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# EFFECT OF TEMPERATURE ON CHLORIDE DIFFUSION IN SATURATED CONCRETE

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## ABSTRACT

The degradation of reinforced concrete structures exposed to marine environment is largely due to the transfer of chloride ions through the material. Indeed, the prediction of the

1 penetration of these ions in the concrete by the diffusion coefficient is a fundamental indicator  
2 for the characterization of its durability. Actually, the tests simulating chloride diffusion in  
3 saturated areas are developed at constant temperature. However, in reality the temperature  
4 fluctuates with the seasons and diurnal variations. In order to simulate the coupled  
5 temperature-diffusion of chloride in reinforced concrete structures in permanent contact with  
6 the Mediterranean Sea, an experimental program was developed in the laboratory to assess the  
7 migration coefficients of a pozzolanic concrete (CPZ10) and compared to ordinary concrete  
8 referenced (OC). The tests of migration are made under electric field, at different  
9 temperatures from 5 to 50°C (41 to 122°F). Also a study of the activation energy was made  
10 and compared with the Arrhenius theory. The test results showed that the migration  
11 coefficient of concrete increase with increasing temperature. The activation energy values of  
12 natural pozzolan incorporated concretes were lower than ordinary concrete.

13

14 **Keywords:** Concrete, Pozzolan, Coefficient of migration of chlorides, Temperature,  
15 Activation energy.

16

17

## INTRODUCTION

18 The corrosion of steel reinforcements is a major cause of the degradation of reinforced  
19 concrete (RC) structures exposed to sea water. It is due to the ingress of chloride ions into  
20 concrete. Indeed, chlorides can penetrate through the porous media of concrete to reach  
21 embedded steel, which leads to depassivation and corrosion initiation. Corrosion of steel can  
22 start when a sufficient amount (i.e., the threshold) of chloride ions accumulates at the steel  
23 surface and breaks down the passive layer of iron oxide that developed due to the high  
24 alkalinity of the concrete medium<sup>1-2</sup>. This phenomenon depends on the speed of chloride  
25 penetration into concrete. This is conditioned by several factors such as the water/binder ratio

1 (w/b), the age of concrete<sup>3</sup>, the type of binder<sup>4-6</sup>, the porosity<sup>7-8</sup> and the environmental  
2 conditions<sup>9-10</sup> (temperature, humidity, etc...). The temperature variations have a significant  
3 effect on the properties of transfer, particularly on the kinetics of chloride diffusion<sup>9</sup>. Hence, it  
4 is judicious to study the impact of the temperature variations on the process of chloride  
5 diffusion in concrete.

6 During the last decades, several researchers have studied the chlorides diffusion coefficient  
7 using different test methods<sup>11-14</sup>, standards<sup>15-16</sup> and numerical prediction models<sup>17-19</sup>. It should  
8 be noted here that the most of the studies focus on the chloride diffusion into cementitious  
9 materials either on effective or apparent diffusion coefficient, at constant temperature<sup>20-23</sup>.  
10 However, the temperature is a catalyst which acts on the kinetics of diffusion. The increase of  
11 the temperature accelerates the chloride diffusion because molecular speed increases with  
12 increasing temperature. In fact, high temperature may both decrease physical binding of  
13 chlorides because of higher thermal vibration and increase the content of chemically bound  
14 chloride ions, because of the increase in the speed of reactions<sup>9, 24-27</sup>.

15 There are few studies concerning the apparent diffusion coefficient which took into account  
16 the temperature effect<sup>9-10,24-27</sup>. This effect was evaluated on samples subjected to heat  
17 treatment before chloride diffusion test or by using a test bench conditioned at desired  
18 temperature for immersion or transient diffusion/migration tests.

19 Some experimental results obtained in previous studies were explained by the theoretical  
20 equation based on the Arrhenius law using the concept of activation energy as shown in Eq.  
21 (1)<sup>10, 26</sup>.

1 
$$D(T) = D(T_0) \exp\left(\frac{E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad (1)$$

2 Where  $D(T)$  ( $\text{m}^2/\text{s}$ ) ( $\text{ft}^2/\text{s}$ ) and  $D(T_0)$  ( $\text{m}^2/\text{s}$ ) ( $\text{ft}^2/\text{s}$ ) are the diffusion coefficients at  $T$  (K) (F)  
3 and  $T_0$  (K) (F) respectively,  $E_a$  (kJ/mol) is the activation energy of diffusing of chloride  
4 transport in concrete,  $R$  (kJ/(mol.K)) (kJ/(mol.F)) is the ideal gas constant.

5 Collepardi et al.<sup>28</sup> studied the chloride diffusion into cement pastes containing natural  
6 pozzolan with water-cement ratio of 0.4: the samples were put in contact with  $\text{CaCl}_2$  solution  
7 and kept at 10, 25, 40°C (50, 77, 104°F). The results shows that the pozzolanic cement paste  
8 offer a higher resistance to the  $\text{Cl}^-$  penetration than the portland cement paste and the  
9 activation energy determined was 35.56 kJ/mol for the cement paste and 4.12 kJ/mol for the  
10 pozzolanic cement paste.

11 Goto et al.<sup>29</sup> has determined a diffusion rates of chlorides ions as a function of several factors  
12 in hardened cement paste such as water-cement ratio, curing age, curing temperature and  
13 diffusion temperature (27, 35, 45 and 60°C) (80, 95, 113 and 140°F) using a diffusion cell. It  
14 is reported there was a significant temperature dependence of apparent diffusion coefficient  
15 and they obtained the activation energy of 50.2 kJ/mol with a water-to-cement ratio of 0.4.

16 Page et al.<sup>30</sup> investigated the cement paste and were using the cells diffusion placed in a water  
17 bath, with five values of temperature in the range 7 to 47°C (44.6 to 116.6°F); the effective  
18 diffusion coefficient measured is affected by the level of temperature and they found that the  
19 activation energy was dependent on water-to-cement ratio (w/c), 41.8 kJ/mol for paste with  
20 w/c = 0.4, 44.6 kJ/mol for paste with w/c= 0.5, and 32.2 kJ/mol for paste with w/c= 0.6.

21 Nguyen et al.<sup>31</sup> investigated the effect of temperature on chloride diffusion into mortars with  
22 cement type I and V using an accelerated test method. They found that chloride diffusion  
23 coefficient and penetration depth increase with temperature level. The activation energy are in  
24 the range of literature values<sup>30</sup>: the values are 35.7 kJ/mol and 32.3 kJ/mol for the mortars  
25 incorporating cement type I and V, respectively.

1 Al-Khaja<sup>25</sup> studied experimentally the durability performance of high-strength concrete mixes  
2 and conventional concrete, exposed to chloride environments (5% NaCl) at temperatures of  
3 20 and 45°C (68 and 113°F). The results noticed that a significant increase in the chloride  
4 ingress into concrete was observed when the exposure temperature was increased from 20 to  
5 45°C (68 to 113°F) in both conventional and high-strength concretes. Furthermore, the effect  
6 of temperature on chloride ingress is more influential in the conventional concrete than in the  
7 high-strength concrete. The activation energy was not determined in this study. Samson and  
8 Marchand<sup>32</sup> proposed a semi empirical function, to estimate variations in diffusion coefficient  
9 of concrete when the temperature of the material fluctuates with the values of 4, 23 and 40°C  
10 (39.2, 73.4 and 104°F). The activation energy obtained from migration test is ranging from  
11 17.9 to 21.2 kJ/mol.

12 Yuan et al.<sup>26</sup> also studied the temperature effect on the transport of chloride ions in concrete  
13 with different water-cement ratio and type of cement. The investigation was carried in non-  
14 steady state condition for both tests, migration and diffusion coefficient, which were  
15 measured at 5, 20 and 40°C (41, 68 and 104°F). They reported that activation energy of  
16 concrete measured from non-steady-state diffusion tests ranges from 17.9 to 39.9 kJ/mol,  
17 while the activation energy obtained from non-steady-state migration coefficient is around 20  
18 kJ/mol and independent of water to cement ratio. Yang and Wang<sup>33</sup> addressed that the use of  
19 accelerated chloride migration test (ACMT) of unheated (20°C) (68°F) and heated concrete  
20 (95°C) (203°F) showed a significant increase of the chloride migration coefficients when  
21 concrete specimens are exposed from 20 to 95°C (68 to 203°F) temperature. The  
22 breakthrough time had reduced at room temperature (20°C) (68°F) to a limited range at 95°C  
23 (203°F).

24 Otsuki et al.<sup>34</sup> studied the influence of temperature on the mortar matrix paste specimens  
25 (5x5x4 mm) (0.19x0.19x0.15 in) from the central part of the cylindrical specimen of concrete

1 (100x200 mm) (3.93x7.87 in), the curing and the test diffusion was conducted under three  
2 levels of temperature (20, 30 and 40°C) (68, 86 and 104°F). The diffusion coefficient was  
3 calculated using Fick's first law of diffusion. The activation energies obtained were from 70.4  
4 to 134.9 kJ/mol.

5 Recently Doutsis and al.<sup>10</sup> focused his work on the influence of exposure temperature ranging  
6 from 22, 35 to 50°C (71.6, 95 to 122°F) on chloride diffusion according to Fick's second law  
7 in control concrete and six different concrete mixtures containing various amounts of silica  
8 fume or natural zeolite. The results obtained by Doutsis et al.<sup>10</sup> have shown significant  
9 differences in diffusion coefficients between ordinary concrete and concrete mixtures from  
10 which the activation energies values were 31.9 kJ/mol and less than 30.9 kJ/mol respectively.  
11 Concerning modelling of chlorides penetration into concrete, there are many approaches in  
12 literature. However, when the temperature effect is considered, there are few models such as  
13 FIB model code<sup>35</sup> and Life-365 model<sup>19</sup>. These models considered that the effect of  
14 temperature on chloride diffusion coefficient is in agreement with the Arrhenius law. The  
15 activation energy values proposed by such models are 40 kJ/mol and 35 kJ/mol, regardless of  
16 concrete mixture type.

17 However, no report was found on studying the influence of coupling directly temperature with  
18 the coefficient of migration under an electric field in steady state in saturated concrete.

19 This work aims to characterize and analyze the effect of temperature upon the chloride  
20 diffusion under electric field of an ordinary and pozzolanic concrete, in saturated conditions;  
21 which leads to the objectives and research methodology adopted in this work.

22 In this study the temperatures selected were 5, 20, 30, 40 and 50°C (41, 68, 86, 104 and  
23 122°F), which reflects the ranged typical ambient temperatures of the Mediterranean Sea.

24

25

## **RESEARCH SIGNIFICANCE**

1 The durability is increasingly decisive for the design of reinforced concrete structures in a  
2 saline environment. In such ambience conditions, the temperature process is known to cause  
3 faster penetration of chloride, and it's relevant for the service life design and reassessment of  
4 reinforced concrete structures. The originality of the present work lies in the new test  
5 experimental setup developed in order to apply a controlled range of temperature at same time  
6 as the chloride migration occurs into saturated concrete conditions. The results presented in  
7 this paper are part of a comprehensive study of ordinary concrete and pozzolanic concrete to  
8 evaluate the porosity, and relationship between the coefficient diffusion subjected to the  
9 variation of temperature. Such information can aid in designing and selecting mixtures  
10 concrete throughout the sea environment by taking into account the fluctuation of the  
11 temperature.

## 12 **EXPERIMENTAL STUDY**

### 13 **Materials**

14 The binder used is a Portland cement composite CEM II/A 42.5 from the factory of Beni Saf,  
15 located in north-west Algeria, as specified in Standard NA 442<sup>36</sup>. It consists of 85% clinker,  
16 and 12% natural pozzolan and 3% gypsum. Its density is 3070 kg/m<sup>3</sup> (191.65 lb/ft<sup>3</sup>) and  
17 Blaine specific surface area is 2705 cm<sup>2</sup>/g (1320.67 ft<sup>2</sup>/lb). Its chemical composition is given  
18 in **Table 1** and its mineralogical compositions is presented in **Table 2**.

19 The natural pozzolan used is extracted from the Bouhmidi deposit of pyroclastic rocky of  
20 volcanic origin located in Beni-saf (north-west of Algeria). It is generally accepted that the  
21 pozzolan sample is chemically suitable with a total content ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$ ) as  
22 mentioned in ACI report<sup>37</sup>, then satisfying the ASTM C 618<sup>38</sup> requirements. And can be used  
23 to replace up to 40% of ordinary Portland cement in accordance with EN 197-1 and ASTM C  
24 595<sup>39</sup> standards.

1 The natural pozzolan was dried at 105°C (221°F) and used as a powder resulting from a  
2 grinding and clipping sieve of 80 µm (0.00314 in). Its density is 2500 kg/m<sup>3</sup> (156.06 lb/ft<sup>3</sup>)  
3 and Blaine specific surface area is 3360 cm<sup>2</sup>/g (1640.46 ft<sup>2</sup>/lb), The chemical analysis of the  
4 resulting powder crushed at 80µm is reported in **Table 1**<sup>40</sup>.

5 The size grading curve for the natural pozzolan was determined by laser granulometry. The  
6 average of three test shown that the diameter at 90% is 69 µm (27.16 x 10<sup>-4</sup> in), at 50% is 16  
7 µm (6.299 x 10<sup>-4</sup> in) and at 10% is 2 µm (0.787 x 10<sup>-4</sup> in) (see **Fig. 1**).

8 The crushed aggregates used are limestone from the career of the National Company of  
9 Aggregates (ENG) located in west of Algeria. The maximum size of coarse aggregate is 25  
10 mm (0.984 in) and their specific gravity is 2.58. The maximum size, fineness modulus and  
11 specific gravity values of sand are respectively 4 mm (0.157 in), 2.95 % and 2.50.

12

### 13 **Mixture proportions**

14 Two concretes designated OC and CPZ10 were used in this study. An ordinary concrete (OC)  
15 which many experimental data are available within our team<sup>41</sup>, was designed with binder  
16 content of 350 kg/m<sup>3</sup> (21.84 lb/ft<sup>3</sup>) and water-binder ratio of 0.55. Another concrete (CPZ10)  
17 containing pozzolanic substitution of 10% of the mass of cement was used to evaluate the  
18 effect of pozzolanic admixture on concrete properties. The details of the concrete mixtures are  
19 summarized in **Table 3**.

20

### 21 **Sample Preparation**

22 In this test campaign, specimens were moulded in 11x22 cm (4.33x8.66 in) PVC cylinders.  
23 After casting, they were demoulding after 24 hours and then immersed in water at 20°C  
24 (68°F) for 28 days for each concrete in accordance with EN 206-1. At the end of the moist  
25 cure, these specimens were cut in order to extract three discs of 5 cm (1.96 in) thick, which

1 are then sealed on their curved surface with epoxy resin to ensure a uniaxial flow inside the  
2 discs and rectified to have plane and cleaned surfaces. Then, they were dried at 105°C  
3 (221°F) until reaching constant weight<sup>42</sup>; the middle disc was chosen and saturated<sup>43</sup> to  
4 evaluate the water porosity and the effective chloride diffusion coefficient.

5

## 6 **Chloride diffusion test**

7 The assessment of diffusion coefficient take long time with natural diffusion test (minimum 9  
8 month), Migration test were developed to accelerate the transport of chlorides<sup>20-21, 44</sup> and  
9 recently standardized as NF XP P18-461<sup>45</sup> according to the following principle : The disc of  
10 concrete was placed between the two compartments of a cell migration. A basic solution  
11 containing NaOH (0.025 M) and KOH (0.083 M) in the downstream compartment; the same  
12 solution laden with NaCl (0.513 M) in the upstream compartment. A 12 V potential difference  
13 was applied between the sides of the concrete sample. The downstream solution was sampled,  
14 and samples were titrated with silver nitrate (0.05 M). As the flux became constant, the  
15 simplified Nernst–Planck relation<sup>20</sup> allowed us to determine the value of the effective  
16 coefficient  $D_{mig}$  (m<sup>2</sup>/s) (ft<sup>2</sup>/s), as in Eq. (2):

$$17 \quad D_{mig} = \left( \frac{RTL}{zFEC_0} \right) J \quad (2)$$

18 Where  $C_0$  (mol/m<sup>3</sup>) (mol/ft<sup>3</sup>) is the chloride concentration of the upstream compartment  
19 (0,513),  $J$  (mol/(m<sup>2</sup>s)) (mol/ft<sup>2</sup>s) is the flux of chloride ions,  $z$  ( $z=1$ ) is the chloride ion valency,  
20  $F$  is the Faraday constant ( $F=96480$  J/(V mol)),  $E$  (V) is the actual potential drop between the  
21 surfaces of specimen,  $R$  is the gas constant ( $R=8.3144$  J/(mol K)) (J/mol F),  $T$  (K) ( $F$ ) is the  
22 absolute temperature,  $L$  (m) (ft) is the sample thickness.

23

## 24 **Evaluation of diffusivity coupling with temperature**

1 To undertake a study that takes into account the diffusion coupling with temperature, an  
2 experimental device has been realized in EOLE laboratory (University of Tlemcen, Algeria).  
3 This experimental apparatus is composed of a caulked water tank of capacity 15 liters (3.96  
4 gal). A heater is disposed on the left side to generate heat and on the right side, a coil for the  
5 circulation of the refrigerant gas which is connected to the compressor and to the evaporator  
6 to generate cold. Both components are flooded in a liquid water mixed with rapeseed oil and  
7 are connected directly to the control panel by two thermostats respectively controlling the  
8 high and low temperatures. The apparatus is also equipped with a variable temperature that  
9 controlled hot and cold temperature (see **Fig. 2**).

10 A circular coil connected to the tank is installed around the disc of concrete for conditioning  
11 specimen at temperature fixed in advance; all pipes are protected by a caulking to prevent loss  
12 of temperature. The circulation of the coolant liquid is provided by a closed circuit provided  
13 with a peristaltic pump. The controlled temperature is maintained constant for at least four  
14 hours, so as to enable the latter to reach the heart of concrete disc. Finally, the migration  
15 under electric field is generated, once the temperature is uniform throughout all the sample of  
16 concrete.

17 One migration test was performed for each temperatures: 5, 20, 30, 40 and 50°C (41, 68, 86,  
18 104 and 122°F). And for each temperature, a diffusion coefficient is obtained. The effect of  
19 temperature on the chloride diffusivity was taken into account, which was often expressed  
20 theoretically by Arrhenius law (Eq. 1). Hence, the relation of the chloride diffusion  
21 coefficients  $\ln(D(T))$  versus the inverse of the absolute temperature ( $1/T$ ) is depicted. These  
22 data can be fitted by linear regression analysis to an unique straight line using the Arrhenius  
23 law . Then, the activation energy  $E_a$  is equal to the slope of the straight line<sup>10,29-31</sup>.

24

25 **Mercury intrusion porosimetry test (MIP)**

1 The mass transport in cement-based materials is largely controlled by the porosity, also  
2 considered as a first durability index. Thus the porosity of cement-based materials and its  
3 microstructure are the main factors that affect the penetration of chlorides<sup>46-47</sup>.  
4 For the characterization of porosity and pore size distribution of the studied materials, an  
5 investigation by mercury intrusion porosimetry (MIP) measurements was conventionally  
6 performed for its convenience and reliable results for all size of pores especially capillary  
7 pores<sup>48</sup>. Moreover, the MIP provides information on the threshold pore size which is  
8 considered relevant for the assessment of the resistance to transport of substance in the  
9 material<sup>49</sup>.  
10 For this test campaign, two cubic samples of each mixtures having dimensions of 1.5x1.5x2  
11 cm<sup>3</sup> (0.59x0.59x0.78 in<sup>3</sup>) cut from cylindrical disc  $\phi$ 110x50 mm ( $\phi$  4.33 x1.96 in) specimens  
12 were prepared and dried by putting them in an oven at T = 40°C (104°F) until reached a  
13 constant weight and stored in sealed containers for the MIP test. The MIP test was carried out  
14 on a Micromeritics AutoPore-9500 mercury intrusion porosimeter capable of generating  
15 pressure in the range of subambient to 414 MPa<sup>50</sup> (60000 psia).

16

17

## RESULTS AND DISCUSSION

18 The accumulation of chloride ions in the downstream compartment is shown as a function  
19 of time for OC and CPZ10 in Figure 3 for different exposure temperatures.

20 From the results obtained in this study, summarized in **Fig. 3** and **Table 4**, the results  
21 emphasize the effect of the type of concrete on diffusion coefficients. The chloride migration  
22 coefficients calculated at the temperature level for the mixture concrete containing pozzolan is  
23 lower than the migration coefficient of chloride through the ordinary concrete. Intuitively, a  
24 lower effective chloride diffusion coefficient value is expected to increase the time to  
25 corrosion initiation, consequently service life of the structure. For all temperature range 5 to

1 50°C (41 to 122°F), the use of 10% pozzolan reduce the CPZ10 migration coefficient by  
2 about 32% compared with OC migration coefficient. This result is in agreement with other  
3 researchers who have studied concrete with pozzolanic additions<sup>10,28</sup>.

4 Moreover, the water porosity of OC concrete is higher than the porosity of CPZ10 concrete  
5 (15.08% vs. 13.79%), as presented in Table 3. As shown by **Fig. 4**, the pore structure of the  
6 two kinds of specimen's concrete is characterized by MIP and presents the pore size  
7 distribution at the age of 90 days. The discussed results below are the average of two tests per  
8 sample concrete. It can be noticed that the cumulative volume of pores for OC (0.0493 ml/g)  
9 (0.75615 fl.oz/lb) showed high values than CPZ10 (0.0393 ml/g) (0.60277 fl.oz/lb), thus the  
10 volume of pores is reduced by about 20%; and the critical pore diameter which corresponds to  
11 the maximum of porosity given by the pore size distribution of CPZ10 report a distinctly  
12 different pore size diameter relative to OC (0.0935 vs. 0.0481  $\mu\text{m}$ ) (0.03681x10<sup>-4</sup> vs.  
13 0.01893x10<sup>-4</sup> in) but still remaining in the range of meso-pores. The reason for these  
14 differences in the main peak and the cumulative pore volume of concrete CPZ10 compared to  
15 OC is related to two effects, first the total volume of capillary is reduced, and second there is  
16 a shift of the curve to the left characterizing the reduction of capillary-sized pores which is  
17 explained by the refinement of the porosity due to lower amounts of pore inter-gel particles  
18 and macro-pores due to the substitution in mass content in cement by pozzolanic addition<sup>47</sup>.

19 Indeed, the substitution of 10% mass content in cement by pozzolan reacts with portlandite  
20 outcome from cement hydration and form additional calcium silicate hydrates which are  
21 filling the voids and thus reduce the interlayer interconnectivity of the pores<sup>51</sup>. Therefore, the  
22 results show that mercury porosity of CPZ10 (9.85%) is less than OC porosity (11.39%) (see  
23 Table3): the decrease of porosity is in accordance with the reduction of water porosity. The  
24 pozzolanic substitution induces a more compact microstructure and a lower pore connectivity.

25 The concrete sustainability performance is improved by substituted Portland cement by

1 pozzolanic admixture. Indeed, the lowest porous concretes (with pozzolan) are less sensitive  
2 to environmental conditions and the mass transport is slower in these concretes<sup>40,52</sup>. As  
3 results, the size of paths of chloride penetration is modified and the transport mode occurring  
4 causes a decrease in coefficient of migration of CPZ10 than OC. This is in accordance with  
5 many researchers which have proposed various relationships between diffusion chlorides and  
6 the microstructure of cement based materials such as its evolution of pore structure<sup>43,53-54</sup>.  
7 Otherwise, by examining the results of migration test for all temperature, it is clear that the Cl<sup>-</sup>  
8 diffusivity of both concretes increased with the temperature rising.

9 Additionally, the time lag  $T_{lag}$  varies with the diffusion coefficient. It was shown that for  $T_{lag}$   
10 of CPZ10 is higher than for OC for the same temperature as shown in Table 4. Firstly, a  
11 higher  $T_{lag}$  may result from a lower porosity, this is an effect of the material composition that  
12  $T_{lag}$  depends on the porosity of concrete as cited in some research<sup>55-58</sup>. Secondly, if we focus  
13 on variation of temperature for the two concretes taken separately, increasing of temperature  
14 of 5 to 50°C (41 to 122°F), has two effect: one, to release of ions binding and to increase the  
15 concentration of free chlorides in the pores and second, catalytic effect of temperature on  
16 diffusion speed, then allows to chlorides to accelerate and reach the downstream part of the  
17 material more rapidly as confirmed by researchers<sup>31,59</sup>. This phenomenon is more marked for  
18 OC than the CPZ10 because the increase of porosity and amount of binding chlorides is lower  
19 which results a great chloride diffusion coefficient evidenced by the significant decrease in  
20 delay time  $T_{lag}$  registered.

21 Furthermore, as shown the experimental results in **Fig. 5**. It can be concluded that there is a  
22 regression relation between the diffusion coefficient and the delay time as mentioned by  
23 Djerbi et al.<sup>44</sup>. This variation is depending on the temperature and it is specific for each type  
24 of concrete. From these results, a major conclusion leads us to think that the important time  
25 lag recorded for low temperature 5 °C (41°F) for both concrete CPZ10 (124 h) and OC (92 h)

1 are due to slowly kinetics chlorides penetration, characterized by small diffusion coefficients.  
2 On the other hand, at temperatures above than 30°C (86°F) the free ions in solution pores  
3 become increasingly more constant amount and are conditioning by the porosity of the  
4 material, then the diffusion is less dependent on chlorides interactions but rather, it is  
5 activated in fact in terms of the speed diffusion by increasing the temperature, it is very clear  
6 that delay times are close, and varying respectively around 12% for CPZ and 21% for OC  
7 passing from 30 to 50°C (86 to 122°F ), with the increase of the diffusion coefficient.  
8 Probably delay time can still evolve, that if the microstructure is modified by a higher  
9 temperature (to beyond 80°C (176°F))<sup>60</sup> or a mechanical damage<sup>43-44,57</sup>, resulting in greater  
10 porosity making penetration most important. it must be examined whether will there be shifts  
11 on time delay for the high temperatures.

12 **Fig. 6**, presents the evolution of migration coefficient as a function of temperature. The results  
13 show that the relationship diffusion - temperature increases regularly. Indeed, we mentioned  
14 that the coefficient of migration increases with increasing temperature from 5 to 50°C (41 to  
15 122°F). This is because the cumulative concentration of chlorides characterized with a  
16 diffusion coefficient respectively for CPZ10 and OC, in one hand, decreases by 58 and 60%  
17 with lowering the temperature from 20 to 5°C (68 to 41°F), in other hand, an increase of 64  
18 and 66% of diffusion coefficient with increasing temperature from 20 to 50°C (68 to 122°F).  
19 in other words, we can see that a penetration kinetics of chlorides is lower at low temperatures  
20 (5°C) (41°F) resulted with an effective diffusion coefficient ( $D_{mig}$ ) of more than about two  
21 times lower in an ambient temperature of 20°C (68°F), and a penetration rate of chlorides  
22 with higher temperature (50°C) (122°F), has led to about three times diffusion coefficient in  
23 relation to a temperature of 20°C (68°F). It is worth to mention that the increase of diffusion  
24 coefficient with the temperature level for each concrete investigated is consistent with some  
25 works without taking reference to the methods used by these authors<sup>10,25,26,32-34</sup>.

1 In fact, at the temperature of 5°C (41°F), the coefficient of diffusion is lower for both  
2 concrete, because ionic diffusion and chemical reaction are showed down; this finding is in  
3 accordance with some works<sup>32,61</sup>.

4 In the case of temperature 20 and 30°C (68 and 86°F) experimentally, the both concrete  
5 diffusion behaved slightly evolution in terms of chloride diffusivity registered; that display  
6 limited to a relative variation of 23%.

7 However, we can also observe that the effect of the increase in temperature causes a large  
8 coefficient in the temperature range from 30 to 50°C (86 to 122°F) then the average variation  
9 is about 33% for a gap of 10°C (50°F). As a consequence, the effect of the speed level of  
10 chloride penetration is due to the impact of the temperature level on the diffusion coefficient  
11 in the temperature range above 30°C (86°F). This was evidenced by a bi-linear trend (see **Fig.**  
12 **6**), which is more representative of the evolution of diffusion temperature.

13 In fact, the diffusion coefficient values tend to increase with temperature; that means the  
14 temperature modify significantly the diffusion coefficient. Such evolution can be expected to  
15 have a substantial impact on the service life of reinforced concrete in chloride environments.  
16 Therefore, structures exposed to hot climates will potentially deteriorate more rapidly due to  
17 increased transport and chemical reaction rates. This observation is in accordance with other  
18 work on slightly different materials<sup>10,32,61</sup>.

19 Of this, it's more important to take role of temperature on ionic transport in cementitious  
20 materials, in order not to underestimate the life of structures.

21 Furthermore, the  $D_{mig}$  of concrete can be estimate based on the energy calculated by the  
22 Arrhenius equation at different temperatures. The relationship of the logarithm  $\ln(D_{mig})$  as a  
23 function of the reciprocal of the absolute temperature is shown in **Fig. 7**.

24 From these Figure, the adjustment of the curve made by linear regression analysis of the  
25 Arrhenius equation, leads us to estimate by means of the slope of this line the value of the

1 activation energy which is respectively about 32.45 kJ/mol for OC and 30.02 kJ/mol for  
2 CPZ10 (see **Fig. 7**). The correlation coefficients for the lines obtained for OC and CPZ10  
3 were calculated to be 0.98. Therefore, it can be concluded that the diffusion of  $\text{Cl}^-$  in concrete  
4 follows the Arrhenius theory and it can be noted that logarithms of the diffusivity of chloride  
5 in concrete, were linearly proportional to the reciprocal of absolute temperature.  
6 The result of activation energy obtained is close to those obtained by some authors<sup>10,26,28,30</sup>  
7 cited, a value that fluctuates between 17.9 and 40 kJ/mol for cement, mortar and concrete  
8 materials.  
9 We mention that the activation energies obtained from cement paste might be different from  
10 those obtained from concrete. Thus, we will compare our activation energies values with  
11 those obtained by Dousti et al.<sup>10</sup>, including control concrete ( $E_a = 29.40$  kJ/mol) and concrete  
12 mixture incorporating 10% of the natural zeolite ( $E_a = 28.88$  kJ/mol), which seems close  
13 natural pozzolan used in this study<sup>56</sup>. Then, it seems that the values obtained for the two kinds  
14 of concretes are relatively close. This fact indicates that the kinetics chloride diffusivity in  
15 concrete apparently agrees with the Arrhenius theory. At the end, from experimental results,  
16 the activation energy calculated can be used into Eq. (1) to estimate diffusion coefficients at  
17 different temperatures. **Fig. 8** shows the comparison between the experimentally data obtained  
18 and the calculated values. Then, we conclude that exists a good agreement as confirmed by  
19 Dousti et al.<sup>10</sup>.

20

21

## CONCLUSIONS

22 The objective of this study was to evaluate the influence of pozzolanic substitution and the  
23 effect of temperature on the effective diffusion coefficient of chloride in the concretes. The  
24 main conclusions of the present study are:

1 1. The characterization by MIP measurements of concrete for substitution of part of the  
2 cement mass proportion (10%) of the pozzolan showed a significant reduction in the  
3 porosity of the CPZ10 concrete than OC concrete. This was explained by the reduction of  
4 the pores volume and the critical diameter, which leads a microstructure more compact;  
5 whole largely conditioning the transport mechanisms in the concrete. In terms of  
6 sustainability, it is systematically confirmed by recording a reduction of diffusion  
7 coefficients.

8 2. The presence of pozzolan in the cement used as mass substitution (10%) can significantly  
9 reduce porosity and effective diffusion coefficient of concrete studied for all temperatures  
10 range.

11 3. The temperature level has an impact on the kinetics of penetration of chlorides. Then, it  
12 always recording an increase of the effective diffusion coefficient of both concrete OC and  
13 CPZ10 studied when the temperature rising. There is a decreasing regression between  
14 coefficient diffusion and time lag. Thus, the time lag ( $T_{lag}$ ) was almost decreasing and the  
15 influence of temperature is well related to the weakness of binding chloride which becomes  
16 minimal above 30°C (86°F) as confirmed by an increase of diffusion coefficient du the speed  
17 diffusion and close time lag.

18 4. The activation energy calculated from the Arrhenius equation remains close to that  
19 presented in the literature.

20 5. Finally, it can be seen that the relationship between the logarithms of diffusion coefficient  
21 and reciprocal of absolute temperature are linearly distributed. Therefore, it can be concluded  
22 that the behaviour of diffusion Cl<sup>-</sup> in concrete follows the Arrhenius theory. Also, a good  
23 agreement was found between the experimental data and the Arrhenius theory.

24

25

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4 Laboratory (France) and EOLE Laboratory (Algeria) for their support.

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## TABLES AND FIGURES

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**Table 1–Chemical compositions of cement and pozzolan (%)**

	CEM II/A 42.5	Pozzolan
SiO <sub>2</sub>	27.95	46.8

Al <sub>2</sub> O <sub>3</sub>	5.43	18.8
Fe <sub>2</sub> O <sub>3</sub>	3.05	10.5
CaO	56.37	9.2
MgO	0.71	3.8
SO <sub>3</sub>	2.53	0.2
Na <sub>2</sub> O	0.30	0.8
K <sub>2</sub> O	0.43	0.5
CaO <sub>Free</sub>	0.75	–
Loss of ignition	3.11	6.5

1

2

**Table 2–Mineralogical (Bogue) compositions of cement**

Bogue composition (%)	
C <sub>3</sub> S	55.65
C <sub>2</sub> S	20.18
C <sub>3</sub> A	9.77
C <sub>4</sub> AF	9.5
Gypsum	3

3

4

**Table 3–Mixture proportions and physical properties**

Mix ingredients	OC	CPZ10
Coarse aggregate, (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	1109 (69.23)	1109 (69.23)
Sand, (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	660 (41.20)	660 (41.20)
Cement CPA-CEM II/A 42.5 (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	350 (21.84)	315 (21.84)
Pozzolan (kg/m <sup>3</sup> ) (lb/ft <sup>3</sup> )	-	35 (2.18)
w/b (%)	0.55	0.55
Slump (cm) (in)	8 (3.14)	7 (2.75)
Compressive strength at 28 days (MPa) (psi)	34.10 (4945.78)	32.50 (4713.72)
Compressive strength at 90 days (MPa) (psi)	37.80 (5482.42)	40.20 (5830.51)
Water porosity (%)	15.08	9.85
Mercury porosity (%)	11.39	11.39

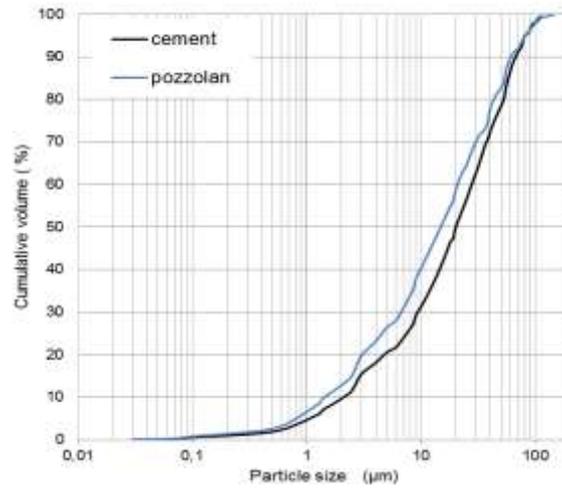
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**Table 4–Coefficients of diffusion at different temperatures.**

Temp. °C (°F)	Coefficients of diffusion		Lag time (Hours)		Activation Energy	
	D <sub>mig</sub> m <sup>2</sup> /s. E <sup>-12</sup> (ft <sup>2</sup> /s)		T <sub>lag</sub>		Ea (kJ/mol)	
	OC	CPZ10	OC	CPZ10	OC	CPZ10
5 (41)	2.03 (21.85)	1.49 (16.03)	92.51	124.04		
20 (68)	5.13 (55.21)	3.56 (38.31)	54.84	57.51		
30 (86)	6.71 (72.22)	4.52 (48.65)	47.04	56.73	32.45	30.02
40 (104)	10.10 (108.71)	6.34 (68.24)	44.18	51.61		
50 (122)	15.32 (164.90)	9.91 (106.67)	41.33	44.34		

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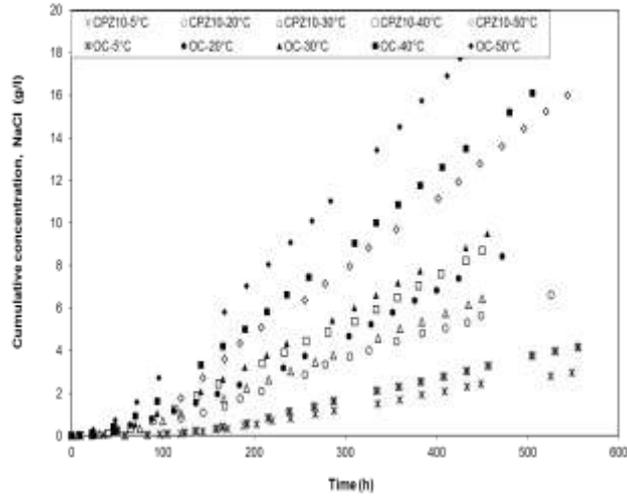
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**Fig. 1– Laser granulometry of Cement and Natural pozzolan (Note :  $1 \mu\text{m} = 3.937 \cdot 10^{-5}$  in.) .**



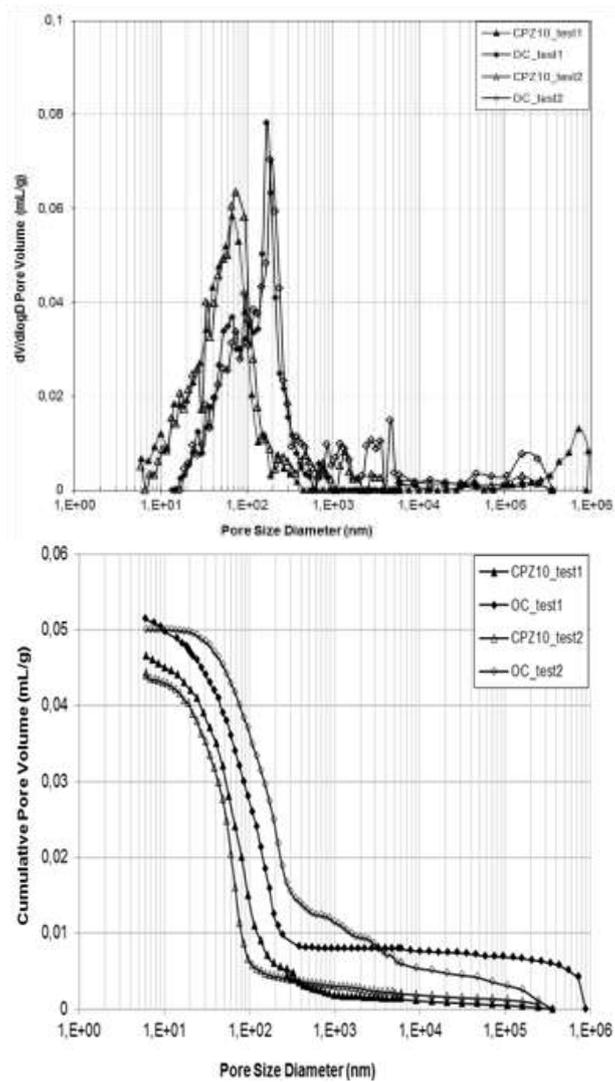
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**Fig. 2–Migration cell with hot and cold device.**



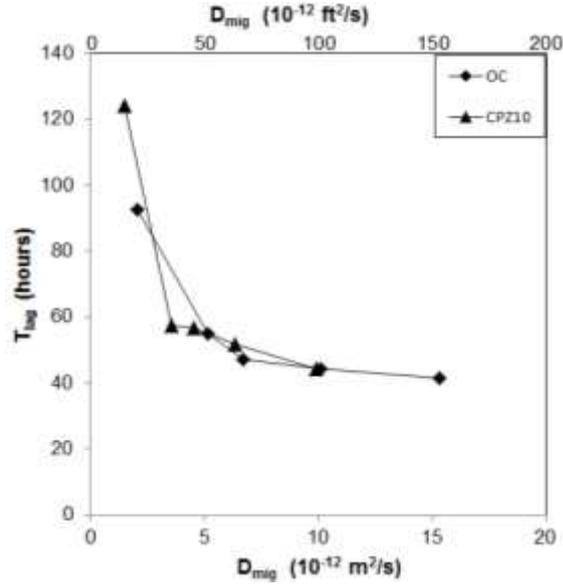
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**Fig. 3–Evolution cumulative increase of chloride concentration in downstream cell of OC and CPZ10 at different temperatures (Note : 1 g/l = 0.0083 lb/gal).**

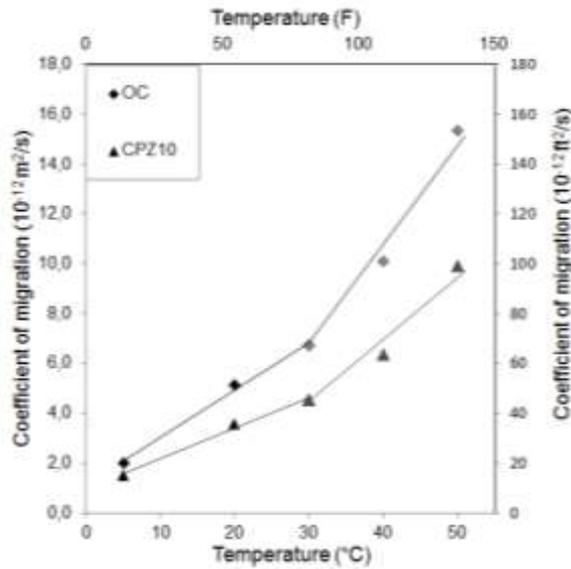


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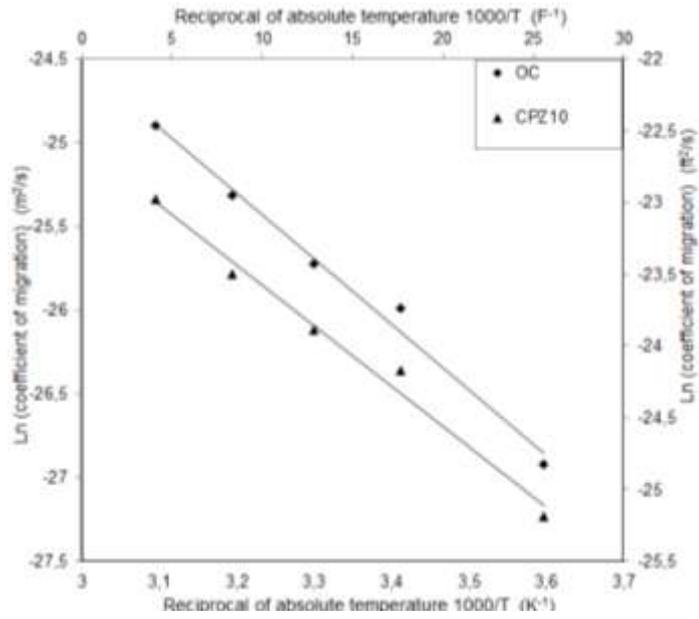
1 **Fig. 4–Measured porosity in OC and CPZ10 specimens using MIP test (Note : 1 nm =**  
 2 **3.937 10<sup>-8</sup> in. and 1 ml/g = 15.337 fl.oz/lb).**



4  
 5 **Fig. 5-Relationship between the time lag and the diffusion coefficient of function of the**  
 6 **different temperatures.**



8  
 9 **Fig. 6–Chloride diffusion coefficient as a function of temperature.**

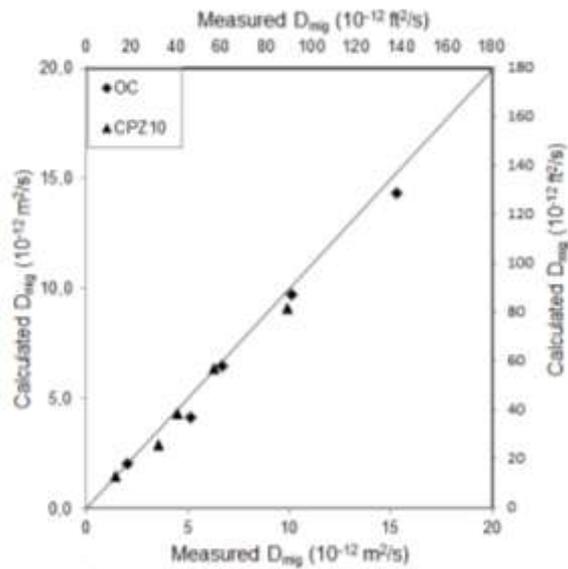


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**Fig. 7–Arrhenius plots of the diffusivity in concrete mixtures.**

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**Fig. 8-Comparison between the experimentally obtained and calculated diffusion coefficients.**

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