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The effects of types of solutions used in accelerated chloride migration tests for concrete

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Abstract

The role of the electrolytic solution used in the accelerated chloride migration test is examined. The findings of this investigation show that the chloride flow through concrete is directly related to the amount of electrical charges transferred during the test and to the chloride transport number. Any change in the type or concentration of the electrolytic solution changes the chloride flow. Consequently, test results from different laboratories cannot be comparable if the tests were not carried out under identical conditions. The findings of this investigation also show that any substitution of solution (anodic or cathodic) could alter the anodic potential and the chloride-ion stabilization (oxidation in chlorine or hypochlorite). © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chloride; Migration; Concrete; Electrochemical properties

1. Introduction

Accelerated chloride migration tests have earned wide recognition as being useful tools in assessing the durability of reinforced concrete [1]. A number of laboratories use different types of diffusion tests to measure chloride concentration profiles and chloride diffusivity in cement-based materials [2]. During the last decade, needs for modeling and predicting durability have spurred the development of a new family of accelerated tests in which chloride penetration is accelerated by low electrical fields applied across the terminals of a diffusion cell [3]. These experimental procedures usually differ with respect to the cell geometry, the choice of the electrodes, the electrical voltage applied and, above all, the types of electrolytes in the solutions in contact with concrete. The following examples illustrate these points.

- ASTM C1202 calls for a 30 g/l NaCl solution in the upstream compartment and a 0.3-N NaOH solution in the downstream compartment [4].
- The procedure developed by Tang uses a lime-saturated solution in the downstream compartment and the same lime-saturated solution with 30 g/l of NaCl in the upstream compartment [5].
- The procedure developed by Andrade and Sanjuan [6] uses a 30-g/l NaCl solution in the upstream compartment and distilled water in the downstream compartment.
- Other labs, including LMDC, use a solution containing NaOH, KOH, and NaCl in the upstream compartment and an NaOH + KOH solution in the downstream compartment [7].

Previously published results have shown that accelerated chloride migration tests behave similarly to electrolytic cells in which the oxidation of OH^- at the anode produces oxygen and reduction of water at the cathode produces hydrogen [8,9]. Under these conditions, it needs to be determined if identical chloride-ion flows can be achieved using the various types of electrolytes listed above. This paper aims to assess the influence of electrolyte solution types and their OH^- concentration on a number of experimental parameters, including current intensity, solution conductivity, anodic potential, and chloride concentration in the downstream compartment.

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2. Experimental setup

The experimental setup includes a DC voltage source, a migration cell, and a multifunction analyzer to monitor the variations in pH, conductivity, and chloride concentration in the solutions. The migration cell is depicted in Fig. 1. The cathode (upstream) compartment contains 2.5 l of a solution containing NaOH (1 g/l), KOH (4.65 g/l), and NaCl (30 g/l). The anode (downstream) compartment contains 2.5 l of a solution containing NaOH (1 g/l) and KOH (4.65 g/l). The concentrations for NaOH and KOH were chosen in order to avoid decalcification and to simulate the pore solutions of the tested concrete; they could be different for other concretes. A graphite cathode and a titanium anode, coated with ruthenium oxide, were selected to reduce the risk of oxidation and corrosion. The potential difference between the electrodes ranged from 10 to 30 V, depending on resistivity and thickness (2 to 3.5 cm) of the concrete sample. Sensors made of coated stainless-steel wires were used to monitor the voltage differentials between the two faces of the concrete sample.

All the migration tests were carried out on samples made from a single batch of concrete with a water/cement ratio of 0.32. Two test specimens were used for each experiment. An ordinary Portland cement (CPA CEM1 52,5 R), two coarse siliceous gravel, a siliceous sand, and a superplasticizer were used to fabricate six 110 × 220 mm concrete cylinders. The mixture characteristics and some physical properties of the concrete are given in Table 1. After 28 days of water curing, the concrete disks used for the migration tests were sawed from the central section of one cylinder and stored in a curing room (100% RH and 20°C) until the age of 5 months.

3. Results

Since migration cells and electrolytic cells operate similarly, it seems logical to expect that changing the anodic solution will modify current intensity. But since the current is partially carried by the ions migrating through the system, changing the anodic solution would probably change the chloride flow through the concrete. The following paragraphs aim to demonstrate the effect of the chemical composition of the anodic solution on current intensity and chloride flow. The results can be justified by theoretical considerations.

Table 1
Mixture characteristics and physical properties of the concrete samples

Cement	425 kg/m^3
Water	136 kg/m^3
Coarse aggregate (10/14 mm)	730 kg/m^3
Coarse aggregate (4/10 mm)	400 kg/m^3
Fine aggregate (0/4 mm)	750 kg/m^3
Superplasticizer	2%[a]
W/C	0.32
28-day compressive strength	92 MPa
28-day water porosity	11.2%

[a] Expressed as dry mass of superplasticizer per mass of cement.

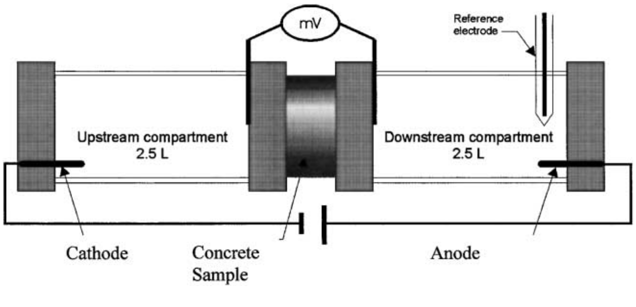

Fig. 1. Diagram of the chloride migration cell.

3.1. Influence of the type of anodic solution on current intensity and on the chloride concentration in the downstream compartment

An initial series of tests was carried out with three 30-mm-thick samples sawn from the middle section of a cylindrical concrete sample. Each migration cell holds one sample with the same cathodic solution and three different anodic solutions. The three migration cells are depicted in Fig. 2. All the samples were vacuum-saturated in the NaOH + KOH solution for 4 h before being stored in the migration cell for 24 h in the same solution. At time t_0, each upstream solution (cathode) was replaced with the NaOH + KOH + NaCl solution and the three downstream solutions (anodic) were respectively replaced with demineralized water (Cell 1), a lime-saturated solution (Cell 2), and a fresh solution of NaOH + KOH (Cell 3). The evolution over time of the current intensity and chloride concentration in the downstream compartment was monitored under a constant potential of 12 V applied across cell terminals.

Fig. 3 gives the evolution of chloride concentration in the downstream compartment of each cell. The curves show clearly that the evolution of chloride-ion concentration varies with the chemical composition of the anodic solution. Of the three solutions, demineralized water yields the lowest concentration, while the NaOH + KOH solution gives the highest. The current intensity curves are also influenced by anodic solution type (Fig. 4). As expected, the lowest intensity was obtained with demineralized water; the highest with the NaOH + KOH solution.

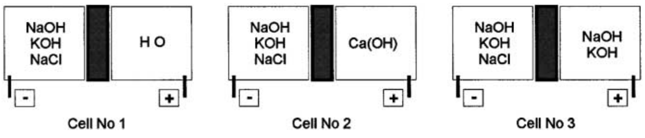

Fig. 2. Diagram of the configuration of three cells used to evaluate the effects of anodic solution on chloride migration.

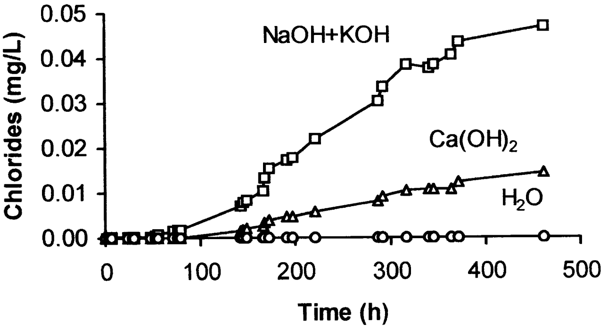

Fig. 3. Influence of the type of anodic solution on the evolution of the chloride concentration in the downstream compartment.

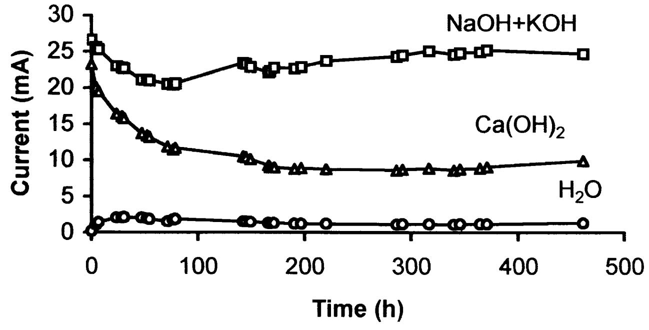

Fig. 4. Influence of the type of anodic solution on the evolution of current intensity.

In each cell, the current intensity is mainly governed by the global electrical resistance of the assembly and it corresponds to the amount of charge transferred in the system per unit of time. When electroactive ions are consumed at the electrodes, the electroneutrality of the solution must be constantly maintained by an equivalent migration of other ions. Therefore, the chloride ions migrating to the downstream compartment are necessarily linked to the number of electrical charges transferred to the electrodes. It will be shown that the chloride-ion flow corresponds to a precise fraction of the charges transferred in the system and that it depends on the chemical composition of the electrolytic solutions.

3.2. Influence of the type of anodic solution on the chloride ions migrating to the downstream compartment

Consider the simple case of a migration test with upstream and downstream compartments containing NaCl and NaOH, respectively. Also assume that a steady state has been achieved and that the ion transport is induced solely by migration, excluding any diffusion processes. All the ions in the solution participate in the current transport and their individual contribution is given by their transport number (t_i) (Eq. (1)):

$$t_i = \frac{\mu_i Z_i C_i}{\sum \mu_i Z_i C_i} \qquad (1)$$

where t_i: transport number of the ion i; μ_i: mobility of the ion i ($m^2\ V^{-1}\ s^{-1}$); Z_i: valence of the ion i; C_i: concentration of the ion i (mol/l).

In the downstream compartment, the transport number can be calculated as: $t_{Na^+} = 0.202$ and $t_{OH^-} = 0.798$. The anodic reaction is:

$$2OH^- \rightarrow 1/2O_2 + H_2O + 2e^- \qquad (2)$$

This indicates that for q charges passing through the cell per unit of time, q/F moles of OH^- will be consumed by electrolysis at the anode ($F = 96{,}450$ C). Since the electroneutrality of the solution must be constantly maintained, this process involves the simultaneous migration of 0.798 q/F moles of Cl^-, from the concrete sample towards the downstream compartment and the migration of 0.202 q/F moles of Na^+ from the downstream compartment towards the concrete sample. Globally, q/F moles of NaOH are replaced with 0.798 q/F moles of NaCl. It follows that, during the process, the electrical neutrality of the solution is maintained, but the pH and the overall ionic concentration are reduced.

In the upstream compartment, the transport numbers are $t_{Na^+} = 0.397$ and $t_{Cl^-} = 0.603$. The cathodic reaction is:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

In these conditions, when q charges pass through the circuit per unit of time, q/F moles of OH^- are generated by electrolysis at the cathode. Simultaneously, 0.397 q/F mole of Na^+ migrates from the concrete sample towards the upstream compartment and 0.603 q/F mole of Cl^- migrates from the upstream compartment towards the concrete sample. Overall, 0.603 q/F mole of NaCl is replaced by q/F moles of NaOH. Again, the electrical neutrality of the solution is maintained, but the pH and the overall ionic concentration are increased.

The experimental results are in good agreement with the above theoretical considerations. The curves in Fig. 5 were obtained with 35-mm-thick samples using voltage levels of 15 and 20 V. According to Eqs. (2) and (3), they show a significant increase in pH and solution conductivity in the upstream compartment and a simultaneous decrease of these

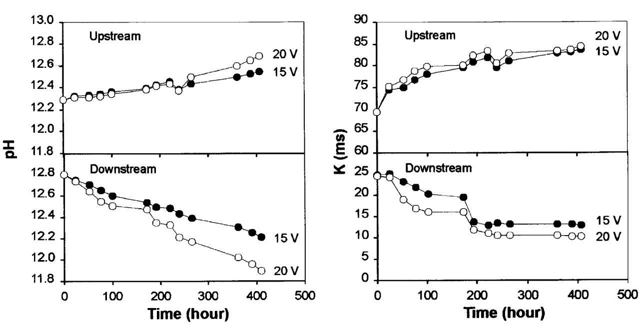

Fig. 5. Evolution of the pH and of the conductivity of the electrolytic solutions at 15 and 20 V.

two parameters in the downstream compartment. These variations are accentuated when the voltage changed from 15 to 20 V.

The main conclusion of this analysis concerns the quantitative assessment of the ionic transport towards the electrodes. The amount of chloride ions migrating in the two compartments is a defined fraction of the total charge transferred at the electrodes. This fraction is defined by the transport number of the chloride ions in the system. Therefore, for a given electrical potential, the total amount of charges transferred varies with the type of anodic solution and cannot be considered an intrinsic property of concrete.

When the NaOH anodic solution is replaced with a KOH solution, the transport numbers become $t_{K^+}=0.487$ and $t_{Cl^-}=0.509$. The number of moles of chloride ions that migrate to the downstream compartment during the transfer of q electrical charges is now 0.509 q/F instead of 0.798 q/F. If a saturated lime solution were used under the same conditions, 0.769 q/F mole of chloride would have migrated to the downstream compartment.

3.3. *Effect of the OH⁻ concentration in the anodic solution*

Generally, the preceding results show that the type of anodic solution significantly affects the flow of chloride ions migrating through the concrete sample and that the magnitude of the flow is proportional to the current intensity. A previous publication demonstrated that current intensity can easily be adapted by changing the OH^- concentration in the anodic solution [10]. Since current intensity is closely related to the anodic potential via the so-called polarization curve, and since the potential, in turn, influences the stability of the chloride ions arriving in the downstream compartment, a test procedure was developed to examine the influence of OH^- concentration on the intensity–potential curve and chloride-ion concentration measurement.

3.3.1. *Effect on the intensity–potential curves*

Three migrations cells were used with the same NaCl cathodic solution (20 g/l) but with three different NaOH anodic solutions having concentrations of 0.1, 1, and 5 N (Fig. 6).

Polarization curves, also called intensity–potential curves, were obtained by voltage measurements using a graphite cathode, a titanium anode coated with ruthenium oxide, and a reference electrode (saturated calomel) (see Fig. 7). These polarization curves can be used to explain the variations in current intensity and potential, and to understand the stability of the chloride ions that reach the downstream compartment.

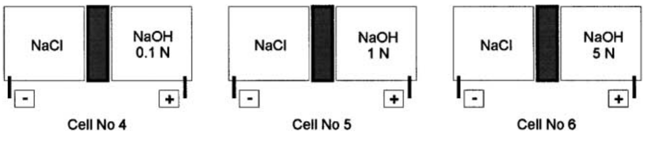

Fig. 6. Diagram of the configuration of the three cells used to evaluate the effect of the NaOH concentration on the anodic solution.

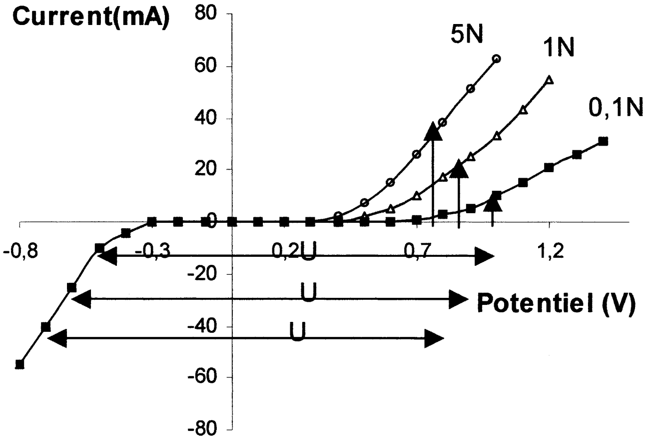

Fig. 7. Influence of the OH^- concentration on the intensity–potential curves.

The cathodic segments of the three curves are identical since the upstream compartments contain the same solution. The three anodic segments, however, are clearly different. When a constant voltage U is applied across the terminals of each cell, the system stabilizes so that the anodic and cathodic currents are equal. The curves in Fig. 7 show that, for a given voltage U, the more dilute anodic solution yields the highest anodic potential and the lowest current, while the more concentrated anodic solution yields the lowest anodic potential and the highest current.

The curves in Figs. 8 and 9 show the experimental evolution of the current and the anodic potential during a typical test run with 30-mm-thick samples under a constant voltage of 12 V. Once the system stabilizes (> 300 h), the experimental results show that increasing the OH^- concentration (from 0.1 to 1 to 5 N) increases the current intensity (17, 25, and 35 mA, respectively) and decreases the anodic potential (0.60, 0.50, and 0.40 V, respectively). These results confirm that the OH^- concentration directly affects current intensity and the anodic potential of an accelerated migration test.

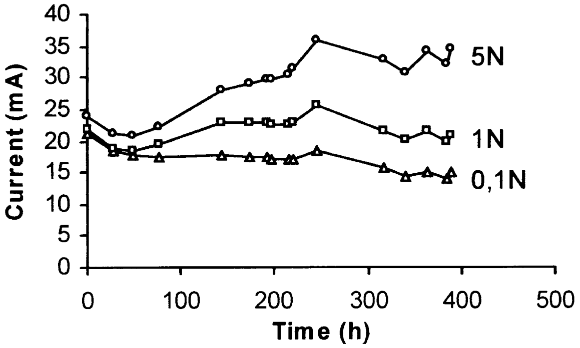

Fig. 8. Influence of OH^- concentration on current intensity in the system.

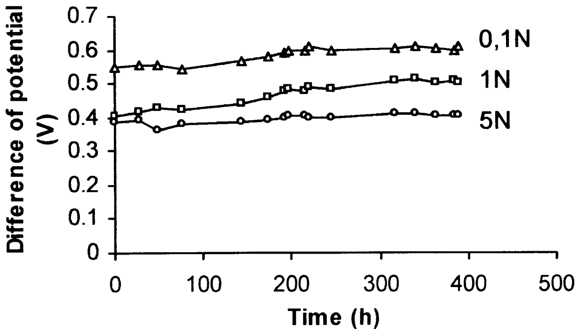

Fig. 9. Influence of OH^- concentration on anodic potential.

3.3.2. *Effect on the quantitative determination of the chloride-ion flow*

Three additional migration cells were prepared with the same upstream solution (NaOH + KOH + NaCl) and three different downstream solutions with NaOH concentrations of 0.1, 1, and 5 N. The variation in OH^- concentration alters the conductivity and pH of the anodic solution. These changes can significantly impact the quantitative determination of the chloride-ion flow.

An increase in the OH^- concentration yields an increase in system current intensity. This was previously shown in Fig. 8, in which current intensity increases proportionally to NaOH concentration. In Fig. 10, the initial chloride concentration increases with NaOH concentration; this is due to the reagent impurities. A comparison of the chloride-concentration curves in the downstream compartment shows that the evolution in time varies from cell to cell (Fig. 10). The chloride-ion concentration in the anodic solution with an NaOH concentration of 0.1 N increases constantly over time, while it fluctuates in the solutions with OH^- concentrations of 1 and 5 N. After several days, the 5 N anodic solution acquires a strong yellowish hue that suggests the formation of other chloride-based products. These results can be explained using a potential–pH relationship usually called the Pourbaix diagram (Fig. 11) [10].

The main consequence of increasing the NaOH concentration is to increase the pH. The analysis of the Pourbaix diagram shows that an increase of the pH decreases the potential required for the oxidation of chloride ions into hypochlorite (ClO^-). Under these conditions, the chloride ions that reach the downstream compartment are more easily oxidized. As a consequence, the Cl^- ion level in the downstream compartment is not entirely representative of the chloride-ion flow through the concrete sample. Overall, these results show that the OH^- concentration in the anodic solution has a direct impact on the quantitative determination of the chloride-ion flow.

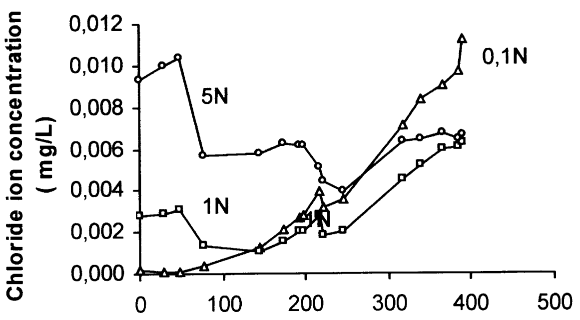

Fig. 10. Influence of OH^- concentration on chloride-ion concentration in the downstream compartment.

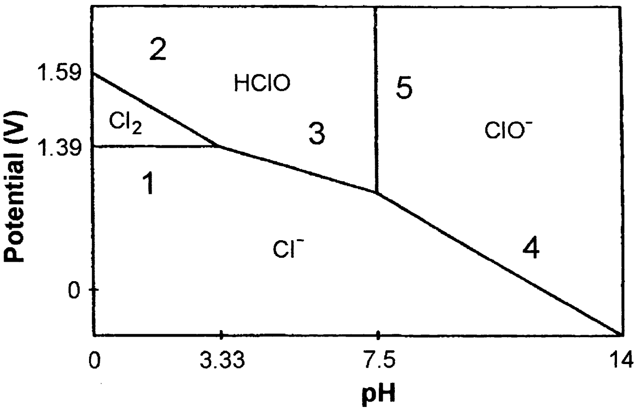

Fig. 11. Potential–pH diagram [10].

3.4. *Practical application for the usual anolytes*

Let us consider the first three migration tests involving the use of a single cathodic solution (NaOH + KOH + NaCl) and three different anodic solutions (water, $Ca(OH)_2$, and NaOH). The anodic segments of the polarization curves are depicted in Fig. 12. The measured anodic potentials for water and for the solutions of $Ca(OH)_2$ and NaOH are 5.3, 0.9, and 0.7 V, respectively.

Analysis of the Pourbaix diagram indicates that high potential values facilitate the oxidation of chloride ions into chlorine (Cl_2), hypochlorite (ClO^-), or hypochloric acid (HClO), depending on the pH of the solution. Therefore, these three anodic solutions are not equivalent, since they generate potential variation and alter chloride-ion stability in the solution. For example, replacing either

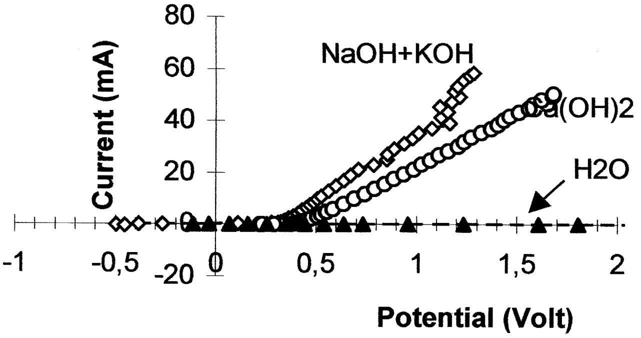

Fig. 12. Influence of the type of anodic solution on the intensity–potential curves.

the NaOH or the $Ca(OH)_2$ solution with water has two main drawbacks: On the one hand, the current intensity and, consequently, the chloride-ion flow are lower; on the other hand, the anodic potential increases. A higher potential facilitates chloride oxidation and alters flow determinations that are based solely on the dosage of chloride ions in the solution.

Generally, these results show that variation in the OH^- concentration in the anodic solution strongly influences the amount of chloride ions available in the solution. This implies that migration test results can only be reliably compared when the experimental conditions are identical. Electrolyte type and concentration figure are among the parameters that affect current intensity and, consequently, the relative proportion of charges transported by the chloride ions.

4. Discussion

Even if emphasis has been placed on the role of the anodic solution, it must be pointed out that the type of cathodic solution has also a significant effect on migration test results. Changing the cathodic solution changes the calculated transport number and, consequently, the variations of the chloride-ion flow. For example, the substitution of the usual NaCl upstream solution by an NaOH + KOH + -NaCl solution decreases both the transport number and the chloride-ion flow penetrating the sample.

The electrolysis occurring in the upstream compartment during long-term testing (no direct evaporation) may influence solution concentration by decreasing solution volume. An increase in chloride concentration in the upstream compartment is not uncommon, even if the total number of chloride ions in the solution decreases. When the determination of the chloride-ion flow is based on the evolution of the chemical composition of the upstream solution, the amount of water electrolyzed must also be calculated.

All the experimental configurations were studied using relatively aged concrete samples with constant properties and under a steady state in which interactions are negligible. The usual testing conditions are obviously different; Na^+, Cl^- and OH^- are not the only diffusing ions. Others ions, especially Ca^{++} and SO_4^{--}, also participate in charge transportation and should be included when calculating the transport number.

5. Conclusion

Ultimately, the chloride migration test must be considered as a conventional test designed mainly for concrete comparison. Since chloride flow depends to a large degree on the operating conditions, it can hardly be deemed an intrinsic parameter of concrete. The type and concentration of the electrolytic solution govern current intensity and chloride flow. The current intensity and chloride flow for a concrete and at a given applied voltage could be reduced by a factor of 10 if sodium hydroxide is substituted for water in the anodic compartment. In addition, changes in the electrolytic solution alter the anodic potential and strongly affect the chloride determination. Indeed, chloride could oxidize to chlorine or hypochlorite if the anodic potential is high.

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