrosion. Recently, a new concept based on smart hydrotalcite containers has been considered as a promising alternative. Modified hydrotalcites (MHTs) may represent a promising option for use in concrete as a new type of functional additive. Deriving from their parent compound, i.e., the naturally occurring hydrotalcites, [Mg₆Al₂(OH)₁₆]CO₃·₄H₂O, MHTs are a group of anion-exchangeable compounds consisting of stacks of positively charged mixed-metal hydroxide layers between which negatively charged anionic species and water molecules are intercalated [37]. The MHTs’ structure can be represented by a general formula:

\[
\left[ M^{II}_{1-x}M^{III}_{x}(OH)_{2} \right]^{x+} \left[ A^{n-}_{x/n} \right]^{x-} \cdot mH_2O ,
\]
in which M
II
 and M
III
 are di- and trivalent metals respectively, (M
II
: Mg
2+
, Ca
2+
, Zn
2+
, Ni
2+
, etc.; M
III
: Al
3+
, Fe
3+
, Ga
3+
, Co
3+
, etc.,) and A
n-
 with valence n is an exchangeable interlayer anion species that could be inorganic or organic. The x value is in the range of 0.22–0.33. The most important key feature of MHTs is their high anionic exchange capacity (2–5 milliequivalents/g) which makes exchange of the interlayer ion by a wide range of both organic and inorganic anions that are versatile and easily achieved. A typical crystal structure of MHT is presented schematically in Fig2.8.

Fig2.8 A typical representation of the crystal structure of hydrotalcite-like compounds [38].

The hydrotalcite-like compounds in corrosion science have been applied in different aspects. In some research, hydrotalcites are produced on the top of metal surface as protective layer [40-46] which consequently provides corrosion protection. A different point of view of using hydrotalcite-like compounds is working as a smart container for corrosion inhibitors for corrosion protection purpose [38, 45]. Hydrotalcite or hydrotalcite-like compounds have been found in hydrated slag cements, which are known to be able to bind more chloride ions than pure Portland cements. In this paper, we will focus on the later perspective used in simulated concrete pore solution. The existence of hydrotalcite-like phases such as Friedl’s salt (a chloride-bearing AFm phase) or its iron analogue and/or Kuzel’s salt (a chloride- and sulfate-bearing AFm phase) have been reported to contribute greatly to chloride binding and thus to enhance the corrosion resistance of reinforced concrete [46]. The beneficial effects of Friedl’s salt on binding chloride in cement support the idea of using MHTs in concrete as an effective chloride scavenger and the increased chloride-binding would definitely slow down chloride transport through concrete matrix. For the envisioned function as an additive to concrete against chloride-induced corrosion, certain inorganic or organic inhibitive anions with known effective inhibition properties could be
intercalated into the structures of MHTs, which then can be slowly released, possibly ‘automatic’ upon arrival of chlorides ions. As expected, such behavior will increase critical chloride content of corrosion initiation and subsequently depress corrosion degradation rate once the corrosion initiated on the steel surface in concrete. Different from other single-function protective inhibitors in concrete, MHTs play a dual role against chloride-induced corrosion: not only release the species that impart active inhibitive properties but also capture the corrosive agents (Cl\(^-\)) in this case simultaneously [47]. Fig.2.9 presents the working mechanism of MHT as an additive in reinforced concrete. Both organic and inorganic inhibitive anions could be intercalated into MHT structure. Due to the nature of different anions, the improvement in terms of critical chloride content of corrosion inhibition provided by could be different compared to the pure inhibitors. In this work, two synthesized MHTs, Mg(2)Al-pAB (MHT-p) and Mg(2)Al-NO\(_2\) (MHT-N) were tested by electrochemical methods to investigate the improvement of MHTs compared to pure inhibitors (pAB and NaNO\(_2\)). The primary objective of the paper is therefore to explore how much enhancement the MHTs can account for with different intercalated organic or inorganic inhibitive species as a new type of smart additive for reinforced concrete to reduce chloride-induced corrosion.

![Fig2.9 Ion exchange mechanism of MHTs in reinforced concrete exposed to chlorides [38]]
2.4 Methods of investigation

2.4.1 OCP map
The open circuit potential (OCP) is the potential of the working electrode relative to the reference electrode when no potential or current is being applied to the cell. Open circuit potential measurements have been used in corrosion studies for many years. OCP values reflect electrochemical properties in electrolytes. In the researches of steel in simulated concrete pore solution it is widely accepted that when OCP values are higher than -270mV vs SCE the metal is considered in passive state [49-53]. It has been often reported that the initiation of pitting corrosion change the corrosion potential or the open circuit potential of the passive metals. Measurement of OCP variation with time is important for estimating passive state of steel in simulated concrete pore solution. A plot of potential as a function of time could be useful to detect the initiation of pitting corrosion on the passive steel surface. Increase of OCP value shows the process of inhibition effect, whereas a drop of OCP values of passive sample indicates the breakdown of the passive layer attacked by corrosive substance.

2.4.2 Potentiodynamic polarization test
Potentiodynamic polarization (PDP) refers to a polarization technique in which the potential of the electrode is varied over a relatively large potential domain at a selected rate by the application of a current through the electrolyte. Potentiodynamic polarization is often used for laboratory corrosion testing. It can provide significant useful information regarding corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. In my experiments, only anodic scan was applied in the anodic direction causing electrons withdrawing from the steel electrode (anode). Fig2.10 illustrates theoretical anodic polarization scan plot which is an idealized representation of features typically observed in practice. Various remarkable features can be figured out on this curve. Point A is the equilibrium potential of steel or corrosion potential in absence of oxygen. Increasing the applied potential to positive direction, it moves into active region where the main reaction is metal oxidation. When the potential reaches point C, with increasing applied potential the current density decreases. Point C is regarded as the passivation potential. In the region E, the current remains stable with increasing applied potential which is known as passive region because the steel is covered by a very thin film of iron oxide that protects it completely (passive film). The corrosion potential (Ecorr) is a mixed potential between the equilibrium potential of the anodic and cathodic reactions and depends mainly on the oxygen availability. With increasing oxygen supply, the corrosion potential will increase. Once the applied potential reaches a sufficiently positive value (Point F), the current density grows dramatically. This critical potential is termed pitting potential (Epit). This pitting potential decrease when there is aggressive species such as chloride ions in the solution (Point F1). When there is increasing concentration of chloride ions, the pitting potential decrease (Point F2). It is worth noting that Epit does not only depend on the chloride concentration but also other factors such as the pH of the solution, temperature, and composition of the solution. The sudden and dramatic current density grow above pitting potential may be due to numerous phenomenon which are dependent of different alloy/environment. For steel in simulated concrete
pore solution with chloride ions, this sudden increase may result from pitting corrosion (localized breakdown of passivity) while for others it may be transpassive dissolution.

Steel in alkaline solution without chloride

Fig2.10 Representative anodic potenio-dynamic polarization curve of passive metal [13]

2.4.3 Electrochemical Impedance Spectroscopy test
As we know, localized corrosion such as pitting corrosion is one of the most common types of corrosion. Although there is great need to qualify the details of localized corrosion, most researches used dc techniques to determine parameters such as the pitting potential and passivation potential which just indicated a potential region where localized corrosion would occur. For the engineering purpose the interested parameter is the corrosion rate once pitting corrosion is initiated. Electrochemical Impedance Spectroscopy (EIS) is a very potent technique to detect the initiation of pitting corrosion and to monitor their growth rate.

During EIS test a perturbation sinusoidal voltage $E_t = E_0 \sin (\omega t)$ is applied at frequency $\omega$ to the electrode system in electrolyte, where $E_t$ is the applied potential at time $t$ and $E_0$ is the amplitude of the voltage. A resultant current $I_t = I_0 \sin (\omega t + \alpha)$ responded from the input is analyzed, where $\alpha$
is a characteristic phase angle shift, $I_t$ is the response current and $I_0$ is the amplitude of the current. Fig2.11. Similar to Ohm’s law, the impedance $Z$,

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$  \hspace{1cm} \text{eq. 2.11}$$

![EIS Test Diagram](image)

**Fig2.11** Applied sinusoidal voltage and resulting current in EIS test

The corresponding complex impedance spectrum $Z(\omega)$, calculated from the variation of the signal frequency $\omega$, is represented in the displacement of the vector $Z(\omega)$. In the Cartesian co-ordinate system, the impedance $Z(\omega)$ is represented by its real part ($Z_R$) and its imaginary part ($Z_I$), i.e.,

$$Z(\omega) = Z_R + jZ_I.$$  \hspace{1cm} \text{eq. 2.12}$$

It is easy to find the value of the modulus and phase angle from eq. 2.13 and eq. 2.14 respectively,
\[ |Z| = \sqrt{Z_R^2 + Z_I^2} \]

\[ \alpha = \arctan\left(\frac{Z_R}{Z_I}\right) \quad \text{eq. 2.14} \]

Two ways are popular when showing the impedance spectrum: Nyquist plot which is made up of a series of vectors representing the total magnitude of the resistance and capacitance (Fig2.12); Bode plots which are made of modulus value and phase shift against signal frequency \( \omega \) (Fig2.13).

Fig2.12 Nyquist plot of EIS response
The impedance spectrum reflects dialectic behaviors, including both redox process and mass migration across the electrochemical interface. This reflection is controlled by the electrical and chemical properties of both electrolyte and the electrode materials. As a necessary part of the EIS analysis, modelling of EIS result using an equivalent circuit is created to describe the electrochemical interface between the metal and the electrolyte. Through equivalent circuit, the impedance spectrum can be derived as a multivariable function. By choosing the proper element, the construction of theoretical spectrum can fit the experimental one with the frequency domain. After constructing the proper equivalent circuit, the information of the electrochemical corrosion can be extracted through the appropriate understanding of the elements.

For inert metals which are stable in molten-salt systems they do not have enough activation to react with the salt in solution to breakdown the passive layer on the metal surface (Fig2.14 (a)). The equivalent circuit for the impedance response of the non-active metals is simply described in Fig2.14 (a), $R_\Omega$ representing the solution resistance, $C_{pf}$ the capacitance of the passive film, and $R_{pf}$ the resistance of the passive film. When the metals are suffering from pitting corrosion from the corrosive substance in solution, the equivalent circuit is different (Fig2.14 (b)). Corrosion substance especially chloride ions often induce localized corrosion instead of uniform corrosion. In the area where localized corrosion happens the passive layer will be destroyed exposing the rare metal to the solution directly; whereas, the rest area is still covered with protective layer. There are two corrosion processes undergoing parallel in this situation: one is on the passive area which is very slow; the other is on the localized corrosion site which is fast. In the area where slow corrosion processes, the charge transfer resistance at the interface between metal and electrolyte can be negligible compared with that on the pitting corrosion site. Therefore, the equivalent circuit in Fig2.14 (b) is used under in this situation, where $R_\Omega$ is the solution resistance, $R_{pf}$ passive film’s resistance, $C_{pf}$ the capacitance of the passive film, $C_{dl}$ the double-
layer capacitance, $R_{ct}$ the charge-transfer resistance. One thing has to be mentioned here is that due to the non-ideal behavior of the double layer in real cells, constant phase element (CPE) is often used instead of a pure capacitor [55-58].

Fig2.15 Equivalent circuit a) Compact oxide film; b) Porous passive layer
3. Experimental aspects

3.1 Materials and solution preparation
Low-carbon steel (St 37) (C<0.13, Si=0.1/0.4, Mn=0.2/0.5, P<0.05, S<0.035, Cr=0.5/0.8, N<0.009, Cu=0.3/0.5 in weight percentage) coupons with an exposed surface area of 3.14cm$^2$ were used as working electrodes. All steel coupons were ground with Nos. 320–2400 emery papers in water and further cleaned with acetone under ultrasonication aiming to obtain an equal steel surface roughness. A common three-electrode system cell, with carbon steel as working electrodes, a saturated calomel electrode (SCE) as a reference electrode, Pt as a counter electrode was employed in electrochemical tests.

0.1M NaOH solution (70mL) was used as the model alkaline solution to simulate the high alkalinity of the concrete pore liquid. Five solutions were prepared for the test:

1. 0.1M NaOH (Ref);
2. 0.1M NaOH+0.1M pAB (pAB);
3. 0.1M NaOH+0.1M Mg(2)Al-pAB (MHT-p);
4. 0.1M NaOH+0.1M NaNO$_2$ (NaNO$_2$);
5. 0.1M NaOH+0.1M Mg(2)Al-NO$_2$ (MHT-N).

All solutions were exposed to atmosphere at ambient temperature without stirring during test. For convenience, the abbreviations, Ref, pAB, MHT-p, NaNO$_2$ and MHT-N are used to represent these five alkaline solutions in this paper. MHT-p and MHT-N were synthesized by my supervisor, Zhengxian, from his previous research. According to his synthesis method, the MHTs (0.1M MHTs) in my test alkaline solutions were added by weight to make the intercalated pure inhibitors reach 0.1M in the solution, the same concentration as the pure inhibitors solution. According to Ormellese, M., Lazzari, L. and etc. [48] it takes 2 days exposure in alkaline solution to reach a good passive state of carbon steel. It is widely accepted that the steel surface is considered passive if OCP is equal or more anodic than −270 mV [49-53]. After 2-day immersion in test solutions when the OCP of steel electrodes was higher than -270 mV, 0.1M NaCl was added to the test solutions and the solution were kept for five days during electrochemical tests. Electrochemical impedance spectroscopy (EIS) measurements were performed at 1h, 1d, 3d, and 5d after NaCl was added. Potentio-dynamic polarization (PDP) tests were performed at 1d and 5d after the addition of NaCl. The concentration of NaCl added was increased to 0.2M, 0.3M, and 0.4M until corrosion was detected. A new passivated steel electrode was used in a new prepared test solution for each NaCl concentration level. Every test was conducted for three times to check the reproducibility of results.

3.2 Test methods
Electrochemical impedance spectroscopy (EIS) and potentio-dynamic polarization (PDP) were performed using Solatron 1286 potentiostat. All the measurements were done after the OCP values stabilized for 5 mins. All potential values were reported vs saturated calomel electrode (SCE).
EIS is one of the most high-frequently employed techniques for the corrosion research in simulated concrete pore solution. EIS measurements in my research were done at the open circuit potential (OCP), the amplitude of the sine wave perturbation was 10 mV in frequency range: 60 kHz to 0.01 Hz. The Zview software was used to plot and fit the EIS data.

PDP test is often used for laboratory corrosion test. It can provide significant useful information regarding corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. The PDP measurement in my research was performed in the range of −0.15 to+ 1.0 V vs OCP at scan rate 0.5 mV/s. Cview software was employed to plot the PDP curves and calculate the corrosion current density.

Olympus BX60M optical microscope was employed for the surface observation. Pictures were taken at several time nodes to compare the surface morphology change and to verify the corrosion spots.
4. Results and discussions

4.1 Anticorrosion evaluation by OCP
In general, the evaluation of the open circuit potential (OCP) determines the time to corrosion initiation. In alkaline chloride-containing medium, the corrosion, in particular localized corrosion, results from the disruption of the passive layer on the steel surface. For steel in simulated concrete pore solution, it is widely accepted that if an OCP value is equal or more anodic than -270mV [49-53] the steel surface is considered in passivation state. Fig 4.1 shows the most representative optical microscopic views of surface of steel. As can be observed, the steel surface became more smooth after five days immersion in alkaline solution (Fig 4.1(b)) than those just after gridding (Fig 4.1(a)).
Fig 4.1 Microscopy images with x20 magnification of steel electrode surface after gridding (a) and 5-day passivation in concrete simulation solution (b).

Fig 4.2 Optical microscopic images with x20 magnification of uncorroded steel electrode surface in the solutions at low chloride concentration levels. (0.1M NaOH+0.1M NaNO₂+0.2M NaCl)
Fig 4.3 depicts OCP evaluation of all series under different concentrations of NaCl at different time intervals in which OCPs have been averaged from three replicate tests per condition. Different concentrations of sodium chloride were added after 48h passivation in alkaline solutions. As can be seen from Fig 4.3 (a) that for all the solutions where no chloride was added, the OCP values were all higher than -270mV (SCE) after two-day immersion indicating that steel electrodes were in passive states. This is also illustrated by microscopic images (Fig 4.1 (b)). It is worth noting that in the following 5 days after passivation the OCP of MHT-p and MHT-N did not significantly change compared to that of reference solutions (Ref) and pure inhibitor solutions (pAB and NaNO₂). However various effects occurred when chloride was added to the test solutions. As can be observed in Fig 4.3 (b), the addition of 0.1M NaCl caused an immediate drop of the OCP of Ref indicating the corrosion initiated on the steel surface (Fig 4.3 (a)). It is interesting to note that the OCP values of other four series with inhibitors behaved similarly to the Ref at chloride concentration up to 0.2M, suggesting that no active corrosion occurred at this chloride concentration. Fig 4.2 shows the representative steel surface with low concentration of chloride addition in alkaline solution with inhibitors. As can be observed, the steel surface was still protected by the passive layer in alkaline solution with chloride concentration below critical chloride content. When 0.3M NaCl was added, the OCP of pAB solution dropped immediately from 1h indicating active corrosion occurred. The corresponding pitting spot can be found in Fig 4.4 (b). Three other series’ OCP values were still more anodic than -270mV which means 0.3M chloride could not break down the passive layer on the steel surface during 5-day measurements. However, when chloride concentration was increased to 0.4M, the rest series’ OCP values dropped to more cathodic values than -400mV during 5 days (Fig 4.3 (d)) which are also confirmed by their corresponding optical microscopic images (Fig 4.4 (c), (d), and (e)). There was a more anodic value for MHT-N compared with NaNO₂ but only at early stage (2d and 3d) which is likely due to the positive effect of MHT structure on the corrosion initiation.
Fig 4.4 Optical microscopic images with x20 magnification of corroded steel electrode surface in the solutions at different chloride concentration levels (a) in 0.1M NaOH+0.1M NaCl, (b) in 0.1M NaOH+0.1M pAB+0.3M NaCl, (c) in 0.1M NaOH+0.1M NaNO$_2$+0.4M NaCl, (d) in 0.1M NaOH+0.1M MHT-p+0.4M NaCl, and (e) in 0.1M NaOH+0.1M MHT-N+0.4M NaCl.

The schematic pictures of chloride induced pitting corrosion on a passive steel electrode in simulated concrete pore solution with inhibitors are shown in Fig 4.5. At first stage, a protective film was developed without chloride addition with inhibitors absorbed in/on the iron oxide passive film or distributed in the alkaline solution due to different working mechanisms of inhibitors. When chloride ions were introduced to the alkaline solutions, they broke the inhibitor film or reacted with inhibitors in the solution; in other words, the chloride ions consumed the inhibitors. Further, the chloride broke down the thin iron oxide layer at specific area on the steel surface with enough chloride content. At last, metal dissolved at the pitting area.
Nevertheless, the OCP evolution results clearly revealed that the chlorides have been exchanged with both intercalated pAB anions and NO\textsubscript{3}\textsuperscript{-} anions. MHT-p subsequently showed some stronger improving inhibiting effect than MHT-N which is indicated by shifting of critical chloride content to a higher level when compared to their pure inhibitors. This probably can be explained by the difference of anion-exchange capacity between MHT-p and MHT-N which was carried out by Zhengxian’s unpublished work (Fig4.6). Taking account of 0.1M pAB intercalated in the MHTs, the maximum amount of pAB that could be released is calculated to be 0.092M which is shown in Fig4.6 (a), and at the same time the chloride that can be accommodated in hydrotalcite host structures can be as high as 0.076M alkaline solution with MHT-p. On the other hand, the maximum released inhibitive anion (NO\textsubscript{3}\textsuperscript{-}) for 0.1M MHT-N was about 0.078M (Fig4.6 (b)) and the maximum accommodated chloride concentration in hydrotalcite host structures was only about 0.065M.
As previously mentioned, it is worth noting that MHTs play a dual role against chloride-induced corrosion: capturing chloride anions and releasing inhibitive anions at the same time to prevent the steel from corrosion initiation. Therefore, the MHTs can be envisioned as both containers of corrosion inhibitors and traps of chlorides. Specifically, we can attribute the high threshold chloride concentration (0.4M) of corrosion initiation of MHT-p to the dual role function of MHT comparing to its pure inhibitor (pAB). The increased 0.1M chloride concentration of threshold value of corrosion initiation is resulted from the ion exchange between chloride and pAB anions in the host hydrotalcite structure. When 0.4M NaCl were added to the solution, nearly 0.076M chloride was captured in the hydrotalcite structure accompanying with about 0.092M intercalated pAB has been exchanged. In MHT-p solution that 0.4M chloride exchanged 0.092M pAB almost gave the same effect as the 0.3M chloride attacked to pure pAB solution which is in accordance with MHTs’ dual roles.

Fig4.6 Ion exchange ratio of chloride and inhibitive anions in MHTs containing solution
4.2 PDP evaluation of anticorrosion performance of MHTs
For chloride free solutions, the potentiodynamic polarization (PDP) tests were conducted after 2-day immersion in alkaline solutions. For solutions with chloride addition, PDP tests were conducted at 1d and 5d after chloride addition with two separate samples for each case. The most representative curves of potentiodynamic polarization were depicted in Fig 4.7, 4.8, and 4.9 for each case.

4.2.1 Solutions without chloride addition:
Fig 4.7 (a) presents the PDP curves for steel electrodes after 2-day exposure in alkaline solutions without chloride addition. As can be seen, all the electrodes exhibited that corrosion potentials were more anodic than -270mV vs SCE and on the other hand the corrosion current density was in the range of 0.022-0.063μA/cm² (Fig 4.7(c)), indicating that all the specimens were in passive state. It is worthy to note that the two MHTs (MHT-p and MHT-N) attained lower corrosion current density than pure inhibitors which indicated their enhanced inhibition effect compared to pure inhibitors.
Fig 4.7 PDP curves for solutions without chloride addition (a) and with 0.2M chloride addition at 5 days (b) with their corresponding corrosion current density (c).
4.2.2 Contamination with different concentration of chloride

As OCP values were almost identical for all the solutions except for Ref solution with 0.1M chloride condition (Fig.4.3 (b)), PDP test just started from 0.2M NaCl for all series with pure inhibitors and MHTs. As expected the behaviors of all series with both pure inhibitors and MHTs under 0.2M chloride contamination for 5 days had similar behaviors compared to their counter solution without chloride addition which means the steel electrodes were in passive state. Whereas, the 0.2M NaCl addition to Ref solution severely damaged the passive layer on the steel electrode surface evidenced by very cathodic corrosion potential and large corrosion current density compared to solutions with inhibitors. The MHTs still gave positive effect on the inhibition effect, evidenced by lower anodic current density in passive region (Fig.4.7 (b)) and lower corrosion current density (Fig.4.7 (c)) compared to pAB and NaNO₂.

When the chloride concentration increased up to 0.3M, significant different behaviors were observed from MHT-p and pAB group. Fig4.8 (a) depicts the PDP curves of four solutions with inhibitors with 0.3M NaCl addition at 1d and 5d time intervals for pAB and MHT-p and only at 5d for NaNO₂ and MHT-N because of their similar uncorroded behaviors in these two days. For both 1d and 5d, pAB group exhibited high corrosion current density (in the range of 0.7-1.4μA/cm²) and low corrosion potential suggesting that the steel in pAB solution with 0.3M chloride has been seriously corroded. On the other hand, MHT-p solution showed lower corrosion current density and higher corrosion potential as well as in NaNO₂ and MHT-N specimens (Fig4.8 (a)). This proved again that the MHTs’ dual role significantly improved the steel inhibition effect especially from MHT-p solution. In other words, capturing chloride anions and releasing pAB inhibitive anions in MHT-p improved the chloride corrosion initiation concentration.
Fig4.8 PDP curves for solutions with 0.3M chloride addition at 1d and 5d (a) with their corresponding corrosion current density (b).
When 0.4M chlorides were added to the solutions for 1d, the MHT-p, NaNO₂ and MHT-N solutions gave similar trend in PDP curved (Fig 4.9 (a)). Further, the positive effect of MHTs was well pronounced by the lower anodic current density. Within prolonged test duration to 5 days, all steel specimens were found corroded evidenced by dramatically increased corrosion current density and decreased corrosion potential (Fig4.9). However, for MHT-N specimen, the corrosion current density remained slightly lower and corrosion potential remained slightly more anodic than NaNO₂ series.
Fig 4.9 PDP curves for solutions with 0.4M chloride addition at 1d and 5d (a) with their corresponding corrosion current density (b).

Fig 4.10 Summary of derived corrosion current density with increasing chloride concentration at 5 days (from 0.2M to 0.4M)
Fig 4.10 depicts a summary of derived corrosion current density with increased chloride concentrations at 5 days (from 0M to 0.4M), only in case of 0.4M NaCl for MHT-p, NaNO₂ and MHT-N. All four solutions with pure inhibitors and MHTs are in passive region with 0.1M and 0.2M NaCl addition at 5 days. There was high corrosion rate on steel surface in pAB solution with 0.3M NaCl addition at 5 days; on the other hand, the steel electrodes in the rest three solutions were still in passive state. With 0.4M NaCl addition, the steel electrode corroded in the rest three solutions (MHT-p, NaNO₂, and MHT-N). As can be observed in Fig 4.10, the corrosion current density remained very low if the added chloride concentration was below the threshold values of corrosion initiation for all four solutions with inhibitors indicating that in this situation the inhibitors could protect the steel in alkaline solution. As previously discussed, the threshold chloride concentration of corrosion initiation of MHT-p is 0.4M which is 0.1M higher compared to its pure inhibitor, pAB. The abnormal low corrosion current density of MHT-p compared to NaNO₂ and MHT-N in 0.4M chloride containing solution at 5 days might result from the insoluble MHT-p inhibitors on the corrosion spots which impeded the development of localized corrosion.

4.3 EIS evaluation of anticorrosion performance of MHTs

In electrochemical impedance spectroscopy the most representative impedance plot curves were used. The fitted parameters (Table 4.1) are presented with normalized values (Ω per cm²) corresponding to the impedance plots (Fig 4.12, 4.13, 4.14). As the EIS responses for 2-day and 5-day passivation for solution without chloride addition were almost identical Fig 13 just depicts EIS responses of the steel electrodes after 5-day passivation in alkaline solution without chloride addition. As obtained from OPC evolutions, EIS responses are almost identical for solutions with pure inhibitors and MHTs under low concentration of chloride. EIS test results were thereby shown from 0.3M chloride. Fig. 14 presents the EIS responses as an overlay of 1h, 1d, 3d and 5d for 4 kinds of alkaline solutions (pAB, MHT-p, NaNO₂, and MHT-N) under 0.3M chloride contamination; Since pAB presented serious corrosion at 0.3M chloride, test at 0.4M NaCl was not conducted. Fig. 16 depicts the EIS response for 3 kinds of solutions (MHT-p, NaNO₂, and MHT-N) at 1h, 1d, 3d and 5d when chloride concentration was increased to 0.4M.

4.3.1 Equivalent circuit

The equivalent circuit depicted in the Fig 4.11 was used to interpret the experimental responses of EIS results for steel in concrete simulation pore solutions with or without inhibitors. In this circuit, there are five elements: Rₖ is the solution resistance, CPEₙ is the constant phase element for passive film, Rₜ is the film resistance, Rₖ is the charge transfer resistance and CPE₀ is constant phase element for metal/solution double layer. Therefore the equivalent circuit, containing two time constants in series with the solution resistance is considered to be sufficiently describing the response of the steel electrode in alkaline model solution. Selected summarized values of each element in the equivalent circuit for each series and time interval are given in Table 1. The physical meanings of each element in equivalent circuit are clarified here to have better interpretation. Rₖ is the solution resistance. As seen from Table 4.1, Rₖ varies due to different inhibitors and Rₖ decreased when higher concentration of chloride was added to the solution. The first time constant (CPE₀, Rₜ) is associated with the whole surface passive film resistance and
pseudodouble layer capacitance respectively [54]. The second time constant (CPE_{dl}, R_{ct}) describes the redox transformations, mainly Fe^{2+}/Fe^{3+}, in the product layer. The use of constant phase element (CPE) instead of pure capacitance (C) is highly accepted in this kind research being attributed to in-homogeneities at different levels [55-58]. This replacement mainly concerns the heterogeneity of corrosion products formed on the surface when corrosion initiates and the participation of inhibitors in the product layer formation. The constant phase element is an empirical mathematical description of the measured impedance response and is defined as [59]:

\[ Z = (j\omega)^n Y_0 \]

where \( Y_0 \) is a parameter with unit \( \Omega^{-1} \text{s}^{n} \) and \( 0 < n \leq 1 \). When \( n=1 \), a CPE will be simplified as a pure capacitor; while on the other hand, when \( n=0 \) CPE simplifies an ideal resistor. The calculated global polarization resistance (R_p) values relating to product layer transformation including oxidation and reduction derived from EIS basing on a well-known, simplified calculation of \( R_p = R_f + R_{ct} \) are presented in Table 4.1 [60].

Fig 4.11 Equivalent circuit for analysis of impedance spectra.
Table 4.1: Fitted parameters from EIS results in alkaline solutions

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<th>Time interval</th>
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<th>R&lt;sub&gt;t&lt;/sub&gt; (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>CPE&lt;sub&gt;0&lt;/sub&gt;,Y&lt;sub&gt;0&lt;/sub&gt; (Ω&lt;sup&gt;-1&lt;/sup&gt;s&lt;sup&gt;1/2&lt;/sup&gt;)</th>
<th>n&lt;sub&gt;t&lt;/sub&gt;</th>
<th>R&lt;sub&gt;ct&lt;/sub&gt; (Ω cm&lt;sup&gt;2&lt;/sup&gt;)</th>
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4.3.2 Solutions without chloride addition
Fig 4.12 EIS response in Nyquist (a) and Bode (b) format for passive steel electrodes in alkaline solutions

As can be seen from Fig 4.12, the shapes of all experimental curves are reflecting similar electrochemical behaviors showing that all steel electrodes were in passive states evidenced by high phase angle (84-85°) and very high impedance values at low frequency. The EIS results confirmed that steel electrodes were well in passive states after 2-day immersion in alkaline solutions. As can be observed in Table 4.1 the values of all elements for all series tend to give passive behaviors of steel from EIS responses. Nevertheless, it is worthy to notice that MHTs (MHT-p and MHT-N) presented higher $n$ than the pure inhibitor indicating that the MHTs gave a thicker and more uniform passive layer [61,62]. On the other hand, the magnitude of $R_p$ and the phase angle for the steel electrodes exposed to MHTs (MHT-p and MHT-N) solutions (Fig 4.12) were higher than those in pure inhibitors (pAB and NaNO₂) which mean MHTs improved corrosion resistance of steel in alkaline solutions.

4.3.3 Contamination with 0.3M chloride

As pre-tested, the EIS responses with inhibitors below critical chloride content were almost identical with the groups without chloride addition reflecting that all were able to protect the steel electrodes in test alkaline solutions in these situation (up to 0.2M for pAB, 0.3M for MHT-p, NaNO₂ and MHT-N) for 5 days. Fig 4.13 presents the EIS responses for pAB and MHT-p series
under 0.3M chloride attack for 5 days. The plots reflect the active corrosion state in pAB series after 1-day with 0.3M chloride attacking, evidenced by the dramatic drop of magnitude of impedance, i.e. semicircle is characteristic for pAB in Nyquist plots, and significant phase angle drop (Bode plots) from approx. 80° at 1h to approx. 55° at 5 days. The response for specimen pAB reflects the evolution of corrosion with time indicating that the system in pAB series changed from capacitive behavior to resistive behavior. On the other hand, steel electrode in MHT-p solution was still in the passive state evidenced by the close to the capacitive behavior at low frequencies (indicating situation of passivity). Both high phase angle and high R_p value indicate that there was still homogeneous protective layer on the steel surface impeding the corrosion initiation.

![Graph showing Nyquist and Bode plots for different conditions.]

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However, when 0.4M chloride were added to MHT-p, NaNO$_2$ and MHT-N series, the EIS responses clearly shown that all series were corroded during 5 days. Fig4.14 represents the evolution of corrosion as a function of time for all three series with 0.4M chloride addition in corresponding figures. As can be observed, NaNO$_2$ and MHT-N (Fig4.14 (a), (b)) exhibited similar EIS responses during the 5-day immersion in 0.4M chloride showing a gradual reduction of impedance with time evolution. In Nyquist plot, the curves of both NaNO$_2$ and MHT-N became lower and shorter during 5-day immersion at 0.4M chloride accompanying by smaller diameters. As can be seen in the Fig4.14 (a) and (b), for NaNO$_2$ and MHT-N in the initial period (1h and 1d) after adding 0.4M chloride the steel were still protected evidenced by high phase angle in low frequency and high impedance value. While, the impedance values of these two solutions experienced a dramatic decrease in 3d after adding 0.4M chloride accompanying by drop of phase angle. These phenomenon suggests that steel lost its protective layers and corrosion initiated on the surface. In the following days, the pits kept growing and propagating which is shown by continuous decrease of impedance values and phase angle. Nevertheless, the MHT-N solution still gave better inhibition effect than the pure NaNO$_2$ solution evidenced by larger diameter of semi-circle and higher impedance values. This is probably due to the dual roles of
MHTs in alkaline solutions. Fig. 4.14 (c) and (d) present the EIS responses in MHT-p solution with 0.4M NaCl addition. As can be observed, MHT-p was almost as effective as NaNO₂ and MHT-N. The impedance and phase angle were still high at 1d after adding 0.4M chloride indicating that there might still be thick and homogeneous protective layer on the steel surface. In the 3d just as NaNO₂ and MHT-N solutions the protective layer broke which is shown by the appearance of small semi-circle in Nyquist plot and dramatic phase angle drop at low frequency in Bode plot. It is noteworthy that the impedance value and phase angle at 5d did not decrease so much when compared to that at 3d indicating that the pitting corrosion did not propagate so much between 3d and 5d.
Fig 4.14 EIS response in Nyquist and Bode format for alkaline solutions with 0.4M NaCl addition at different time intervals. NaNO$_2$ and MHT-N in Nyquist (a) and in Bode (b) format; MHT-p in Nyquist (c) and in Bode (d) format.
4.3.5 Discussion of elements’ evolutions in equivalent circuit

![Graph A](image1)

**Fig 4.15** $Y_{0f}$, $Y_{0dl}$ (a) and $R_p$ (b) evolution for pAB and MHT-p with 0.3M NaCl addition during 5d

**Fig 4.15** (a) depicts a comparison of capacitance values ($Y_{0f}$ and $Y_{0dl}$) for both pAB and MHT-p series under 0.3M chloride attack for 5-day evolution. As can be observed, the values of $Y_{0f}$ and $Y_{0dl}$ for pAB series experienced an obvious increase in semi-logarithmic coordinate associating with the decrease in the exponent ($n_1$) from 0.99 to 0.88 for CPE$_f$ and ($n_2$) 0.75 to about 0.45 for CPE$_{dl}$. The gradual increase of $Y_{0f}$ of pAB suggested that the passive film was becoming thinner and less homogeneous because of the attack of chloride ions. The dramatic increase of $Y_{0dl}$ of pAB solution after 1d indicated that a significant corrosion initiated on the steel surface which dramatically increased the capacitance of the double layer on the corrosion spots. In the following test day, the capacitance of double layer continued growing indicating that the corrosion spots expanded to larger area. In contrast, for specimen MHT-p, as observed both $Y_{0f}$ and $Y_{0dl}$
remained lower values compared to those for pAB specimen without big fluctuation accounting for homogeneous protective film under this chloride concentration. Fig4.15 (b) depicted R_p evolution of pAB and MHT-p solutions with 0.3M NaCl for 5d. As can be observed the polarization resistance of pAB solution decreased of more than 2 orders of magnitude during 5d immersion suggesting the corrosion initiation and dramatic propagation. Although there was small fluctuation on the evolution of R_p of MHT-p solution during 5d, R_p remained high values indicating a solid protective layer on the steel surface during 5d. The recorded values of polarization resistance correspond very well to the capacitance values (Y_{0f} and Y_{0dl}) for both pAB and MHT-p series under 0.3M chloride attack for 5d evolution.

Fig4.16 Y_{0f}, Y_{0dl} (a) and R_p (b) evolution for MHT-p, NaNO_2 and MHT-N with 0.4M NaCl addition for 5d
Fig 4.16 (a) gives evaluations of capacitance values \((Y_{0f}, Y_{0dl})\) for MHT-p, NaNO\(_2\) and MHT-N solutions with 0.4M NaCl addition for 5d. For all three series both \(Y_{0f}\) and \(Y_{0dl}\) increased significantly during 5d indicating that weakening of protective film on the steel surface and initiation and propagation of corrosion during 5d. What is worthy to note is that in the first day after adding 0.4M NaCl both \(Y_{0dl}\) of MHT-N solution did not increase and \(Y_{0f}\) of MHT-N just increased a little bit indicating the delay of corrosion initiation in MHT-N solution. This phenomenon might result from the MHTs dual roles against chloride induced corrosion. Fig 4.16 (b) depicts the \(R_p\) evolution of three series during 5d. As can be observed, \(R_p\) decreased significantly during 5d which corresponded very well with their capacitance values indicating significant corrosion on the steel surface. What is worthy to notice is that the \(R_p\) values of MHT-p and MHT-N experienced smaller decrease in the last two test days compared to NaNO\(_2\) solution. As a result, the corrosion propagation might be slowed down or impeded in MHT-p and MHT-N solutions during the last 2 test days. This might be resulted from the MHTs dual roles at which captured chloride ions decreased the chloride concentration in the test solutions and released inhibitive ions impeded propagation of chloride induced corrosion. The inhibition effect of MHT-p was almost as competitive as NaNO\(_2\) and MHT-N series evidenced by the trends of both \(Y_{0f}\) and \(Y_{0dl}\) (Fig 4.16 (a)) and \(R_p\)’s evolution (Fig 4.16 (b)) during 5-day test in 0.4M chlorine alkaline solution.

After 5-day immersion in different concentration of chloride, MHT-p series represent superior properties compared to pAB series. In 0.3M chloride solution MHT-p series maintained stable protective layer for 5 days evidenced by close to capacitive behavior at low frequencies and high \(R_p\) values during 5 days; on the other hand, the response for pAB specimen reflected serious corrosion indicated by dramatic drop of \(R_p\) values and phase angle drop, and this was also evidenced by the semi-circle in Nyquist plots in 5 days. Moreover, MHT-p series almost gave the same effective inhibition performance compared with NaNO\(_2\) and MHT-N series. This significant improvement inhibition effect which is also evidenced by OCP test and external polarization is probably due to the dual roles of MHTs: capturing chloride anions and releasing inhibitive anions. As for MHT-N, a small improvement of inhibition effect compared to pure inhibitors (NaNO\(_2\)) was observed. This could probably be explained by the small anion-exchange capacity of MHT-N between chloride ions and NO\(_2\) ions.

### 4.3.6 Corrosion rate

As mentioned, the corrosion rate of steel is very important for the engineering target. In EIS test the polarization resistance \(R_p\) can determine the corrosion current density by using the equation \(i_{corr} = B/R_p\) (B is the Stern-Geary constant dependent on the nature of corrosion reactions) [63]. The value of B is 52mV for passive steel while equals to 26mV in corroded situation. If the corrosion current density is known, the corrosion rate is obtained as well. Table 4.2 represents the polarization resistance, corrosion current density and its corresponding corrosion rate with
different chloride concentration at the fifth day. As can be observed, the MHT-p series really protected the steel very well evidenced by much lower corrosion rate compared with pAB series with 0.3M chloride contamination. MHT-N gave a lower corrosion current density compared with the pure inhibitor NaNO₃ group at their corporate critical chloride concentration of pitting corrosion threshold value.

Table 4.2 Polarization resistance, corrosion current density and corrosion rate of five simulated concrete pore solutions with/without inhibitors of different chloride concentration at 5d

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<th>Rp (kΩ cm²)</th>
<th>i_corr (μA cm⁻²)</th>
<th>corrosion rate (μm y⁻¹)</th>
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5. Conclusions and recommendations

5.1 Conclusions
MHTs (MHT-p, MHT-N) represented superior corrosion inhibition effect against chloride induced pitting corrosion in simulated concrete pore solution when compared with the pure inhibitors (pAB, NaNO$_2$). Among them, MHT-p exhibited a better improvement of inhibition effect than MHT-N. This result is probably caused by the bigger ion exchange capacity between pAB ion and chloride ion in MHT-p. MHT-p was almost as effective as NaNO$_2$.

In PDP test, both corrosion potential and corrosion current density indicated that steel electrodes in all solutions were well protected at chloride concentration below threshold chloride concentration of corrosion. Steel electrode in pAB solution was badly corroded under 0.3M chloride attack with high corrosion current density and low corrosion potential. While the steel in MHT-p solution was still in passive state at 0.3 M chloride attacks. When chloride concentration increased to 0.4M, specimens in MHT-p, NaNO$_2$, and MHT-N solutions exhibited high corrosion current density and low corrosion potential. A little lower corrosion current density was observed in MHT-N group compared with NaNO$_2$ group in almost all chloride concentrations.

The EIS responses of all solution with inhibitors showed inhibition performance of corrosion with the concentration of chloride addition that was below threshold values of corrosion initiation for corresponding inhibitors. Pure pAB inhibitor showed corroded EIS performance with 0.3M chloride addition; nevertheless, the EIS response of MHT-p inhibitor with 0.3M chloride addition indicated the steel was well protected. 0.4M chloride could induce the breakdown of passive film in the steel surface in all other three solutions (MHT-p, NaNO$_2$, and MHT-N). Some improvement of MHT-N can still be observed through the equivalent circuit parameters compared to pure NaNO$_2$ inhibitor.

The microscope images confirmed the occurring of pitting corrosion on the steel surface by showing big pitting spot when high concentration of chloride was added to the test solution.

5.2 Recommendations
As the exact working mechanism of MHTs as inhibitors in concrete is not very clear now, more effort can be made on the understanding of inhibition mechanism of MHTs in the future to develop more effective inhibitors in concrete.

A rough critical chloride concentration with 0.1M chloride interval was investigated in this thesis. More details should be studied on the concentration of chloride corrosion threshold with low chloride concentration interval.

As the use of the inhibitors is in civil constructions, real test in concrete should be studied in more details before commercial application. If there is possibility to find a model to construct the relationship between the accelerate test in simulated concrete pore solution and the real corrosion test in concrete, it will save a lot of time to verify the inhibitor’s efficiency in concrete.
Reference


