

## Chloride Diffusion in Mortars - Effect of the Use of Limestone Sand Part I: Migration Test

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**Abstract:** In order to determine the effect of the use of limestone sand on chloride ion ingress in mortar, specimens were cast with two different sands: siliceous sand (used as reference) and limestone crushed sand (used for this study). To compare and assess the resistance of this mortar to chloride penetration, two different diffusions tests were employed: slow migration and rapid migration (AASHTO test). In this study, calculation of the effective diffusion coefficient is proposed using a model based on Nernst-Planck equation. The diffusion coefficients from each sample were compared. The results for all tests show that the diffusion coefficients for siliceous sand mortar are larger than those obtained with limestone sand. It appears also that the diffusion coefficient varies as a function of the W/C ratio.

**Keywords:** limestone sand, diffusion coefficient, transport properties, chloride, mortar.

### 1. Introduction

Limestone has been increasingly used in concrete as filler or as a main cement constituent for many years. It is applied in high performance concrete as well as in normal or low performance concrete. Most of the studies were focused on the effects of limestone on concrete durability. In particular, it has been reported that the use of large quantities of limestone filler in concrete may lead to an increased probability of sulphate attack.<sup>1</sup> It has been known that by neutralising the acidic environment, limestone aggregates could be used to extend the service life of concrete structures exposed to sulphuric acid attack.<sup>2</sup>

The use of limestone as a dominant local material is an increasing of public interest, because it reduces the use of siliceous sand which is in rarefaction, notably in countries like Tunisia. So limestone was employed as sand replacement since previous research has shown that this use can give satisfactory compressive strength of concrete.<sup>3</sup>

Furthermore, chloride ions, contained in an environment surrounding the concrete, can penetrate this material and induce the corrosion of embedded reinforcing steel. Thus, it is important to know the diffusion coefficient of chloride in order to predict the initiation time of corrosion. This critical time depends on the con-

crete cover thickness and on the diffusion coefficient of chloride in the concrete of the studied structure. Diffusion coefficient is mostly determined experimentally for many cases.<sup>4</sup>

In the present study, the effect of replacement of siliceous sand by crushed limestone on chloride attack was investigated. An experimental study was developed to obtain conclusive data on the effects of limestone sand in mortar resistance to chloride penetration. This penetration would be measured and then compared with different water/cement (W/C) ratios and sand types.

### 2. Corrosion initiation time

The diffusion-based corrosion initiation time is expressed by the following function, which is based on Fick's second law of diffusion<sup>5</sup>:

$$T_i = f(C_s, C_{th}, D, d_c) = \frac{d_c^2}{4D \left[ \operatorname{erf}^{-1} \left( 1 - \frac{C_{th}}{C_s} \right) \right]^2} \quad (1)$$

Where  $T_i$  is the time to onset of corrosion (equivalent to time to corrosion initiation),  $d_c$  is the depth of concrete cover over the reinforcing steel,  $C_{th}$  is the chloride threshold level,  $C_s$  is the chloride concentration at the surface and  $D$  is the diffusion coefficient.

Differential sensitivity analysis is based on using a Taylor series to approximate the model under consideration. The first order sensitivity is determined as follows<sup>5</sup>:

$$S_j = \frac{\partial f(X_0) X_{j0}}{\partial X_j T_{i0}} \quad J = 1, \dots, 4 \quad (2)$$

Using Eq. (2), the first-order sensitivity coefficients of corrosion initiation time  $T_i$  to  $C_s$ ,  $C_{th}$ ,  $D$ , or  $d_c$  is obtained as follows:

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$$S(D) = f(D) \frac{D}{T_i} = -1 \quad (3)$$

$$S(d_c) = f(d_c) \frac{d_c}{T_i} = 2 \quad (4)$$

$$S(C_c) = f(C_s) \frac{C_s}{T_i} = -\frac{C_{th}}{C_s} \frac{\sqrt{\pi}}{\text{erf}^{-1}\left(1 - \frac{C_{th}}{C_s}\right) e^{-\left[\text{erf}^{-1}\left(1 - \frac{C_{th}}{C_s}\right)\right]^2}} \quad (5)$$

$$S(C_{th}) = f(C_{th}) \frac{C_{th}}{T_i} = \frac{C_{th}}{C_s} \frac{\sqrt{\pi}}{\text{erf}^{-1}\left(1 - \frac{C_{th}}{C_s}\right) e^{-\left[\text{erf}^{-1}\left(1 - \frac{C_{th}}{C_s}\right)\right]^2}} \quad (6)$$

The Eq. (2) is used to obtain Eqs. (3, 4, 5, 6) by just replacing X by the parameter tested D,  $d_c$ ,  $C_s$  and  $C_{th}$ . The objective of this part of study is the comparison between all this parameters. Furthermore, linear regression analysis is carried out on the steady state portion of the concentration time curves. The use of curve and Eq. (7) give the  $K_a$  which used in Eq. (8) to determine the diffusion coefficient  $D_e = D_{eff}$ . The effective diffusion coefficient is the result of this study and is calculated by Eq. (8) and mentioned in Table 2.

As expected, it can be seen from Eqs. (3) to (6) that  $S(d_c)$  and  $S(C_{th})$  are positive, which means that increasing  $d_c$  or/and  $C_{th}$  will increase  $T_i$ . On the other hand,  $S(C_s)$  and  $S(D)$  are negative, which means that increasing  $C_s$  or/and D will make  $T_i$  decrease.

The values of  $S(d_c)$  and  $S(D)$ , are constant and equal to 2 and 1, respectively, which indicate that  $T_i$  is much more sensitive to  $d_c$  than D. On the other hand, the values of  $S(C_{th})$  and  $S(C_s)$  are both functions of the  $C_{th}/C_s$  ratio, which depends primarily on the corrosion resistance of the reinforcing steel and environmental expo-

**Table 1** Mix proportions and strength.

| Mix                        | MCF  | MCP  | MSF | MSP  |
|----------------------------|------|------|-----|------|
| Type of sand               | CS   | CS   | SS  | SS   |
| Sand/Cement                | 3    | 3    | 3   | 3    |
| W/C                        | 0.5  | 0.65 | 0.5 | 0.65 |
| Slump (mm)                 | 30   | 23   | 8   | 19   |
| Compressive strength (MPa) | 36.8 | 29.5 | 19  | 16   |

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

**Table 2** Different test results.

| Mix | AASHTO (coulombs) | Migration test E-12 ( $m^2/s$ ) |
|-----|-------------------|---------------------------------|
|     | Q                 | $D_{eff}$                       |
| MCF | 3,107.5           | 3.78                            |
| MCP | 4,173             | 5.54                            |
| MSF | 3,706             | 17.4                            |
| MSP | 4,776             | 40.7                            |

**Table 3** Bogue's composition (mass percentage), density and fineness of cement.

| $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ | Density (-) | Blaine fineness ( $m^2/kg$ ) |
|--------|--------|--------|---------|-------------|------------------------------|
| 71.18% | 5.95%  | 6.93%  | 8.98%   | 3.02        | 318                          |

sure.

In our study, the effect of the diffusion coefficient D is considered in particular. It appears that this coefficient which is an indicator of the accessibility of concrete to chloride penetration influences adversely in the time of the initiation of corrosion. And that a gain of reduction of this coefficient appears fundamental to protect the concrete from the chloride corrosion.

### 3. Experimental program

#### 3.1 Materials and specimen preparation

Four different types of mortar with a different W/C ratio and two types of sand were manufactured. Cement matrix was made of CEM 32.5 Type I Portland cement, Siliceous Sand (SS) as reference aggregate and the Crushed limestone Sand (CS) as a local material, and water. The densities of the employed cement, the SS and the CS are 3.02, 2.63 and 2.66  $g/cm^3$  respectively. The mixture proportion of mortar is shown in Table 1 and the chemical properties are mentioned in Tables 3 and 4. Two types of W/C ratio in mortar, ranging from very Plastic (labelled P) to non plastic "Firm" (labelled F), were selected in the mixture. These types were adjusted to obtain the required slump.

For each mixture, four cylindrical specimens ( $\phi 110 \times 220$  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 at 28 days of age were obtained from three specimens (average) and as listed in Table 1.

After curing, three 20 mm thick discs were cut from the central portion of the cylinders for the migration and AASHTO tests.

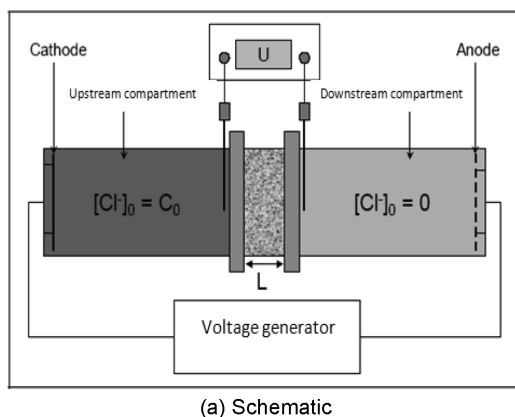
#### 3.2 Testing conditions and measurements

The experimental activity has been focused on the two type of Accelerated Chloride Migration Test (ACMT) and (AASHTO test, migration test) to evaluate the chloride ions penetration through concrete slices, accelerated by an electric field. To perform the Accelerated Chloride Migration Test (ACMT), a two-compartment cell as shown schematically in Fig. 1 was used.<sup>6,7</sup> Before the test, specimens were prepared following the specification in ASTM C1202-05.<sup>8</sup>

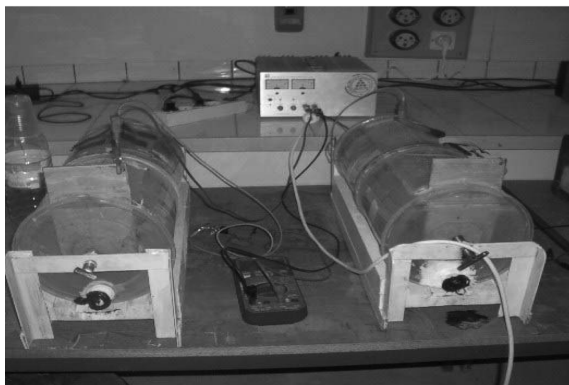
AASHTO tests were conducted according to the standard.<sup>9</sup> This test is known as a short time test. Electrical charge passed through specimens during six hours is determined at 60 V. The solution used is the same as used in migration test which is indicated after.

For the migration test, the concrete sample were kept under vacuum for more than four hours and then saturated with a basic solution containing NaOH (1 g/l) and KOH (4.65 g/l) for more than 24 hours. Then they are placed between the two compartment of the migration cell.

The cathodic cell contained a solution of NaOH (1 g/l), KOH (4.65 g/l) and NaCl (30 g/l) solution. While the anodic cell contained only NaOH (1 g/l), KOH (4.65 g/l) solution; the difference of electric potential between the two faces of the concrete sample is maintained up to 10 volts. Each day, a sample of anodic solution was taken out, in order to measure ion concentration and the solu-



(a) Schematic



(b) Photo of two cells

Fig. 1 Experimental set-up for the migration and AASHTO test cell.

tion in the anodic compartment was totally renewed. Once a week, the two compartments are renewed after their withdrawal.

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 indicated the equivalence point.<sup>10</sup>

## 4. Experimental results and discussion

### 4.1 Effective chloride diffusion coefficient

Typical results of chloride concentration gain in the anode solution are shown in Figs. 2 and 3. These figures show the chloride concentration profile as a function of time.

Three stages of non-steady state (1), steady state (2), and attenuate (3) are identified (Figs. 2 and 3), with respect to literature results.<sup>7</sup> In the non-steady state, the chloride ions have not yet reached the anode cell which explains a few concentrations at the test start. The time period of the non-steady state is defined as the necessary time for chlorides to pass through the specimen, saturating it.<sup>7</sup> In the steady state, the flux of chloride ions passing through the specimen becomes constant. In the attenuate stage, however, the amount of chlorides emerging to the anode cell starts to decrease.

In order to calculate the chloride migration rate of anode solution, linear regression analysis is carried out on the steady state portion of the concentration time curves:

$$C_a = K_a t + a \quad (7)$$

Where  $C_a$  is the chloride concentration in anode cell in mole/l,  $t$

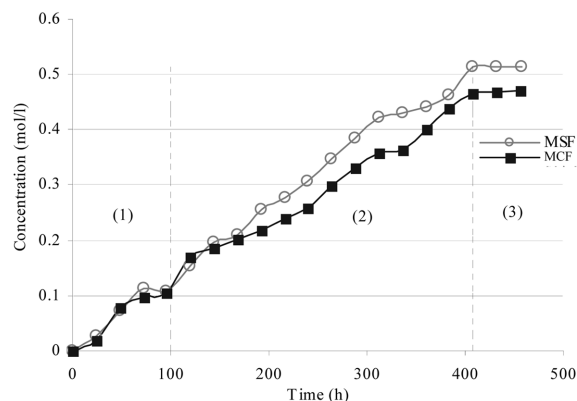


Fig. 2 Variations of chloride concentration gain in the anode cell - effect of sand type (S,C)

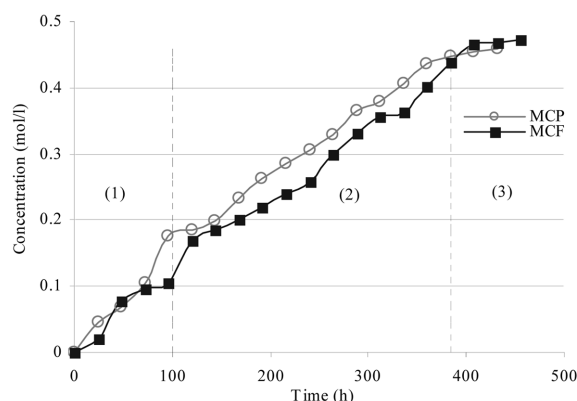


Fig. 3 Variations of chloride concentration gain in the anode cell - effect of workability (fluid and plastic).

is the elapsed time in seconds (s),  $K$  is the chloride migration rate of anode solution in mole/l/s.

As the chloride flux becomes constant, the effective chloride diffusion coefficient  $D_e$  ( $m^2/s^2$ ), is calculated as:

$$D_e = \frac{RT}{|z|C_0 F \left(\frac{E}{l}\right)} J_a; \quad J_a = \frac{K_a V_a}{A} \quad (8)$$

Where  $C_0$  is chloride concentration in the upstream cell at cathode,  $E/l$  is the electrical field (V/m), and  $J_a$  is a constant flux of chloride in the anode cell ( $mole/m^2/s$ ).

In this test, the solution volume of each cell's compartment is about 5 liters. The increasing volume may minimize the temperature effect on the test result.<sup>7</sup> It is found that both of the effective chloride diffusion coefficients (Table 2) in the mortar with different plasticity P and F decrease with the use of limestone sand. Substitution of siliceous aggregate with limestone enhanced the resistance of the mixture to chloride penetration.

Furthermore, it is noted that the chloride amount decreases with decreasing of W/C ratio so that it is clear that permeability and porosity are favourite factors to chloride infiltration as confirmed also by many authors.<sup>4,11-13</sup> Indeed, the increase of the porosity leads those ions finding more liberty to migrate in the porous cementer sample.

### 4.2 Charge passed- AASHTO T277

The current across each cell was measured during 6 hours

**Table 4** Chemical analysis of crushed limestone sand.

| Components       | Mass percentage (%) |
|------------------|---------------------|
| CaO              | 37.24~37.50         |
| MgO              | 13.16~13.35         |
| SiO <sub>2</sub> | 0.79~0.89           |
| SO <sub>3</sub>  | 0.17~0.70           |
| K <sub>2</sub> O | 0.00~0.02           |
| Si               | 1.75~1.91           |
| Al               | 0.10~0.12           |
| Fe               | 0.16~0.17           |
| Cl               | 0.0487~0.0501       |
| Organic matter   | None                |
| Loss on ignition | 46.01~46.21         |

experiment. The charge passed,  $Q$ , is determined by integrating the current–time curve and calculated by:

$$Q = \int I(t) dt \quad (9)$$

where  $I(t)$  is time-dependent total electrical current and  $t$  is the elapsed time.

The obtained value is the resistance of the concrete/mortar since in fact the faculty of the sample is measured to resist the passage of a current (resistance) or again what quantity of current the cylinder of concrete/mortar let pass (conductivity).<sup>14</sup> This test permits to classify the concrete.

Referring to the ASTM standards<sup>15</sup> and Table 2, and for any type of sands, the plastic mortar present a strong penetrability to chlorides ions ( $Q > 4000C$ ), while when the W/C ratio is increased, the permeability to ions chlorides increases. This test provides only the comparative data permitting an ordering of the different types of mortar/concrete.

## 5. Conclusions

The variations in time to onset of corrosion induced by realistic variations of the four governing parameters were determined. These results have important applications both in modeling and in practice.

Considering a feasible range of chloride diffusion coefficients that are relatively easy to achieve in practice for normal concrete, say from  $10^{-12}$  to  $10^{-11}$  m<sup>2</sup>/s, decreasing the chloride diffusion coefficient is considered as an effective measure of extending the time to onset of corrosion. A 50% decrease in the chloride diffusion coefficient increases the time to corrosion by 100%.

A reduction of the Diffusion coefficient  $D$  is observed for mortar/concrete prepared with crushed limestone sand leading to a favourable delay in the time of corrosion.

Finally, it is concluded that the crushed sand can replace the siliceous sand as to ensure a good use of local waste materials.

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