

The relation between electrokinetics and chloride transport through cement-based materials

D. Voinitchi^{a,b}, S. Julien^a, S. Lorente^{a,*}

^a *Laboratoire Matériaux et Durabilité des Constructions, INSA-UPS, Toulouse, France*

^b *Technical University of Civil Engineering, Bucharest, Romania*

Received 18 May 2007; received in revised form 24 August 2007; accepted 13 November 2007

Available online 21 November 2007

Abstract

The objective of this study is to determine how the use of an electrokinetic technique (migration) has an impact on chloride transport through cement-based materials. Electrokinetic transport of ions is the transport of ions under the influence of an electrical current, and is also named migration. The paper emphasizes the impact of electrokinetics on the total chloride concentration profile through saturated mortar both in transient regime, and in steady state during chloride penetration, and chloride extraction. For chloride decontamination, an explanation is proposed for the different shapes of the curves representing the chloride mass flow rate and the amount of chloride extracted in time from the mortar, measured with or without an electrical current. The efficiency of the electrokinetic dechloruration is proposed in terms of amount of removed chloride.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Electrokinetics; Mortar; Chloride

1. Introduction

The penetration of chloride through cement-based materials represents a major threat to the integrity and performance of reinforced concrete structures. If the amount of chloride is sufficiently high in the vicinity of the reinforcement bars, the passivity film may be altered, and rebar corrosion may be initiated.

Because of this threat, the chloride diffusion coefficient measured for a given material became an indicator of the durability of cementitious materials. Several methods to measure this coefficient exist, including electrokinetically accelerated chloride tests in steady and non-steady states. Among them are the AASHTO [1] or ASTM [2] test, the non-steady test migration test proposed by Tang and Nilsson [3], the LMDC-Test, which is a steady state migration test initially proposed by Truc et al. [4] and improved later by Khitab et al. [5]. The calculation of a diffusion coefficient

based on the combination of a multi-species model and on the electrical current measurement was proposed by Samson et al. [6]. More recently, Yang et al. [7] proposed to calculate the non-steady state chloride diffusion coefficient by measuring the electrical current in an electrokinetic test. While the steady state migration tests are not affected by the relationship between chloride and the solid phase, the situation is different in the non-steady state. The key question therefore is to determine whether the application of an electrical current has an impact on the chloride binding to the solid phase of the cement-based materials.

Electrokinetics, as far as chloride is concerned, has another domain of application in addition to the accelerated chloride diffusion coefficient tests. Once chloride has penetrated the cementitious material, one way to prevent the corrosion of the reinforcement bars in concrete is to force the chloride to leave the structure by using an electrical current. The reinforcement bars are polarized as cathode, while an external electrode (a grid) is placed against the material which plays the role of an anode. Under the influence of the applied electrical current the chloride is

* Corresponding author. Tel.: +33 5 61 55 99 14; fax: +33 5 61 55 99 49.
E-mail address: lorente@insa-toulouse.fr (S. Lorente).

attracted toward the outside because it is an anion. Details on the electrokinetic removal of chloride can be found in Refs. [8–12]. The advantage of using migration to extract chloride from concrete is to reduce significantly the time required by the process. But, does the electrokinetic removal have also impact on the efficiency of the decontamination, namely on the decontamination rate?

The present work addresses the effect of migration, an electrokinetic technique on the chloride transport through cement-based materials. By using a CEM-I type mortar, the study documents the impact of an external current on the chloride ingress through the materials (interactions with the solid phase, and total chloride concentration profile). In dechloruration, the effect of the electrical current on the chloride decontamination rate is also revealed and compared to extraction by diffusion.

2. Experiments

The experimental procedure consisted in contaminating mortar samples with chloride by means of migration (with constant current density). Next, chloride was extracted from the samples in two ways: in one case, the driving force was only a chloride concentration gradient with the outside (diffusion), in the other case a constant current density was added to the first driving force. The characterization of the process was done through the measurements of the total chloride concentration profiles, chloride binding, and amount of extracted chloride.

2.1. Material and samples preparation

The material used in this study was a mortar with CEM-I cement which composition is given in Table 1 together with the cement composition (Table 2). The water:cement ratio was 0.43. After mixing (following EN 196-1), the mortar was poured into cylindrical moulds (11 cm diameter and 22 cm height), and kept in a wet room (20 ± 1 °C, 90% relative humidity) for 24 h. After this period, the mortar cylinders were demolded and kept in the same wet room for three months. The water porosity and the apparent dry density were measured at the end of the curing period following the AFREM-AFGC recommendations [13]. The resulting water porosity and apparent dry density were, respectively, 17.7% and 2131 kg/m^3 . The cylinders were then cut into 3-cm thick slices. To avoid wall effects, the

Table 1
Mortar composition

CEM-I 52.5 R	618 kg m^{-3}
Sand 0/4 mm,	1365 kg m^{-3}
Superplasticizer (Glenium 27)	7.7 kg m^{-3}
Water	264 kg m^{-3}
Total density	2255 kg m^{-3}
W/C (water/cement)	0.43
C/A (cement/aggregate)	0.45

Table 2
Chemical composition of the cement

% by mass	CEM-I
SiO ₂	20.3
Al ₂ O ₃	5.2
Fe ₂ O ₃	2.1
CaO	60.8
MgO	2.1
K ₂ O	0.62
Na ₂ O	0.21
SO ₃	2.95
Loss on ignition (1000 °C)	1.31

two ends of the mortar cylinders were not used in the experiments, though wall effects may be to some extent still present close to the cylindrical face.

2.2. Experimental procedures

Part of the mortar samples were tested in migration cells, the principle of which is sketched in Fig. 1. The lateral surface of the cylinders was coated with an epoxy resin. Once the sample was sandwiched between the two compartments, the assembly was tested for leaks. Each compartment was filled with 2.5 L of solution. The upstream compartment solution (cathodic compartment) was made of 1 g/L of sodium hydroxide, 4.65 g/L of potassium hydroxide and sodium chloride. The NaCl concentration added to the cathodic compartment was in one case 20 g/L (for 3-cm thick specimens), and in the other 30 g/L (for 2-cm thick samples). For the sake of maintaining constancy of the boundary conditions for ionic species, the cathodic solution was periodically renewed. In each case, three samples of mortar were tested in parallel. The anodic compartment contained a solution of NaOH (1 g/L) and KOH (4.65 g/L). The solution of NaOH (1 g/L) and KOH (4.65 g/L) was chosen in order to meet (at best) a typical pore solution for CEM-I type materials, as reported by Schmidt and Rostazy [14]. Electrodes, one in each compartment, were allowed to create an electrical potential difference through the mortar samples. If in the case of diffusion, the ionic transport through the material is driven by concentration gradients, in a migration process, the ionic transport is driven not only by concentration

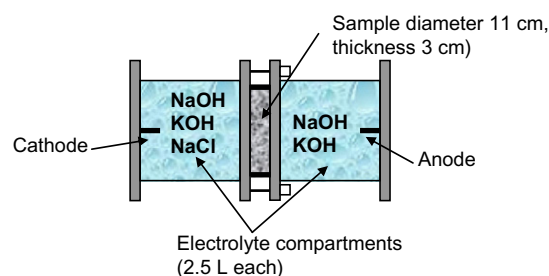


Fig. 1. Migration cell ($[\text{NaOH}] = 1 \text{ g/L}$, $[\text{KOH}] = 4.65 \text{ g/L}$, $[\text{NaCl}] = 20$ or 30 g/L , current density = 3 A/m^2).

gradients but also by the electrical field [15,16]. The electrical current density applied over the mortar samples had to be a compromise between the duration of the experiments that can be shortened with an electrokinetic test, and the temperature rise that may occur through the sample if the electrical current is too high (Joule effect). Based on preliminary experiments, a value of 3 A/m^2 was chosen. This value was maintained constant during the tests.

Before the tests, each disk of mortar was vacuum saturated with a NaOH–KOH solution. The NaOH concentration was 1 g/L , and the KOH concentration was 4.65 g/L . First the samples were placed in a sealed container linked to a pump. A void was created and maintained for 4 h. Next the NaOH–KOH solution was slowly introduced until the samples were totally covered by the solution. The void was maintained for 24 h. This procedure corresponds to the AFREM-AFGC recommendations [13].

The total chloride concentration profiles were measured after the migration tests from powders obtained after grinding the core samples of mortar following the procedure described in [17]. The method to get the total chloride is the one described in [13], which consists of extracting chloride with nitric acid: 5 g of homogenized mortar powder was mixed with 50 mL of distilled water, and agitated for 2 min by means of a magnetic agitator. 100 mL of 20% diluted nitric acid was added to this solution. The suspension was allowed to agitate at 80°C for half an hour. The hot solution was cooled down to 20°C . The cold mix-up was vacuum filtered. Approximately 150 mL of the solution was prepared for further analysis in potentiometric titration, to determine the total chloride concentration. The chloride concentration in the pore solution (free chloride) was measured with potentiometric titration after extracting the pore solution by pore pressing. The mortar sample was broken into small pieces and placed in the cell of a mechanical device that crushed the pieces with a pressure of 1 GPa. A few mL was extracted for each sample, and the obtained solution was analyzed right after the extraction.

The chloride interactions with the mortar solid phase were determined through the measurement of the chloride binding isotherm. Because all the experiments were carried in a solution made of 1 g/L of NaOH and 4.65 g/L of KOH, it was decided to keep the same solution for the binding isotherm test. To the solution of NaOH and KOH was added 1, 3, 7, 10, 20, and 30 g/L of NaCl. The mortar was crushed into very tiny pieces, and was vacuum dried. The resulting mortar pieces (50 g) were then saturated in vacuum with the contaminated solution (200 mL), before being placed in a sealed beaker with the same contaminated solution. Each container was vibrated daily to ensure the homogeneity of the solution. The chloride concentration of the solution was checked regularly until the measured value became constant. The amount of bound chloride was calculated as the difference between the initial chloride content and the final chloride content per weight of mortar.

3. Results and discussion

3.1. Contamination phase

One of the objectives of the study was to determine whether the use of an electrical field has an impact on the total amount of chloride that can be extracted from a sample of cementitious material, this is in comparison with the chloride extraction by diffusion only. The first part of the work was therefore designed to quantify the initial state to be certain that the initial state for decontamination in migration is the same for the diffusive chloride removal.

It was decided that equilibrium was obtained through the material when the amount of chloride reaching the anodic compartment became constant. At this stage, the total chloride concentration profiles were measured according to the procedure described in the preceding section. The results are presented in Fig. 2a for the cases of 20 g/L and 30 g/L of NaCl. These two cases were chosen to get two points of comparison with the chloride binding isotherm. The use of an electrical current to force an ionic species to penetrate mortar leads to a horizontal concentration profile whatever, the concentration level chosen. Such results were previously proposed by Frizon et al. [18,19], who studied cesium contamination of mortar samples by electrokinetics in the context of nuclear safety. Note that for the same boundary conditions in chloride, namely, a constant value upstream and a null concentration in the downstream compartment (and in the pore solution as initial condition), penetration due to natural diffusion would not permit the establishment of a horizontal profile. Instead, the total chloride concentration profile would decrease linearly from the highest chloride content on the face in contact with the compartment containing chloride to zero on the opposite face [20].

The way chloride enters the material under the influence of the electrical current is stressed in Fig. 2b (in non-steady state) for an NaCl level of 20 g/L . Fig. 2b shows the total chloride concentration profile measured after the constant electrical current is applied for 2 days, the corresponding current density being 3 A/m^2 . Again, three samples of mortar were tested in parallel. The chloride concentration profile exhibits a plateau on the cathodic side, combined with a classical diffusive profile towards the anodic side. The effect of the electrical current is to force chloride to fill entirely the available pores in the vicinity of the cathodic compartment, before diffusing through the material. The diffusion front is therefore displaced in the direction of the anodic side by the progression of the plateau. Note that such behavior can be predicted by multi-species numerical models such as the ones developed by [5,20–22].

The contamination of mortar samples with 20 and 30 g/L of NaCl was then repeated until steady state was reached for the purpose of measuring the amount of chloride available in the porous network in steady state (free chloride content). The measurement of chloride concentration in the pore solution obtained after pore pressing led,

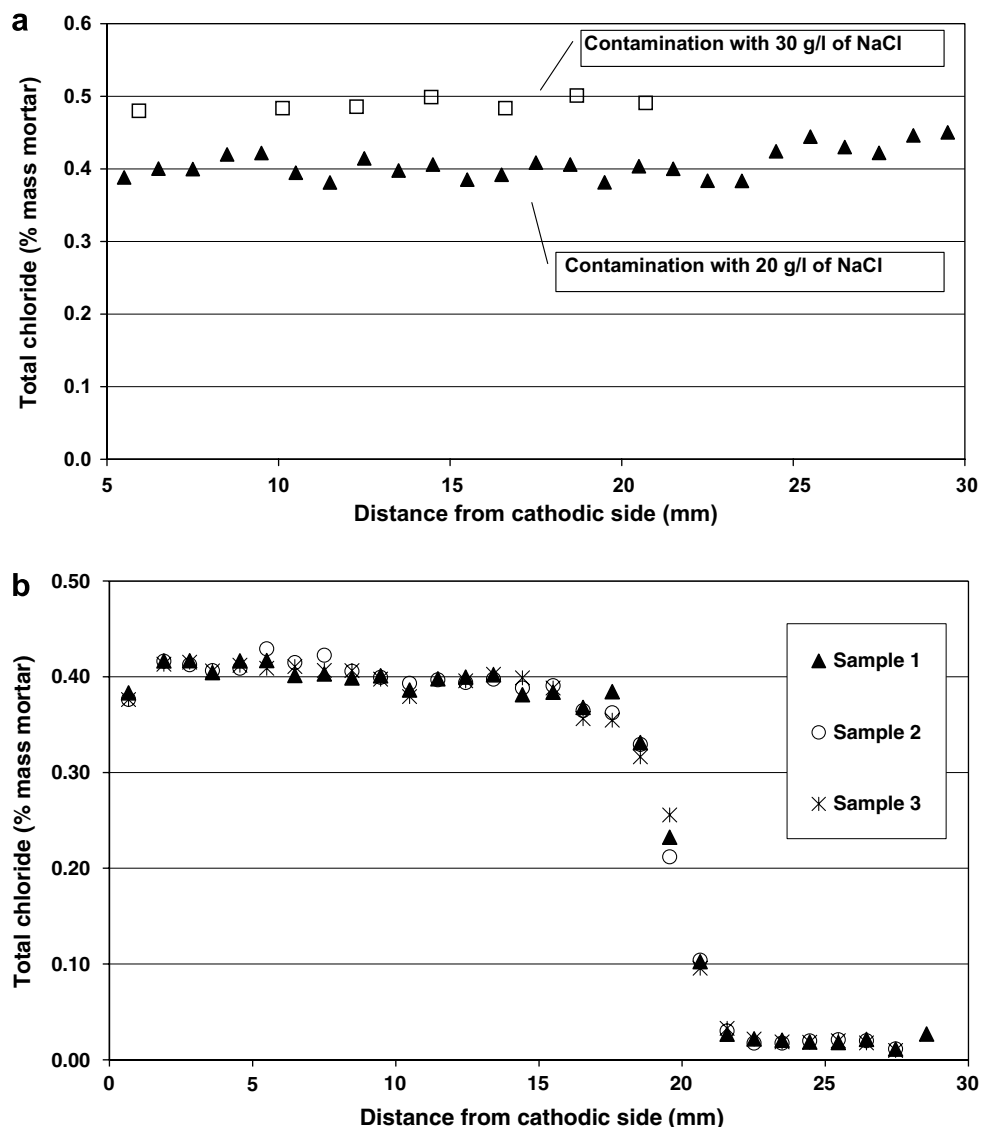


Fig. 2. Total chloride concentration profile in (a) steady state when the NaCl concentration is 20 g/L (3-cm thick specimens), and 30 g/L (2-cm thick samples), and (b) non-steady state, after 2 days of migration when the NaCl concentration is 20 g/L.

respectively, to 11.4 and 19.13 g/L of chloride. Because the total chloride concentration exhibits a plateau, it is reasonable to suggest that the free chloride concentration would also present a horizontal profile. Therefore, the measurement of the chloride concentration in the solution obtained by pore pressing is representative of the free chloride concentration for a given amount of total chloride.

The difference between the total and the free chloride is the amount of chloride bound to the solid phase of the mortar during the electrokinetic test. A value of 0.30% of bound chloride per weight of mortar was obtained in the case when 20 g/L of NaCl was added to the NaOH–KOH solution, while 0.33% of chloride was bound to the solid phase of mortar when 30 g/L of NaCl was added to the NaOH–KOH solution. The two results are plotted in Fig. 3 together with the binding isotherm obtained from the mortar left in solution with NaCl, NaOH and KOH until equilibrium. Though the time to reach equilibrium

was different, the equilibrium itself is the same. The choice of the driving force during chloride contamination, namely, concentration gradient in diffusion or electrical field combined with a concentration gradient in migration, seems to have no impact on the interactions between chloride and the solid phase of cementitious materials, at least at a macroscopic level. Note that such a conclusion was also reached by Frizon et al. [19] on cesium contamination of CEM-I type mortar. In sum, the external electrical current has no impact in the steady state on the amount of chloride that binds to the solid phase of mortar based on CEM-I type cement.

3.2. Decontamination phase

The uniformly contaminated samples were then ready for the decontamination phase. Part of the samples were tested in the migration cells, two compartments of which

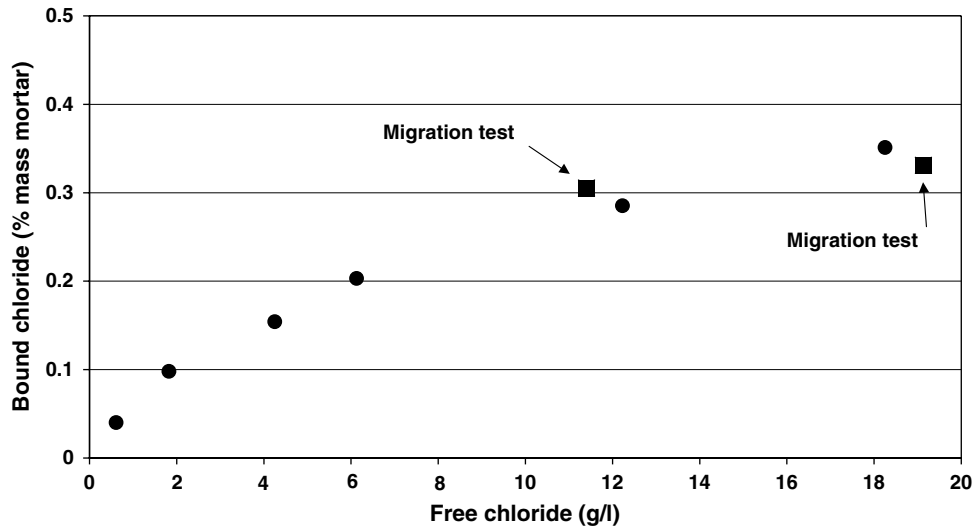


Fig. 3. Chloride binding isotherm during diffusion and the amount of bound chloride during migration.

were filled with the same sodium hydroxide and potassium hydroxide solution that was used previously. The same 3 A/m^2 current density was applied through the mortar cylinders. The solution in the anodic compartment where the chloride was expected to be detected was regularly pipetted and analyzed. Other contaminated samples were subjected to decontamination driven by a chloride concentration gradient only. Because of this, the samples were mounted on diffusion cells. Diffusive transfer being very slow through cement-based materials, the samples tested in diffusive decontamination were cut into 12 mm thick slices. One face of the cylinders was sealed with epoxy resin while the other face was in contact with a compartment containing the sodium hydroxide (1 g/L) and potassium hydroxide (4.65 g/L) solution. Because the lateral surface of the sample was already coated with epoxy resin, the ionic exchanges were unidirectional, from the sample to the only compartment filled with a solution (Fig. 4). The solution was repeatedly pipetted and the chloride content measured.

The chloride mass flow rate was regularly calculated from the measurement of the chloride content reaching the compartments. Steady state was considered to be achieved when the mass flow rate of chloride extracted from the mortar samples became null. This steady state corresponds to about 30 days in the case of diffusive decontamination but the experiments were pursued for 20 more days.

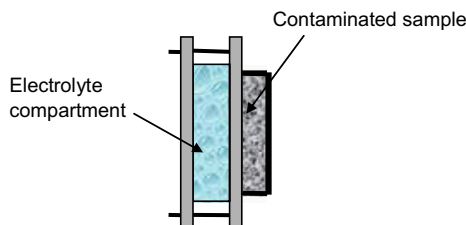


Fig. 4. Cell for decontamination by diffusion (the initial solution is made of deionized water).

The electrokinetic removal of chloride was also monitored for 50 days approximately. Fig. 5 shows the evolution of the chloride flow rate in time for both diffusive chloride decontamination and migration. When the extraction is driven by a concentration gradient only, the mass flow rate is one order of magnitude lower than the chloride flow rate obtained in electrokinetics. During the diffusion test, the mass flow rate goes to zero after one month approximately indicating that no chloride is available for extraction. In the case of the migration experiments a plateau seems to be reached after the same period meaning that the chloride is still transferred from the sample. The shapes of the two curves are consistently different. The chloride mass flow rate in migration exhibits a plateau in the beginning of the experiment, which does not appear in the case of diffusive decontamination.

The chloride mass flow rate can be calculated as the product of the flux at the interface material/downstream compartment and the cross-section of the sample. The flux is given by the Nernst–Planck equation which reads [20,23]

$$J_i = -D_i \left(\nabla c_i + z_i \frac{F}{RT} c_i \nabla \varphi \right) \quad (1)$$

where J is the flux of ionic species i ($\text{mol/m}^2 \text{ s}$), D is the diffusion coefficient (m^2/s), c is the concentration (mol/m^3), z is the charge number, F is the Faraday constant ($96,480 \text{ J/V mol}$), R is the gas constant (8.32 J/K mol), T is the temperature (K), and φ is the electrical potential (V). In the case of a natural diffusion process, the electrical potential is the membrane potential, i.e. the potential created between the different ionic species in the pore solution [24]. In migration, the electrical potential is both due to the membrane potential and the externally applied electrical potential. $\nabla \varphi$ can be expressed from the current law [23,25]

$$j = F \sum_i z_i J_i \quad (2)$$

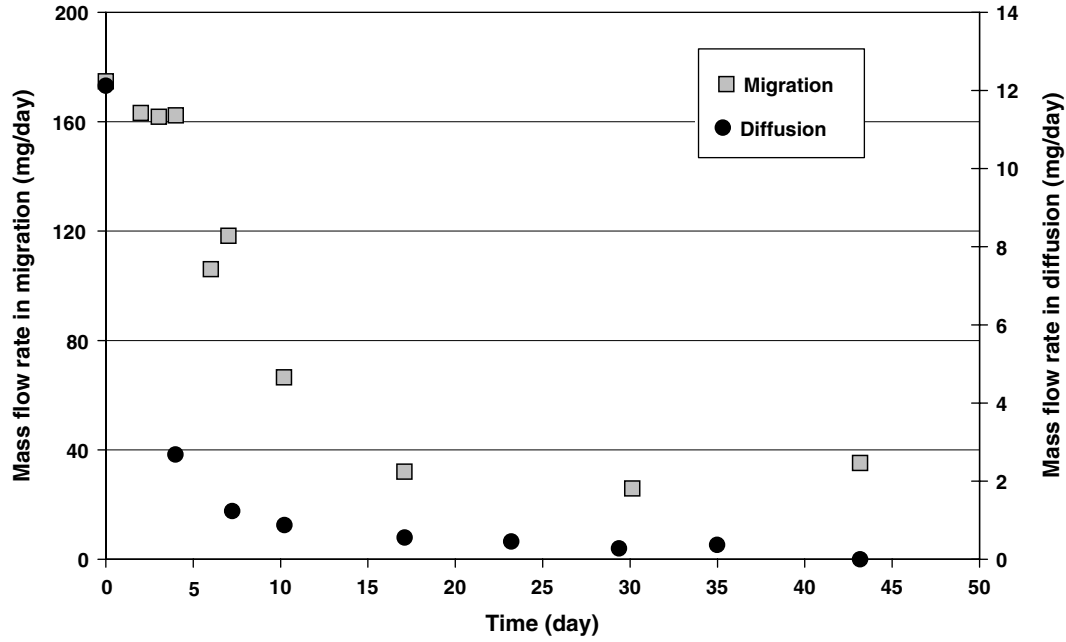


Fig. 5. Chloride mass flow rate during decontamination by diffusion and migration.

where j is the current density (A/m²), and

$$\frac{\partial \phi}{\partial x} = \frac{RT}{F} \frac{\sum_i z_i D_i \frac{\partial c_i}{\partial x}}{\sum_i z_i^2 D_i c_i} \quad (3a)$$

$$\frac{\partial \phi}{\partial x} = \frac{RT}{F} \frac{j + \sum_i z_i D_i \frac{\partial c_i}{\partial x}}{\sum_i z_i^2 D_i c_i} \quad (3b)$$

Eq. (3a) is the electrical potential in diffusion (the membrane potential), while Eq. (3b) gives the electrical potential when the electrical current density j is added.

Let A be the sample cross-section (m²). For chloride we write the flow rate \dot{q} (mol/s) as

$$\dot{q} = AJ \quad (4)$$

In an order of magnitude sense, $c \sim c_0$, $D \sim D_0$, where c_0 is the highest ionic concentration in the system, and D_0 is the highest ionic diffusion coefficient. The scale analysis of Eq. (3) for migration leads to [20,22]

$$\frac{\partial \phi}{\partial x} \sim \frac{RT}{F^2} \frac{j}{D_0 c_0} \quad (5)$$

The scale analysis is now applied to the flux of chloride on the face of the material in contact with the anodic compartment. Recall that the chloride concentration profile is horizontal, therefore,

$$j \sim \frac{D_0 c_0}{x}, \quad D_0 \frac{F}{RT} c_0 \frac{RT}{F^2} \frac{j}{D_0 c_0} \quad (6)$$

More details on the scale analysis technique can be found in [16,26]. We have

$$j \sim \frac{D_0 c_0}{x}, \quad \frac{j}{F} \quad (7)$$

and

$$\dot{q} \sim A \frac{D_0 c_0}{x}, \quad A \frac{j}{F} \quad (8)$$

Here the thickness x is an infinitely small thickness of material in which the gradients are present. On the right-hand side of Eq. (8), the first term shows the effect of diffusion, while the second term accounts for the effect of the electrical field. The thickness x (which is related to the chloride concentration profile) tends to increase in time as the concentration gradient decreases. See the total chloride concentration profile in Fig. 7 which will be commented on later. The variation of x with time can be calculated from the scale analysis of the continuity equation written for chloride at the scale of the material [22].

$$\frac{\partial c}{\partial t} = \frac{D}{p + \partial C_B / \partial c} \left(\frac{\partial^2 c}{\partial x^2} + z \frac{F}{RT} \frac{\partial c}{\partial x} \frac{\partial \phi}{\partial x} \right) \quad (9)$$

where p is the porosity, and C_B represents the concentration of chloride (mol/m³ of mortar) that interacts with the solid matrix. Eq. (9) holds for unidirectional transfer through a saturated porous system in the absence of pressure gradient. The details of this scale analysis can be found in [16,22]. The diffusive part of the continuity equation, namely, the first term in parentheses on the right-hand side of Eq. (9), gives the relation between the thickness and time:

$$x \sim \sqrt{\frac{D_0 t}{p}} \quad (10)$$

Combining Eq. (10) with Eq. (8), we obtain

$$\dot{q} \sim A c_0 \sqrt{\frac{D_0 p}{t}}, \quad A \frac{j}{F} \quad (11)$$

The flow rate \dot{q} of extracted chloride is due to the combination of two driving forces: diffusion and electrical effects. Yet, in the early stages of electrokinetic decontamination, the chloride flow rate is driven by the electrical effects ($A \frac{j}{F}$), which explains the plateau-shaped curve in the flow rate versus time (Fig. 5). Later the flow rate is dominated by diffusion, and the curve follows an equation in $t^{-1/2}$. An estimation of the transition between the two different regimes can be obtained by equating the two terms $Ac_0\sqrt{\frac{D_0p}{t}}$, and $A \frac{j}{F}$:

$$t_{\text{transition}} \sim D_0p \left(\frac{c_0F}{j} \right)^2 \quad (12)$$

Plotted in Fig. 6 is the amount of chloride measured in the anodic compartment in time in the case of a chloride extraction by migration. Also plotted in Fig. 6, but with a different scale on the ordinate, is the amount of chloride reaching the compartment when the driving force is the concentration gradient (diffusion). In the case of electrokinetic removal, from Eqs. (7) and (10), we have

$$J \sim c_0 \sqrt{\frac{D_0p}{t}}, \quad \frac{j}{F} \quad (13)$$

and

$$Q \sim Ac_0\sqrt{D_0pt}^{1/2}, \quad \frac{j}{F}t \quad (14)$$

where Q is the amount of chloride (mol).

In diffusive decontamination, the amount of chloride reaching the anodic compartment is given in an order of magnitude sense by $t^{1/2}$, while when an electrical current is added to the concentration gradient, the amount of chloride leaving the sample varies first linearly in time ($\frac{j}{F}t$) before being controlled by diffusion and shaped as $t^{1/2}$. This trend is highlighted in Fig. 6, where the amount of chloride extracted in diffusion varies as $t^{1/2}$. We also plotted

in Fig. 6 a line curve the slope of which is proportional to $\frac{j}{F}t$. This line matches the experimental data in migration, and this indicates that in the beginning of the electrokinetic extraction process the main driving force is the electrical current. Later, the diffusive part takes over.

At the end of the decontamination period, the experiments were stopped and the samples were used to control the remaining total chloride content. The results are presented in Fig. 7a and b in dimensional values. Fig. 7a shows the total chloride concentration profile measured after 50 days when the chloride contamination was driven by the concentration gradient created between the material and the outside solution of NaOH–KOH. Fig. 7b shows the total chloride concentration profile after the same 50 days for the case of the electrokinetic chloride removal. Fig. 8 presents the same results in a non-dimensional way to account for the difference in thickness of the samples decontaminated by diffusion or by migration. The sample surface in contact with the compartment corresponds to the origin of the abscissa axis for diffusion, while in the case of decontamination by migration the origin of the abscissa is taken on the anodic side.

The profile measured before the start of the decontamination phase represents the initial state, where chloride was uniformly distributed (0.41% per weight of mortar). The shapes of the two total chloride concentration profiles after decontamination are different. In electrokinetic extraction, the chloride concentration profile is shaped by two different fronts. The decontamination front on the right side (see Fig. 8) moves from the cathodic compartment towards the anodic compartment, and represents the chloride transport due to migration. The left side of the curve shows the presence of a leaching front due to the concentration gradient between the mortar sample (the left-hand side of Fig. 8) and the anodic compartment. The combined effect of two fronts, decontamination and leaching, drives the removal of chloride from the mortar sample. Interesting is the fact

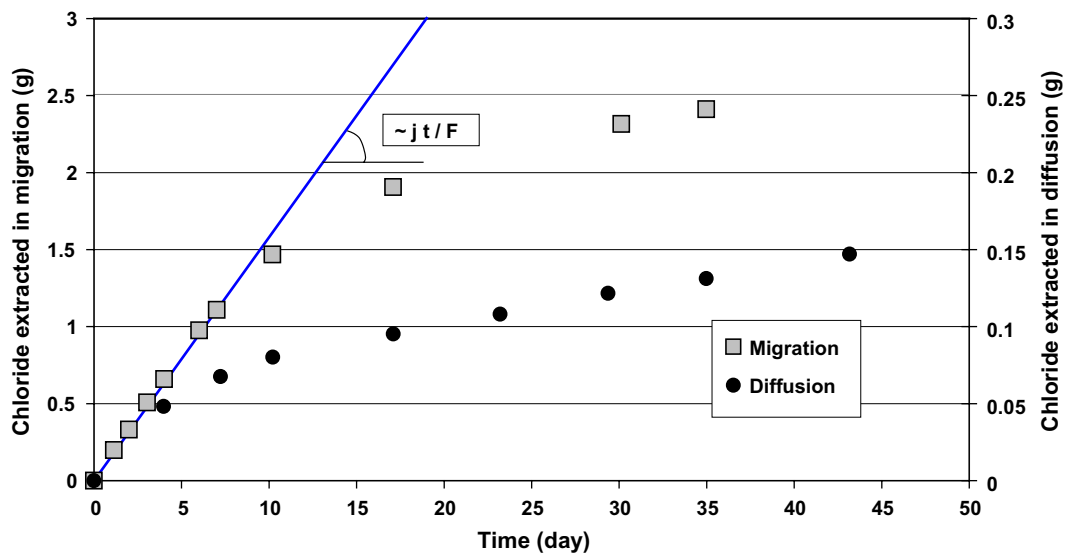


Fig. 6. The amount of chloride extracted during decontamination by diffusion and migration.

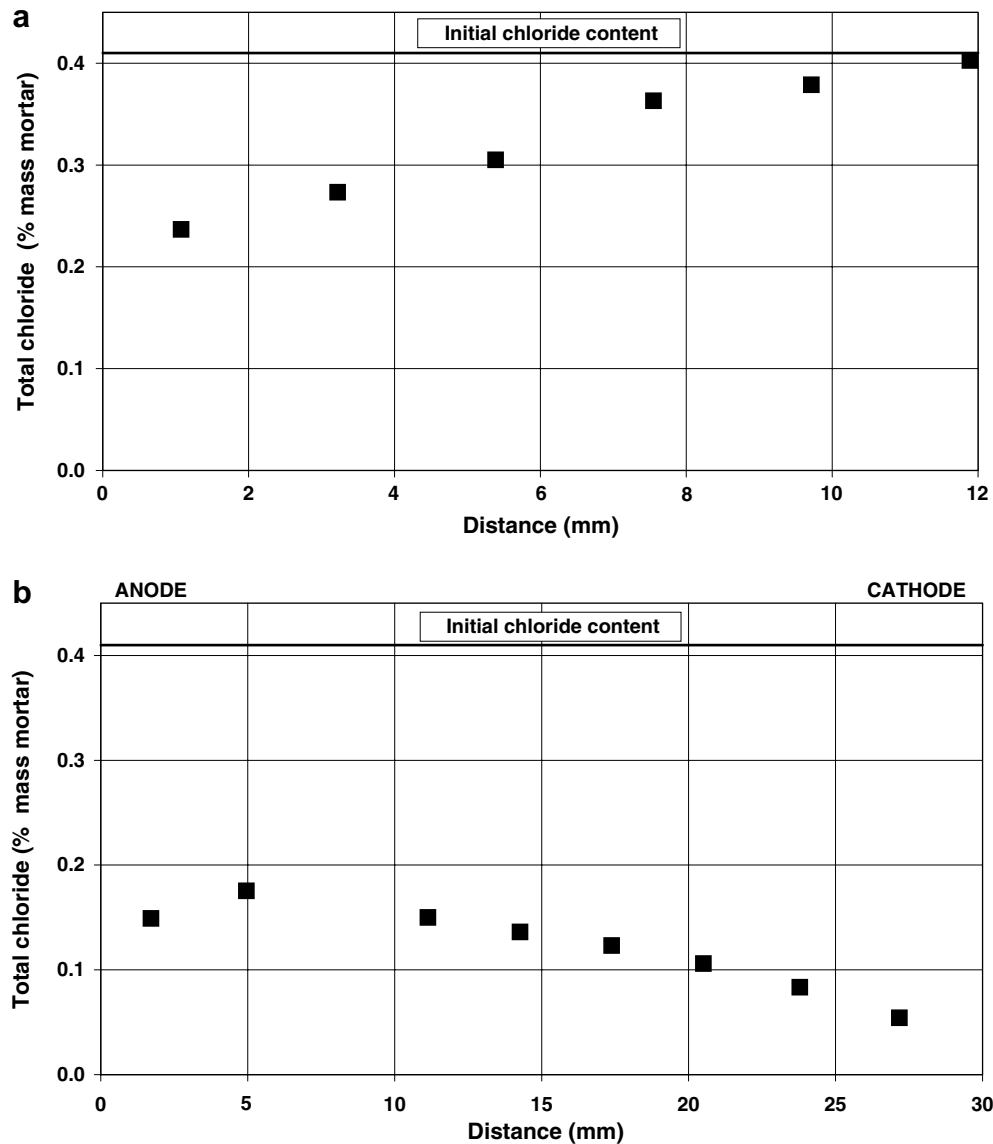


Fig. 7. The total chloride profile at the end of decontamination, (a) diffusion, and (b) migration.

that the concentration profile for chloride extraction by means of an electrical current resembles the one obtained for cesium decontamination [19].

In the case of diffusion, the 12 mm thick cylinder of mortar (11 cm diameter) contained 1 g of chloride before decontamination. Indeed, the total chloride concentration profile indicates as an initial state a uniform contamination of 0.41% of chloride per weight of mortar. Combined with the apparent volume of mortar and with the apparent density, the chloride content amounts to a total mass of chloride of 1 g. From the total chloride concentration profile remaining in the sample after decontamination (zero mass flow rate), it was calculated that 0.86 g of chloride still remained in the sample. This corresponds to an extraction rate of 20%.

In the case of decontamination by electrokinetics, the concentration profile of the total chloride remaining in

the sample is no longer uniform. A peak value of chloride (0.18% per weight of mortar) was measured at 5 mm from the anodic compartment. After 50 days of decontamination, the average residual contamination was 0.63 g of chloride, while the initial content was 2.5 g. This corresponds to a decontamination rate of 74%.

In the case of chloride extraction by diffusion, the steady state was reached after one month, meaning that no more chloride was available for removal from the mortar samples. The chloride amount that remains inside the mortar is mainly bound to the pore walls, though some free chloride may still be in the porous network but not leached out due to a weak concentration gradient with the outside. In electrokinetic extraction, the fact that the decontamination rate is 74% suggests that a certain amount of bound chloride, which is not available to chloride extraction by diffusion, becomes available to chloride removal by migration.

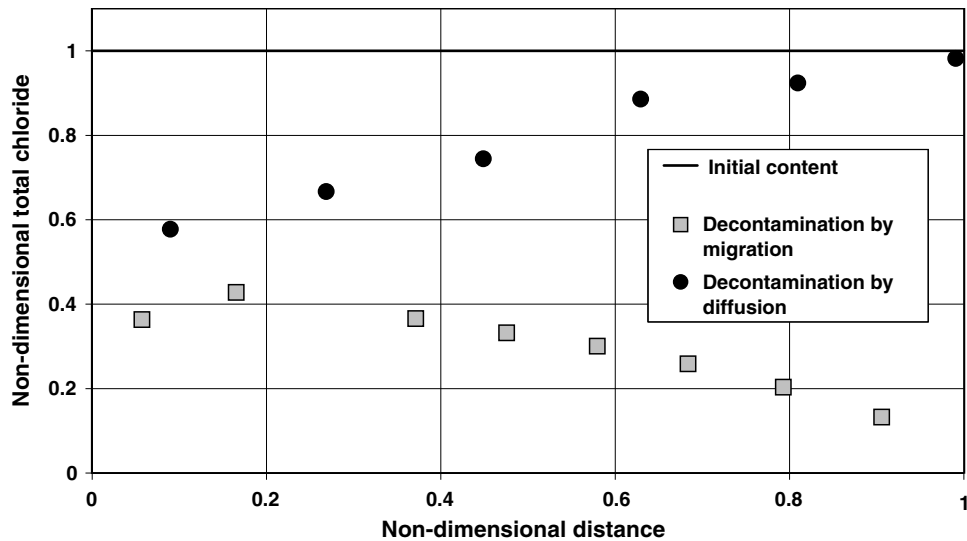


Fig. 8. Non-dimensional total chloride profiles at the end of decontamination by diffusion and migration.

Consequently, the current has an impact on the chloride desorption capacity of the material. This behavior may be attributed to the nature of the interactions between chloride and the C–S–H of the solid phase. Physical interactions of chloride with cement-based materials are explained mainly based on physical adsorption [27]. Considering that a certain number of sites are available for chloride binding on C–S–H in a sorption process, the effect of the electrical current is to enhance the kinetic of the chloride sorption. In decontamination, the electrical current modifies the electrical equilibrium of the system and chloride becomes available for extraction.

4. Conclusion

This work was dedicated to the study of the relations between chloride transport (penetration and extraction) through CEM-I type mortar and external current. The main conclusions are:

- In contamination, the electrical current forces chloride to penetrate the mortar samples leading to constant total chloride content through the specimen in steady state.
- In non-steady state, the total chloride concentration profile exhibits a plateau close to the cathodic side of the sample, then a diffusive profile in the direction of the anodic side, indicating that the porous network is filled by chloride before chloride diffuses through the material.
- In decontamination by diffusion, steady state was reached after one month leading to a decontamination rate of 20%, while electrokinetic extraction allows a decontamination rate of 74% after the same period.
- By applying scale analysis to the Nernst–Planck equation of the ionic flux, it is possible to predict the shapes of both the chloride mass flow rate in time, and the

amount of chloride extracted in time. The impact of the electrical current relative to the results obtained by diffusive extraction was highlighted.

- The interactions between chloride and mortar were measured. It was shown that the electrical current has an impact on the kinetic of the chloride absorption to the solid phase. Yet, the binding capacity of the mortar is not affected by the electrical current. The electrical current does have an effect on the chloride desorption, which explains the higher efficiency of the electrokinetic technique.

Acknowledgement

The authors would like to thank the Agence Universitaire de la Francophonie which supported this work through a grant to Prof. D. Voinitchi.

References

- [1] Standard method of test for rapid determination of the chloride permeability of concrete, AASHTO T277-86. Washington, DC: American Association of State Highway and Transportation Officials; 1996.
- [2] Standard test method for electrical indication of concrete's ability to resist chloride ion penetration, ASTM C 1202-97. American Society for Testing and Materials; 1994.
- [3] Tang L, Nilsson LO. Rapid determination of the chloride diffusivity in concrete by applying an electrical field. *ACI Mater J* 1992;89(1):49–53.
- [4] Truc O, Ollivier JP, Carcasses M. A new way for determining the chloride diffusion coefficient in concrete from steady state migration test. *Cement Concrete Res* 2000;30(2):217–26.
- [5] Khitab A, Lorente S, Ollivier JP. Predictive model for chloride penetration through concrete. *Mag Concrete Res* 2005;57(9): 511–20.
- [6] Samson E, Marchand J, Snyder KA. Calculation of ionic diffusion coefficient on the basis of migration test results. *Mater Struct* 2003;36:156–65.

- [7] Yang CC, Chiang SC, Wang LC. Estimation of the chloride diffusion from migration test using electrical current. *Constr Build Mater* 2007;21(7):1560–7.
- [8] Benson J, Eccles H. A novel technique for the decontamination of concrete and steel. *Int Mech Eng Conf Trans* 1995;7:363–9.
- [9] Dickenson KS, Ally MR, Brown CH, Morris MI, Wilson-Nichols MJ. Demonstration recommendations for accelerated testing of concrete decontamination methods. DOE; 1995.
- [10] Fajardo G, Escadeillas G, Arliguie G. Electrochemical chloride extraction (ECE) from reinforced concrete specimens containing chloride penetrated from “artificial” sea water. *Corros Sci* 2006;48(1): 110–25.
- [11] Tritthart J, Petterson K, Sorensen B. Electrochemical removal of chloride from hardened cement paste. *Cement Concrete Res* 1993;23(5):1095–104.
- [12] Swamy RN, McHugh S. Effectiveness and structural implications of electrochemical chloride extraction from reinforced concrete beams. *Cement Concrete Compos* 2006;28(8):722–33.
- [13] AFGC-AFREM. Méthodes recommandées pour la mesure des grandeurs associées à la durabilité. Toulouse, France; 1997.
- [14] Schmidt F, Rostasy FS. A method of calculation of the chemical composition of the concrete pore solution. *Cement Concrete Res* 1993;23:1159–68.
- [15] Lorente S, Voinitchi D, Bégué-Escaffit P, Bourbon X. The single-valued diffusion coefficient for ionic diffusion through porous media. *J Appl Phys* 2007;101(2):024907.
- [16] Lorente S. Constructal view of electrokinetic transfer through porous media. *J Phys D: Appl Phys* 2007;40(9):2941–7.
- [17] NORDTEST. Concrete, hardened: accelerated chloride penetration. NT BUILD 443; 1995.
- [18] Frizon F, Lorente S, Ollivier JP, Thouvenot P. Modeling the decontamination by electromigration of a porous medium. *J Porous Media* 2004;7(3):213–27.
- [19] Frizon F, Lorente S, Auzuech C. Nuclear decontamination of cementitious materials by electrokinetics: an experimental study. *Cement Concrete Res* 2005;35(10):2018–25.
- [20] Lorente S, Ollivier JP. Scale analysis of electrodiffusion through porous media. *J Porous Media* 2006;9(4):307–20.
- [21] Marchand J. Modeling the behaviour of unsaturated cement systems exposed to aggressive chemical environments. *Mater Struct* 2001;34:195–200.
- [22] Bégué P, Lorente S. Migration versus diffusion through porous media: time dependent scale-analysis. *J Porous Media* 2006;9(7):637–50.
- [23] Rubinstein I. Electro-diffusion of Ions. Philadelphia: SIAM; 1990.
- [24] Révil A. Ionic diffusivity, electrical conductivity, membrane and thermoelectric potentials in colloids and granular porous media: a unified model. *J Colloid Interf Sci* 1999;212:503–22.
- [25] Masliyah JH. Electrokinetic transport phenomena. AOSTRA technical publication series # 12. Alberta, Canada; 1999.
- [26] Bejan A. Convection heat transfer. 3rd ed. New York: Wiley; 2004.
- [27] Larsen CK. Chloride binding in concrete. PhD Thesis. Trondheim, NTNU; 1998.