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Chloride Diffusion in Mortars - Effect of the Use of Limestone Sand Part II: Immersion Test

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Abstract: Part I of this study was devoted to the electrical accelerated chloride diffusion in mortars. In this second part, natural chloride diffusion has been investigated for four types of mortars under exposure to a 0.5 mol/L NaCl solution for a period of up to 35 days. Two different types of sand were used for the production of test samples: siliceous sand (used as a reference) and limestone sand (used in this study). The effect of water to cement ratio and exposure time on the diffusion coefficients of mortars was also investigated. In this study, the total and free chloride content and penetration depth of mortar were measured after immersion, and Fick's second law of diffusion was fitted to the experimental data to determine the diffusion coefficient. Their results show that the use of crushed limestone sand in mortar had a positive effect on the chloride resistance. The apparent diffusion coefficient in all specimens was smaller than that in siliceous sand mortar. However, the chloride penetration of these mortars was increased as exposure time progressed.

Keywords: limestone sand, chloride diffusion, immersion, corrosion, mortar.

1. Introduction

The increasing building's sector development in Tunisia is consuming a massive natural concrete/mortar aggregates use such as siliceous sand. The uncontrolled exploitation of these resources is disturbing environmental equilibrium in the aggregates' production areas. Face by this situation, an enormous study laid down research which aims to use crushed limestone in concrete/mortar production. Some studies[1,2] found that the use of this available local material, as a substitution of siliceous sand, gives a concrete/mortar with equivalent quality compared to ordinary concrete/mortar. But the issue of the durability, and mainly corrosion effect, remains still under investigation.

Ion transport through a hydrated cement system often becomes a primary factor to degrade concrete/mortar in an aggressive environment. Chloride Ion diffusion has become a center of attention for research on ion transport in concrete. This is because of the fact that corrosion of steel bars embedded in concrete/mortar is caused by chloride ingress resulting in the most detrimental effect on the degradation of concrete structures.[3,4]

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Chloride in concrete may be present in either of the following forms:

- *Acid soluble chloride*, which is equal to the total amount of chloride present in the concrete/mortar or that is soluble in nitric acid, and *Bound chloride* which is the sum of chemically bound chloride with hydration products of the cement, such as the C_3A (tricalcium aluminate) or C_4AF (tetracalcium aluminoferrite) phases, and loosely bound chloride with C–S–H gel,
- *Free or water-soluble chloride* which is the concentration of free chloride ions (Cl^-) within the pore solution of concrete/mortar.

It is generally recognized that only the 'free chloride' ions influence the corrosion process. It is reported that the resistivity decreases and corrosion rate increases with an increase in the chloride content.[5]

Thus, chloride diffusivity is a complex phenomenon, as the movement of chloride ions through the concrete is slowed down by other ions present in the pore solution of concrete/mortar. Therefore, convenient determination of the chloride diffusion coefficients of concrete/mortar is rather difficult. Two different methods, such as long-term immersion tests and electrically accelerated chloride ingress tests, have recently been used to accomplish this purpose.[6,7] Long-term immersion tests require chloride extractions from different levels of concrete/mortar samples, and quantification of chloride contents by using this method is rather tedious and time-consuming. On the other hand, although they provide rapid information about the diffusion properties of concrete/mortar, electrically accelerated test procedures may not be reliable due to the possible adverse effects of the relatively high voltage imposed on the rebar in concrete.[6]

This paper studies the influence of crushed limestone sand (CS) on chloride diffusion in mortars. It is to be recalled that in the previous paper (part I),[8] the accelerated chloride diffusion test and a study of different mortar constituents were presented. The results obtained showed that the incorporation of crushed limestone sand (CS) in mortar improved the resistance of mortar to chloride penetration by decreasing the effective chloride diffusion coefficient. In the same manner, this paper investigates the influence of the CS sand in the apparent chloride diffusion coefficient. This part presents the immersion test which is known as the slow chloride diffusion test.

2. Testing conditions and measurements

Four different types of mortar were produced. The materials used for the composition of these samples are the same as those presented in part I.[8] Four cylindrical specimens (ϕ110 × 220 mm) were cast and cured. After demoulding, the specimens were cured in water (at 22°C) until the time of testing. The compressive strengths of specimens, obtained from three specimens for each type (through an average), are presented in Table 1.

For the pure diffusion test (immersion test), the samples were exposed by their diameter to the NaCl solution with the concentration of 30 g Cl^- in 1 liter of the solution as shown in Fig. 1. The other remaining faces were water-proofed and insulated by an epoxy cover. The long time test (35 days) was performed for two different groups of samples. After immersion time, the samples were cut into 5 mm-thick pieces as illustrated in Fig. 2 and in each piece chloride concentration were measured.

In the determination of chloride concentration, the particular samples were, after drying, crushed into a powder. In order to determine that the free chloride ion existed in the sample, 2 g of the ground sample was leached for 3 minutes in 80 ml of distilled water, a magnetic stirrer was used to speed up the leaching process. To extract the total chloride, 2 g of the sample were put in 10 ml of distilled water and 3 ml of concentric acid and was leached for 10 min in which distilled water was added so as to obtain 60 ml and leaching was continued to complete 30 min according to AFREM specifications.[7]

The content of chlorides in the leach was determined by a turbidity method, i.e., titration of the volumetric solution of mercuric nitrate on the sodium nitroprusside indicator. The first turbidity indicates the equivalence point.[9]

Table 1 Strength and Immersion test results.

Mix	Compressive strength (MPa)	Immersion test ($\times 10^{-10}$) (m^2/s)	
		$D_{app}T$	$D_{app}F$
MCF	36.8	1.162	1.117
MCP	29.5	1.201	1.157
MSF	19.0	1.216	1.172
MSP	15.8	1.269	1.178

MCF: Mix Crushed sand Firm; MCP: Mix Crushed sand Plastic; MSF: Mix Siliceous sand Firm; MSP: Mix Siliceous sand Plastic.

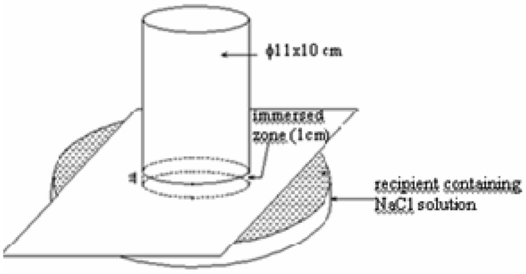

Fig. 1 The pure diffusion test on a cylindrical test-tube (ϕ 110 mm). Immersion in a NaCl solution (0.5 M).

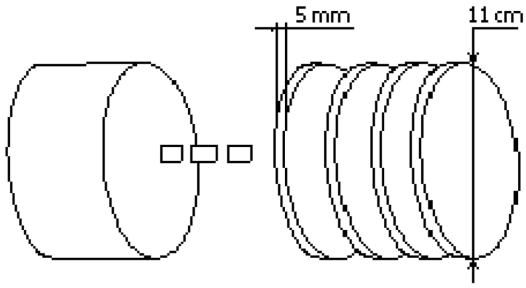

Fig. 2 Carving of a cylindrical test-tube (ϕ 110 mm x 220 mm) after the immersion test.

3. Free and total chloride

Chloride ion diffusion into the micropores of concrete can be modelled to predict chloride concentration at the reinforcing bar surface in concrete. Fick's second law of diffusion is frequently used for this purpose where chloride ion diffusion into concrete is from one direction only.[6,9,10-13] This enables prediction of the apparent chloride diffusion coefficient of concrete/mortar, D_a, when the chloride concentration, C, at any time is known as a function of depth, x.

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{1}$$

An analytical solution to Eq. (1), assuming that the flux of chlorides at any time is proportional to the chloride concentration gradient in the concrete/mortar of a semi-infinite medium, is as follows when reasonable assumptions are specified as proposed by Browne[6,10-14]:

$$C_x = C_s\left[1 - erf\left(\frac{x}{2\sqrt{D_a t}}\right)\right] \tag{2}$$

where C_x is the chloride ion concentration at depth x after exposure time t for a surface chloride concentration of C_s at the concrete surface, D_a is the apparent chloride diffusion coefficient, and the expression *erf* is the Gaussian error function.

The apparent chloride diffusion coefficient of concrete/mortar, D_a, is calculated for a free and total chloride concentration by:

$$D_a = \frac{1}{3t}\left[\frac{x}{1 - \left(\frac{C_x - C_0}{C_s - C_0}\right)^{0.5}}\right]^2 \tag{3}$$

where C_s is the surface chloride concentration, equal to 0.5 mol/l and C_0 is the initial concentration within the material ≈ 0.

4. Results and discussions

The obtained total (T) and free (F) apparent chloride diffusion coefficient of mortar, $D_{a,T}$ and $D_{a,F}$ are presented in table 1 for the two types of sand (and for fluid (F) and plastic (P) cases). This table shows that D_a coefficients were in the range of 1.16×10^{-10} to 1.2×10^{-10} m^2/s for mortar specimens prepared with CS and they were in the range of 1.21×10^{-10} to 1.26×10^{-10} m^2/s for the specimens with the SS. The lowest chloride diffusion coefficients were noted for the specimens prepared with CS sand which shows a better resistance of this mortar to chloride penetrability. This is resulting from the fact that CS presents less void pores than SS, due to its fine granulometry. It is also found that free D_a is lower than total D_a indicating a presence of some bound chloride. Furthermore, while increasing the W/C ratio to 15%, the apparent chloride diffusion coefficient increases by 3.2% for the limestone sand (Cl. Total) and by 4.2% for siliceous sand (Cl. Total). This increase is more important, for total chlorides, than for free chlorides.

Total (T) and free (F) chloride contents profiles are presented in Fig. 3 (as a function of depth from surface, x). For both the chloride contents (T and F), Fig. 3 shows that as chloride concentration in the mortar with CS sand increases, the resistance to diffusion also increases.

Fig. 4 shows the total chloride profiles for the SS and for different workability (F and P). An increase in the water quantity gives an increase in chloride concentration.

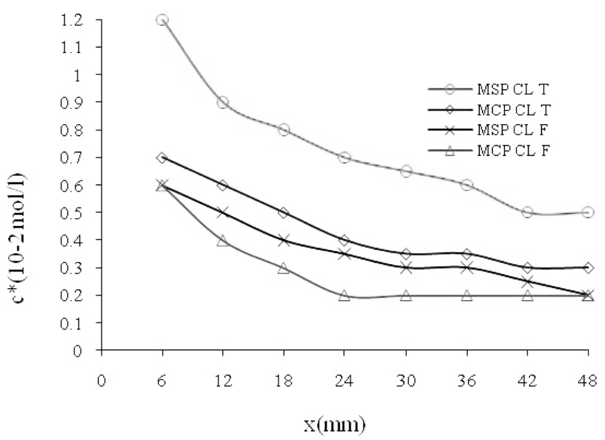

Fig. 3 Totals and free chlorides contents profiles for SS and SC.

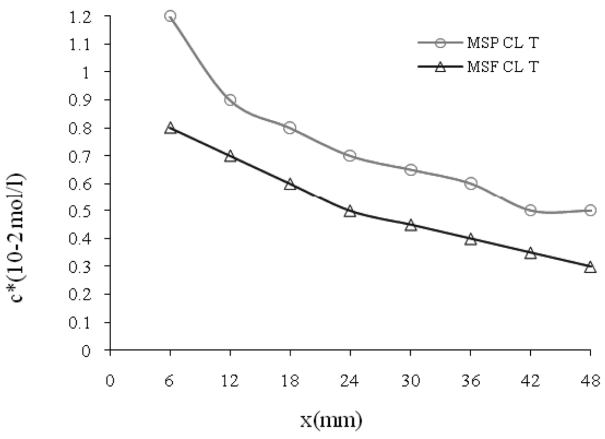

Fig. 4 Totals chlorides contents profiles for two different plasticity (P and F) and SS mortar.

5. Conclusions

The present work aims to study the diffusion of chlorides ions in the Tunisian mortar made with the CS as to investigate its long-term performances, compared to those of SS. This paper completes a previous study [8] by the use of pure diffusion tests. These tests show that the substitution of SS by CS slow down the chloride penetration due to less pore voids of the CS. Thus, the CS contributes an improvement of the mortar characteristics against chloride ions penetration.

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