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Numerical and Experimental Study of Chloride Ion Transport in Recycled Aggregates Concrete

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ABSTRACT

This paper analyses, both experimentally and numerically, the transport of chloride ions inside concrete. The samples are made from either 100% Natural Aggregates (NA) or 100% Recycled Concrete Aggregates (RCA). The goal of this research is to quantify the loss of durability of Recycled Aggregates Concrete (RAC) with respect to Natural Aggregates Concrete (NAC), possibly promoting their use in long-term building.

The experimental campaign focused on evaluation of transfer properties of concrete: water absorption, retention curves, intrinsic permeability, chloride diffusion under steady and unsteady state and conduction experiments were performed. The results depict that RAC tends to have higher exchange rates with the environment than NAC, mainly due to the increased paste content from the recycled aggregates.

Keywords Chloride ions, Durability, Recycled Concrete Aggregates, Multiscale Modeling, Experimental Study

I. INTRODUCTION

Recycled Concrete Aggregates (RCA) are produced from the recycling of Construction and Demolition Waste (C&DW), providing a sustainable source of aggregates. RCA contains Natural Aggregates (NA) as well as residual adherent mortar. This gangue decreases their properties both mechanically and from a durability point of view. Literature has proven that RCA have an increased porosity and water absorption compared to NA, which favours the penetration of water and chloride ions, increasing its diffusivity inside Recycled Aggregates Concrete (RAC) (Akbarnezhad, Ong., Tam, & Zhang, 2013) (Hu, et al., 2018) (Rao, Jha, & Misra, 2007) (Sun, Chen, Xiao, & Liu, 2020).

RCA have been studied for many years, mainly focusing on their mechanical properties. In this study, the focus is rather on the durability of concrete made from RCA, and specifically its resistance to chloride attacks. Chloride attacks are a major cause of degradation in coastal areas as well as where de-icing salts are used (Mangat & Molloy, 1994) (Morga & Marano, 2015). The chloride ions penetrate the concrete through its porous system, concentrate near the steel rebars and possibly corroding them. This corrosion is called pitting corrosion due to its local aspect, and induces a loss of section for the reinforcements, possibly leading to a structural failure (Angst, Elsener, Larsen, & Vennesland, 2009).

This paper analyses concretes made from 100% NA (NAC) or 100% RCA (RAC) experimentally as well as numerically. The dual approach is necessary nowadays to ensure the development of a model representative of the reality.

II. MATERIALS AND METHODS

A. Compositions of the material used

Several materials have been characterised experimentally, to better understand the chloride ingress inside the microstructure of concrete:

- NAC: a micro-concrete with natural 2/7 aggregates of limestone origin;
- RAC: the same micro-concrete, whose particle size distribution is reconstructed with recycled aggregates to mimic the one of the natural aggregates, keeping a constant volume fraction;
- E-M: an equivalent-mortar with natural 0/2 Rhine sand;
- E-CP: an equivalent plain cement paste.

The compositions and important fresh properties are visible in the Table 1.

Table 1 - Compositions and water-to-cement ratios of the materials used

Composition	M_agg (kg/m ³)	M_sand	M_cement	M_water	W/C	Efficient W/C
NAC	1111	643	320	172.5	0.54	0.5
RAC	946	643	320	201.5	0.63	0.5
E-M	-	1337	622.5	336	0.54	0.54
E-CP	-	-	1240	647	0.52	0.52

The main compositions of interest are the NAC and RAC. Their efficient water-to-cement ratio are equal, allowing a better comparison of the results obtained experimentally.

B. Description of the experiments performed

The experimental plan performed in this study yields macroscopic homogenized properties for our compositions. By comparing those results between the compositions developed, we may be able to observe differences in properties due to the substitution/addition of a particular ingredient. A focus is done on the experiments on chloride diffusion.

The first test performed is Water Absorption by Immersion (WAI) (NBN B 15-215:2018 and NBN EN 772-4). It allows the determination of the dry and humid densities of our compositions, as well as inform us on their water absorption and water-accessible porosity.

Secondly, we also want to determine how easily fluids can percolate within the porous structure of our materials. This is achieved by means of a water permeability experiment (NBN EN ISO 17892-11:2019), yielding results in terms of intrinsic permeability of the porous media. It is based

on the constant head method and analysed with Darcy's law under the hypothesis of a permanent flow in saturated porous media.

Once this is achieved, we focus on the exchanges the media can have with its environment, which is studied through static sorption and desorption experiments. The results of those tests can be interpreted into Water Retention Curves (WRCs): these are curves linking the saturation degree of the porous system with the external environmental conditions, such as the relative humidity and the temperature, through the expression of the suction. More information on this test can be found in (Fanara, Courard, Collin, & Hubert, Transfer properties in recycled aggregates concrete: Experimental and numerical approaches, 2022).

In addition to those experiments that are purely oriented on the properties of the microstructure of concrete, chloride-related experiments are performed, under steady-state and unsteady-state. Furthermore, a conduction experiment is performed to measure the electrical resistance of our concretes, resistance that can be transformed to a resistance to chloride ions' penetration inside the porous structure. These three experiments are detailed below.

B. 1. Chloride Diffusion under Steady-State

The experiment of chlorides' diffusion under steady-state yields the effective diffusion coefficient of chloride ions inside concrete, noted D_{eff} .

Each sample ($\varnothing 80\text{mm}$ - H20mm) is saturated in a lime solution to ensure that the chloride ingress is solely due to the diffusion and not to capillary suction. The samples are then used to create diffusion cells (Figure 1): they are sealed between two compartments that contain two solutions of with different compositions. The first chamber contains a saturated lime ($\text{Ca}(\text{OH})_2$) solution whose concentration is equal to 3g/L while the other one contains, in addition to the saturated lime solution, an aqueous solution of sodium chloride (NaCl) whose concentration is equal to 3M.

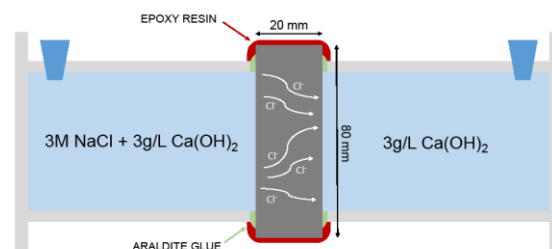


Figure 1 - Representation of a cell for the diffusion of chloride ions under steady-state

Once a week, 10ml of solution is collected in the first chamber that contained, initially, no chloride ions. The concentration in chloride content can then be determined by means of potentiometric titration, revealing the amount of chloride ions that has passed through the sample after a certain period of time. After each sampling, 10ml of solution must be added back to the cell in order to keep an equal volume between the two compartments and therefore keeping a constant concentration gradient. Obviously, the added solution must contain the same chloride concentration as the one that was sampled for the potentiometric titration.

The effective diffusion coefficient is calculated from the ion flow that has reached a steady-state. The constant flow J [kg/m².s] parallel to the direction of ion diffusion is given by the first law of Fick:

$$J = \frac{D_{eff}}{e} (C_1 - C_2) \#(1)$$

where D_{eff} [m²/s] is the effective diffusion coefficient, e [m] is the height of the sample, C_1 [kg/m³] is the chloride concentration in the initially saturated compartment while C_2 is the chloride concentration in the other compartment where the sampling was performed.

Another way to express the ionic flow is with the help of the following equation:

$$J = \frac{V_2}{A_2} \frac{dC_2}{dt} \#(2)$$

where V_2 [m³] is the volume of the solution in the second chamber and A_2 [m²] is the area of that chamber in contact with the sample.

By matching the two equations written above and then integrating with respect to time, from the first time where chlorides enter the second chamber (t_0) to the duration of the experiment (t), one obtains the following expression:

$$\int_{t_0}^t \left(\frac{D_{eff}}{e} (C_1 - C_2) \right) dt = \int_{t_0}^t \left(\frac{V_2}{A_2} \frac{dC_2}{dt} \right) dt \rightarrow \ln \left(1 + \frac{C_2}{C_1 - C_2} \right) = \frac{D_{eff} A_2 (t - t_0)}{e V_2} \#(3)$$

And finally, if the chloride concentration in the second chamber is smaller than the concentration in the first chamber ($C_2 \ll C_1$), which is always the case, one can write:

$$C_2 = C_1 \frac{D_{eff} A_2 (t - t_0)}{e V_2} \rightarrow D_{eff} = \frac{V_2}{A_2} \frac{C_2}{(t - t_0)} \frac{e}{C_1 - C_2} \#(4)$$

B. 2. Chloride Diffusion under Unsteady-State

The diffusion test can also be performed under transient conditions: it consists of determining an apparent diffusion coefficient (D_{app}) from the total chloride concentration profile in the sample.

The samples (Ø80mm – H50mm) are initially saturated with a lime solution to ensure the diffusion of ions and no other convective movements. Sides that will not be in contact with the chloride solution will be covered with an epoxy resin to ensure a one-dimensional penetration of the chloride ions. The samples are then immersed in a saline solution of NaCl whose concentration is equal to 165±1 g/L. They are stored in a closed chamber whose temperature is maintained constant to 23°C. The experiment is represented in the Figure 2.

Sampling is performed after a 15, 29 and 91 days on three separate samples. It requires to grind the sample perpendicularly to the exposed surface at different depths to determine, from the powder obtained, a chloride profile inside the sample. The powder is then completely dried in an oven, weighed and the chloride concentration is determined by potentiometric titration using the "AgNO₃ SOL" method.

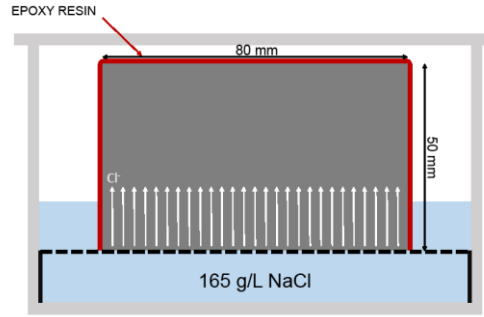


Figure 2 - Diffusion experimental device for chloride diffusion under transient conditions

The unidirectional ingress of chloride ions inside our sample can be approximated by Fick's second law, yielding an analytical solution using the error function:

$$\frac{\partial C}{\partial t} = D_{app} \frac{\partial^2 C}{\partial x^2} \rightarrow C(x, t) = C_s - (C_s - C_i) \times \operatorname{erf}\left(\frac{x}{2\sqrt{D_{app}t}}\right) \quad \#(5)$$

B. 3. Electrical conductivity

The conduction experiment is intended to measure the electrical current flowing through a sample in a given period of time. A total penetration charge can be determined for each sample, and then used to estimate the chloride ion permeability of our compositions, according to the standard ASTM C 1202-05. The samples ($\varnothing 100\text{mm} - \text{H}50\text{mm}$) are covered in an epoxy resin on their lateral side. They are then saturated in water before starting the experiment. To ensure the saturation, the water absorption is performed under a vacuum, according to the standard NBN B 24-213.

The standard recommends using a voltage of 60V, however our cells are not equipped with temperature probes and this higher voltage would be increasing the "Joule effect", creating heat and modifying the relations to be used. Therefore, a reduced voltage is used, decreasing the temperature increase inside the sample and the solutions used. The positive terminal is connected to the cell that contains the solution of NaOH while the negative terminal is connected to the other cell. An ammeter is then connected between those two terminals to measure the intensity of the electric current flowing through the sample. Due to our reduced voltage, the readings are to be corrected according to the Ohm law. The experiment lasts 6 hours at a constant voltage, and measurements are performed every 300 seconds. A representation of the setup is shown in the Figure 3.

The total electric charge passed through the sample, noted Q (in coulombs), is calculated by integrating the results (intensity over time). One way to perform this integration is by using the trapezoidal rule (with one point every 30 minutes as given in the standard, to be adapted for our case):

$$Q_{initial} = 900 \times \left(I_0 + 2 \times \left(\sum_{i=30}^{300} I_i \right) + I_{360} \right) \quad \#(6)$$

where I_0 is the current (in amperes) measured immediately after the application of the voltage, and I_i is the current at time i (in minutes).

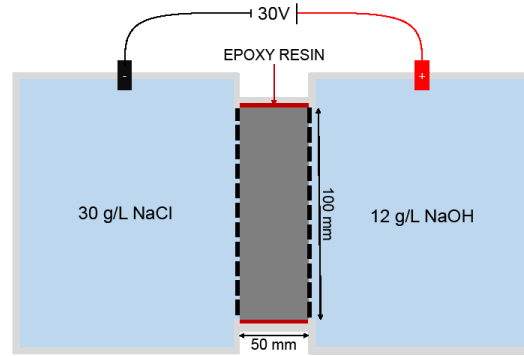


Figure 3 - Representation of the conduction experiment

This law is based on a sample whose diameter is equal to 95mm. Our samples being 100mm in diameter, it is thus required to modify the total electric charge according to the following equation:

$$Q_{diameter} = Q_{initial} \times \left(\frac{95}{100}\right)^2 \quad \#(7)$$

A final correction is then made to account for the reduced voltage used. The Ohm law ($V = R \times I$) states that, at equal resistivity (which we assume here), doubling the voltage means doubling the current passing through the sample. Therefore:

$$Q_{voltage} = 2 \times Q_{diameter} \quad \#(8)$$

This total electric charge ($Q_{voltage}$ after the two corrections) that has flowed through the sample can be linked to several chloride permeability class through the Table 2 [Whiting, 1981].

Table 2 - Chloride permeability class regarding the total electric charge flowing through a sample in a conductivity experiment (from [Whiting, 1981])

Chloride permeability	Charge passed [Coulombs]
High	>4000
Moderate	2000-4000
Low	1000-2000
Very low	100-1000
Negligible	<100

III. RESULTS AND DISCUSSION

The results of the experimental campaign, for all the experiments performed, are visible in the Table 3. For the chloride diffusion experiments, an in-depth analysis is available below.

For the water absorption experiment, it resulted that the E-CP has the greater porosity and water absorption, followed by the E-M, then the RAC and finally the NAC. This is not surprising as the porosity is mainly found inside the mortar matrix of the concrete, the aggregates and sand

particles being rather not porous. However, the porosity of the cement paste is less permeable than the one of the mortar, as proven by the water permeability experiment. It means that the porosity of the mortar is more connected than the one of the cement paste. Following this information, the NAC is therefore less permeable to water than the RAC, due to the adherent mortar brought by the recycled aggregates. Moreover, the concretes are both less permeable to water due to the impervious nature of natural aggregates.

For the static sorption and desorption experiment, the RAC has the lower air entry pressure of all the compositions, followed by the E-CP and E-M, and finally the NAC. This proves that the RAC has a greater exchange rate of moisture with its environment than the NAC.

Table 3 - Results of the experimental campaign

Parameter	E-CP	E-M	NAC	RAC
<i>Water absorption experiment</i>				
Dry density [kg/m ³]	1463	2025	2263	2061
Saturated density [kg/m ³]	1914	2253	2405	2266
Water Absorption [% Mass]	30.87	11.27	6.26	9.95
Porosity [% Volume]	45.01	22.83	14.16	20.5
<i>Water permeability experiment</i>				
Intrinsic Permeability [10 ⁻¹⁹ m ²]	3.82	38.7	1.73	2.58
<i>Static sorption and desorption experiment</i>				
Air entry pressure [MPa] for sorption/desorption	3.84/10.95	2.75/11.55	3.45/13.83	3.56/10.43
Parameter n_{vG} (slope) [-] for sorption/desorption	1.50/1.51	1.49/1.51	1.51/1.53	1.51/1.48
<i>Diffusion under steady-state</i>				
D_{eff} [10 ⁻¹³ m ² /s]	6.22	8.17	5.99	15.4
<i>Diffusion under unsteady-state</i>				
D_{app} [10 ⁻¹¹ m ² /s] at 15/29/91 days	1.63/1.51/-	1.71/1.43/0.92	1.77/1.41/2.77	2.46/1.65/1.78
C_s [% total mass]	4.15	1.45	0.79	1.27
Depth of [Cl] = 0.4% total mass [mm] at 15/29/91 days	12.1/16.2/-	11.9/15.1/21.5	12.2/15.1/37.5	15.8/18.0/33.1
<i>Conduction</i>				
Charge passed [Coulombs]	/	5808	3141	5290

A. Diffusion under steady-state experiment

The Figure 4 represents the evolution of the chloride content with time. The effective diffusion coefficient D_{eff} is obtained by finding the linear part of those curves, then using the Equation 4. One can see that the curves are relatively linear, proof of the stationary state obtained.

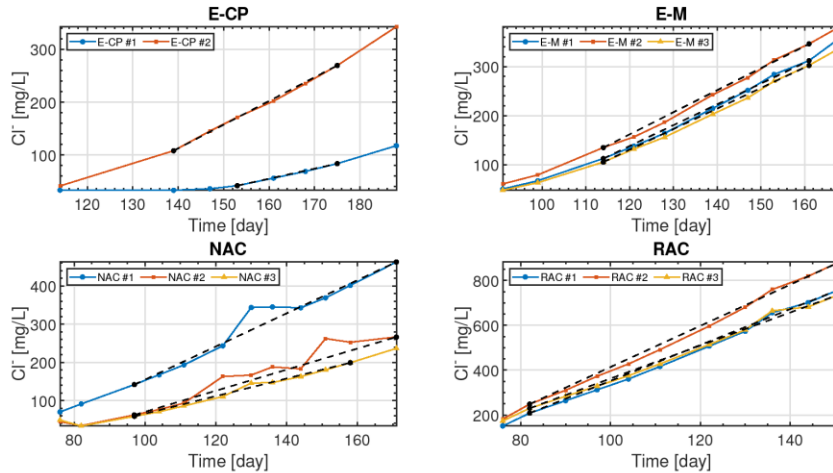


Figure 4 - Results of the diffusion experiment under steady-state

B. Diffusion experiment under unsteady-state

The Figure 5 represents the experimental results obtained for the chloride diffusion experiment under unsteady-state. The chloride content, in % of total mass, is given with respect to the depth inside the sample, after 15, 29 and 91 days.

Those results are then analysed and fitted by Fick’s second law of diffusion (Equation 5). The results are displayed in the Figure 6 and Figure 7. The parameters of the equation are also noted in the legend: the diffusion coefficient, the surface concentration, the depth at which the critical chloride content (0.4% of binder mass) is reached and, finally, the R² value assigned to the fitting.

The first point of each series of measure is neglected, as recommended by the standard. For the RAC, a sample gave inconclusive results and was therefore not used in the analysis.

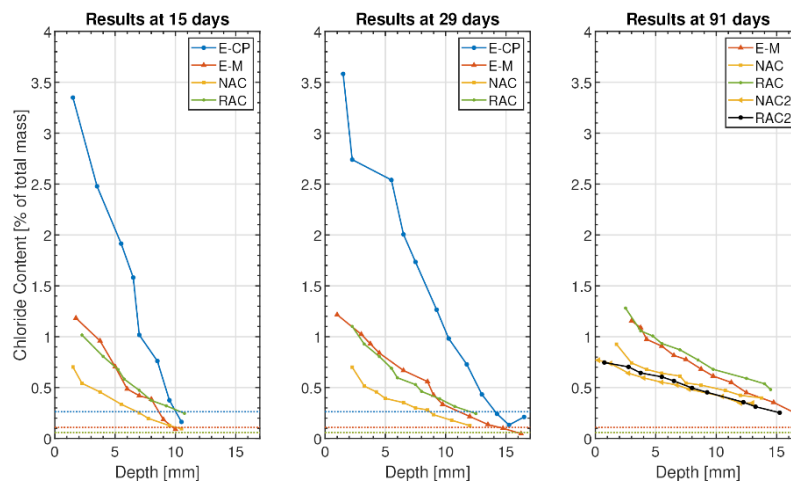


Figure 5 - Experimental results of the chloride diffusion under unsteady-state

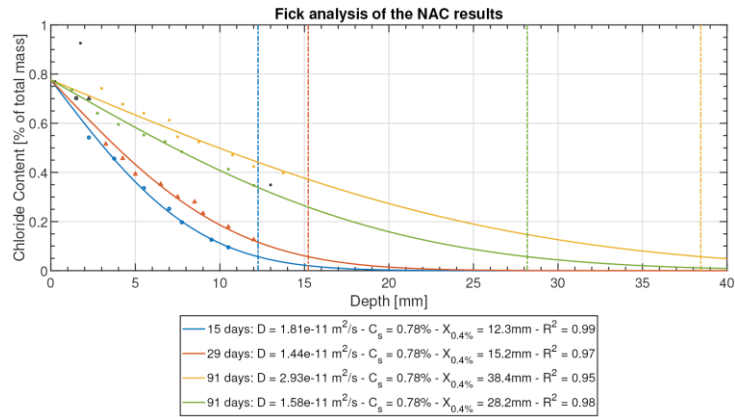


Figure 6 - Fick analysis of the NAC results for the chloride diffusion under unsteady-state

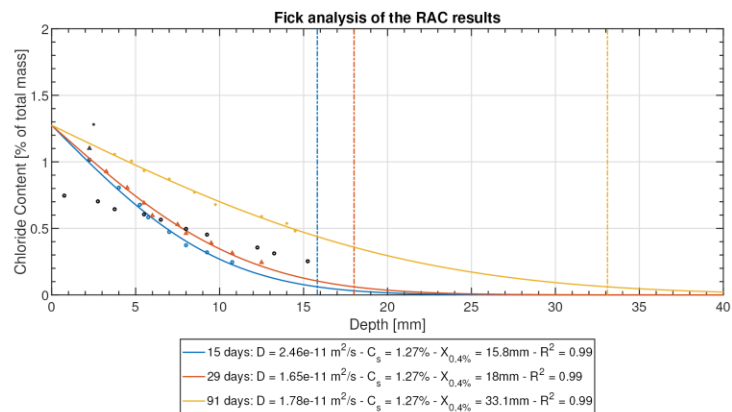


Figure 7 - Fick analysis of the RAC results for the chloride diffusion under unsteady-state

The surface concentration is determined by fitting in this case. However, knowing the chloride content in the solution, it would be possible to determine it theoretically based on the porosity and dry density of our compositions. The exercise has been done and it resulted in a porosity approximately 20% greater with this experiment than with the Water Absorption by Immersion experiment.

IV. CONCLUSION

This paper analysed experimentally the chloride ingress inside concretes made from Natural Aggregates and Recycled Concrete Aggregates, as well as an equivalent cement paste and an equivalent mortar. The results show that:

- The greater the volume fraction of mortar paste there is, the greater the porosity and water absorption: the adherent mortar of the RCA renders the RAC more porous than the NAC;
- The substitution of NA by RCA increases the intrinsic water permeability of concrete, even though the results are relatively close;

- The water retention curves of the RAC exhibits greater water exchange rates with its environment than the NAC;
- The RAC displays a greater diffusion coefficient (either apparent or effective) than the NAC, which is also confirmed by the conduction experiment. **A study of the chemical and/or physical absorption of chloride ions inside the porous structure of concrete is foreseen to better analyse this difference in diffusion.**

The use of RCA inside concrete therefore results in worse properties with respect to the chloride ingress inside the porous system. However, the results are not excessively different than for a concrete made from NA. Thus, substituting NA by RCA would indeed decrease the durability of concrete, but not dramatically. Further numerical results would be necessary to assess the lifetime decrease and better balance the loss of durability with the environmental advantages of this substitution. The first results of our numerical model can be seen in (Fanara, Courard, & Collin, FE² multiscale modelling of chloride ions transport in recycled aggregates concrete, 2022).

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