Construction and Building Materials 141 (2017) 589–597

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of Na_3PO_4 inhibitor on chloride diffusion in mortar

H. Nahali [a,b,1], H. Ben Mansour [a,b,1], L. Dhouibi [b], H. Idrissi [a,*]

[a] MATEIS CNRS UMR 5510 (Équipe CorrIs), INSA-Lyon, F-69621 Villeurbanne, France
[b] Unité de Recherche Mécanique-Energétique (Équipe COPROMET), ENIT, Université de Tunis- El- Manar, BP 37, Tunis Belvédère 1002, Tunisia

HIGHLIGHTS

- The Na_3PO_4 addition in mortar increases the critical period of pitting initiation.
- The presence of phosphate in mortar reduce significantly the chloride diffusion.
- The chloride diffusion coefficient is very low when mortar contain Na_3PO_4 inhibitor.

ARTICLE INFO

Article history:
Received 10 June 2016
Received in revised form 7 February 2017
Accepted 26 February 2017

Keywords:
Mortar
Chloride diffusivity
Diffusion coefficient
Steel corrosion
Phosphate inhibitor

ABSTRACT

The penetration of chloride ions by diffusion has become among the most important factors that lead to concrete reinforcement deterioration. To solve the corrosion problem and achieve the expected service life of reinforced concrete structures, many procedures can be employed such as the use of corrosion inhibitors. In this paper a phosphate based inhibitor ($Na_3PO_4{\cdot}12H_2O$) has been used to study its effectiveness against corrosion and its influence on chloride ions diffusion. This study has been conducted in steady-state conditions using a specific diffusion cell. This simple and effective technique was complemented by the use of a non-destructive method for measuring the concentrations of free chloride ions, diffused through the mortar containing or not phosphate inhibitor, which is the specific chloride electrode (ORION 96-17). The Inhibitor effect, the period and the chloride corrosion threshold of steel reinforcement has been followed using electrochemical techniques. Characterization methods were employed in order to study the behavior of the mortar in absence and presence of phosphate inhibitor. From these methods, it was possible to calculate the evolution of chloride diffusivity over the whole range of chloride concentrations. Results show that the addition of phosphate inhibitor in mortar can reduce significantly the corrosion rate of steel reinforcement in chloride solution, and also increases the critical period of pitting initiation from 30 to 100 days. In these conditions, the calculated chloride diffusion coefficient was estimated at 0.103×10^{-11} m^2/s, value obviously lower than that obtained in the case of the mortar without inhibitor (0.22×10^{-11} m^2/s), during the same period. Thus it can be concluded that the presence of this phosphate inhibitor in mortar reduces the chloride diffusion rate.

1. Introduction

Corrosion of steel reinforcement has been and will be always a major cause of deterioration of reinforced concrete structures. The steel reinforcements corrode whenever the cover concrete does not protect them sufficiently against corrosion. This lack of protection can have many causes [1–4]. Chloride ions are the primary agents that are able to destroy the natural passivity of reinforcement in alkaline concrete condition and therefore, shorten the life of the structure. These chlorides can penetrate into the concrete by various mechanisms. Indeed, in partial saturated concrete, chlorides dissolved in the micro drops of marine fogs, can penetrate by absorption and capillary forces, this mechanism is related to the concrete permeability. However, when concrete is completely water saturated, chloride ions penetrate by a pure diffusion mechanism, according to their concentration gradient [5–11]. This process is very complex. It can be described as some approximations by simple laws of diffusion, the most used is that Fick equation. In this condition, it was important to evaluate the permeability of concrete to predict its service life. In Cl^- rich environment, chloride ions diffuse and react with the constituents of the cement paste. Hydrated calcium silicate can absorb these ions. The tricalcium aluminate C_3A is the most influential. It reacts chemically and produces the hydrated calcium monochloroaluminate or Frie-

---

* Corresponding author.
E-mail address: hassane.idrissi@insa-lyon.fr (H. Idrissi).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.conbuildmat.2017.02.147
0950-0618/© 2017 Published by Elsevier Ltd.

del salt $C_3ACl_2{\cdot}10H_2O$ At the crystalline level, the Cl^- ions insert in the calcium silicate CSH and transform it into a porous and cellular structure which leads to the fracture of the concrete [12].

To delay or prevent the chloride ions diffusion and thus to minimize the reinforcement corrosion process, many procedures can be assessed, such as the use of corrosion inhibitors, in particular the phosphate corrosion inhibitors [13–15]. The literature [16,17] showed that the presence of sodium monofluorophosphate in concrete can protect steel reinforcements against corrosion. It slows down the chloride ions diffusion and reduces the corrosion rate. Montecelli et al. [18] have demonstrated using several techniques that the use of sodium β-glycerophosphate as steel corrosion inhibitor, leads to the formation of a film on the metal surface which increases the corrosion resistance.

Several studies have been made in order to determine the rate of chloride ions diffusion in concrete [19–21], but very few works have investigated the influence of the presence of corrosion inhibitor on these chlorides penetration, which is the objective of this paper.

In our previous work [22], it was demonstrated that Na_3PO_4 based inhibitor in simulated mortar pore solution increases strongly the critical ratio $[Cl^-]/[OH^-]$ of corrosion initiation. The addition of this inhibitor in mortar leads to the decrease of corrosion rate [23].

This paper deals with the role of Na_3PO_4 inhibitor on the chloride diffusion through the mortar. To do so, the apparent chloride diffusion coefficient has been determined. Further, electrochemical techniques, SEM observations and EDS analysis were carried out in order to ascertain the critical period of corrosion initiation.

2. Apparatus and experimental procedures

2.1. Materials

2.1.1. Diffusion cell

The diffusion cell is designed in order to detect the corrosion start, and to determine the chloride concentration threshold which causes the corrosion initiation. This phenomenon is assessed by electrochemical methods in relation to the critical content. The purpose of this technique is to determine the chloride diffusion rate in mortar without and with phosphates. This cell is made of plexiglass. It consists of two compartments, each one equipped with a cylindrical groove. These two compartments are filled with two different solutions, the first one containing distilled water and the other one containing sodium chloride solution (3% NaCl). The compartment containing distilled water (named “test compartment”) is pierced to allow the electrodes location: a saturated sulfate electrode (SSE) as reference, a platinum electrode as auxiliary and a working electrode which is the steel sample (Fig. 1). All potential values were referred to saturated calomel electrode (SCE).

The assembly of these two compartments is made after having placed the mortar sample in between (Fig. 1). A silicone gasket was casted at the edge of the mortar specimen test in order to eliminate the risk of solution leak between the two cell compartments. The experimental study is conducted at room temperature around 22 °C and without stirring.

2.1.2. Specimen preparation

The mortar specimen used is cylindrical with 6 cm in diameter and 1.5 cm of thickness.

Two types of mortar are prepared. The first one is the reference mortar (reference cell). It is prepared with a water/cement (w/c) ratio of 0.5 and cement/sand (c/s) ratio of 0.3. The second sample is prepared with water/cement (w/c) ratio of 0.5, cement/sand (c/s) ratio of 0.3 and phosphate content of 0.3 mol/1 kg of cement (Table 1).

The cement used is Type II PC-32.5 provided by the cement plant of Djebel Oust (Tunisia), its composition is shown in Table 2. The sand, silica based, is normalized.

The produced paste of each sample is poured into a polyvinyl chloride (PVC) cylindrical mold (6 cm in diameter and 1.5 cm of thickness). After that all specimens were dried in air for 24 h, and then cured in water for 7 days. After curing days, specimens were placed in the diffusion cell.

2.1.3. Working electrode

The working electrode is a carbon steel rod of 6 mm in diameter normally used as concrete reinforcement (Chemical composition:

Table 1
Mortar mix design.

	Reference mortar	Mortar containing Na_3PO_4
water/cement (w/c)	0.5	0.5
cement/sand (c/s)	0.3	0.3
Phosphate content	–	0.3 mol/1 kg of cement

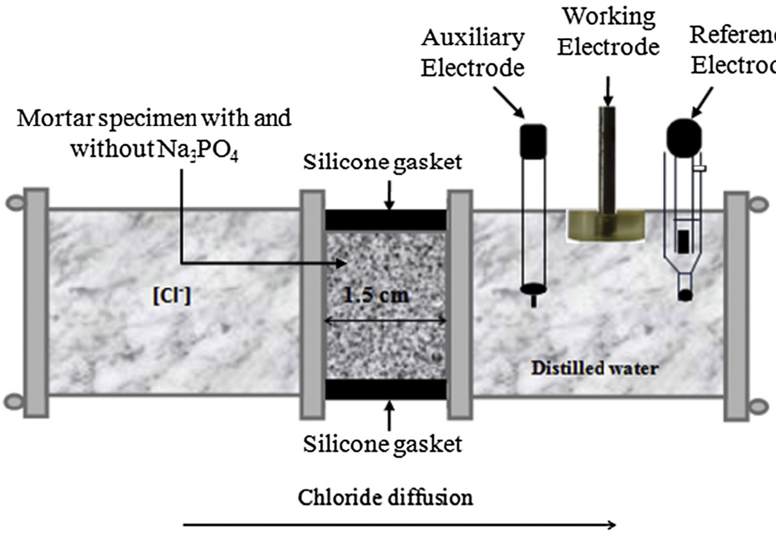

Fig. 1. Diffusion cell.