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Mechanisms involved in the accelerated test of chloride permeability

William Prince [a,*], René Pérami [b], Marguerite Espagne [b]

[a]Laboratoire de Matériaux et Durabilité des Constructions, UPS-INSA Génie Civil, Complexe Scientifique de Rangueil, 31077 Toulouse cedex, France
[b]Laboratoire de Minéralogie et Matériaux, Université Paul Sabatier, 39, Allées Jules Guesde 31000 Toulouse, France

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Abstract

This paper describes a specific device that allows good assessment of the mechanisms involved in the standardized test of the accelerated determination of chloride permeability. Current, pH, conductivity, and chloride concentration were regularly monitored during the test. It appears that electrolysis is the main process involved in this test and that the role of hydroxide ions is essential. We underlined the analytical precautions of chloride determination in the anodic compartment. The AASHTO test detects correctly the interconnected pores network in which ions migrate, but it does not determine the true importance of the chloride ions that flow through the material. Consequently, if concrete samples of different compositions are to be compared, a simple determination of the amount of electrical charges could lead to serious misinterpretation. © 1999 Elsevier Science Ltd. All rights reserved.

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The test currently used to characterize the chloride permeability of concrete is the one developed by Whiting and standardized by the American Association of State Highway and Transportation Officials (AASHTO T277-831) [1]. This test quantifies the amount of electrical charges that passes through a slab during a period of 6 h. The result is expressed in coulombs and is generally drawn by the curve giving the variation of the current. Several works [2–6] were devoted to this test, and a good correlation were underlined between the results of this test and the compactness of the concrete. Concrete with a high water-to-cement (w/c) ratio is more permeable to chloride than concrete with a low w/c ratio. However, some authors wondered about the basis of this test and the mechanisms involved in it. For example, Whiting [7] in his first publications, thought that chlorides are stopped in the concrete and do not pass through the sample. In contrast, Cabrera and Claisse [8] indicated that the charge transfer is mainly due to the hydroxide of the concrete and not to the chloride. However, determinations carried out in the downstream compartment of the diffusion cell showed that chlorides migrated surely in this compartment. Therefore, it seems that the contribution of chloride is not clearly established. The aim of this study is to examine thoroughly the mechanisms involved in this test. For that purpose, we developed a special device that allows continuous determination of the main parameters of the system.

1. Experimental device

A schematic diagram of the device used in this study is shown in Fig. 1. The whole experiment requires a voltage generator, potentiometric analyzer, milliampermeter, diagram recorder, magnetic agitator, and diffusion cell. The diffusion cell is a cylindrical PVC tank covered with a lid. The test tube is a cylindrical core of concrete (100-mm diameter and 100-mm height) in which a secondary drilling produces a central cavity (C) of 40-mm diameter. This tube is fixed firmly in the cell by the intermediary of a hollow PVC roll. The sample delimits two compartments sealed by two elastomer membranes. The external compartment contains about 1.2 L of NaCl of definite initial concentration. This solution is homogenised periodically by mechanical agitation or blowing of air. A cylindrical stainless steel electrode dips in this solution and is connected to the negative pole of the generator. The internal compartment contains about 0.2 L NaOH uninterruptedly homogenised by magnetic agitation. A carbon electrode dips in this solution and is connected to the positive pole of the generator. The amount of chlorides that diffuses through the porous tube of concrete is followed with a great sensitivity using a chloride probe.

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* Corresponding author. Tel.: 33-5-61-55-77-66; Fax: 33-5-61-55-03-93; E-mail: prince@cict.fr.

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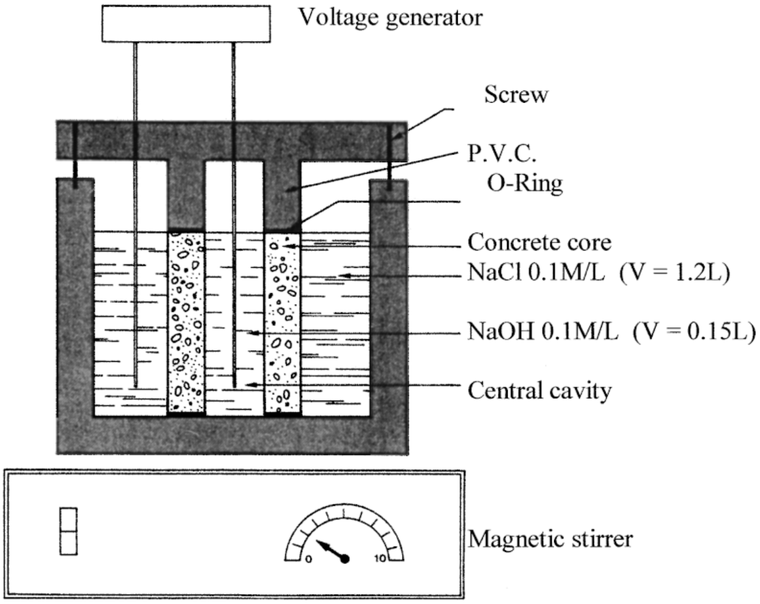

Fig. 1. Chloride migration device.

2. Results

The typical test in this study consists of filling up the cathodic compartment with NaCl 0.1N and the anodic compartment with NaOH 0.1N. The voltage applied between the two electrodes is limited to 30 V to avoid any abnormal heating of the sample and to reduce the risk of chloride oxidation on the anode. During the test, which lasts several days, we carry out regular determinations of the pH, conductivity, and chloride concentration. The current is recorded uninterruptedly. The electrolytic solutions were renewed daily so that the temperature increase did not exceed 1.5°C.

The compositions of the concrete are summarised as follows:

CPA-CEM I-42.5 300 kg/m^3
Silica fume 30 kg/m^3
Calcareous filler 80 kg/m^3
Silico-calcareous aggregate
0.5 mm 762 kg/m^3
5/12.5 mm 312 kg/m^3
12.5/25 mm 860 kg/m^3
Water 127 kg/m^3
Plasticizers 10.5 kg/m^3
Water/Cement 0.30

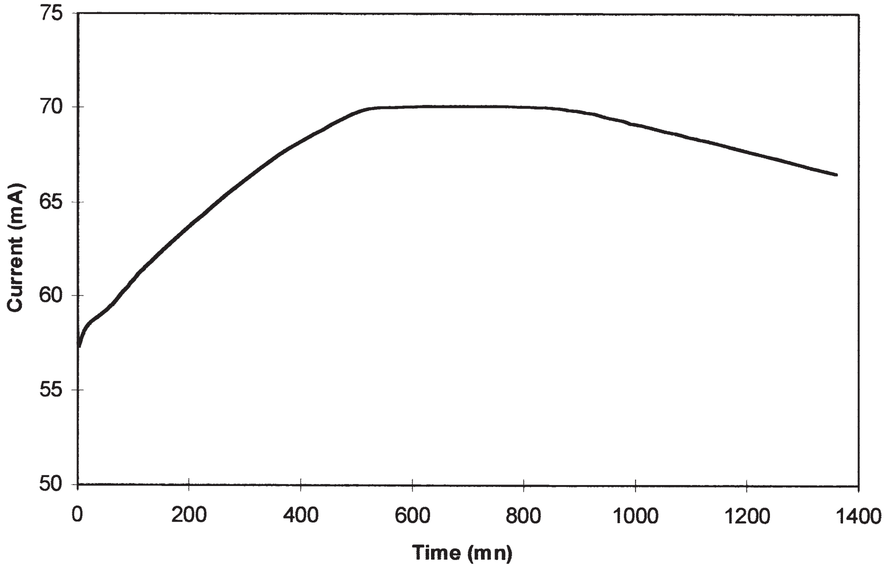

Fig. 2. Variations of current.

2.1. Variations of the current

An example of a daily variation of the current is shown in Fig. 2. The current increases rapidly during the first hours and decreases after about 15 h of test. This variation is attributed to a polarization of the cell. During the test, the concentration of OH− in the solution downstream becomes increasingly weak and the kinetics of migration of the ions through the sample is not enough to compensate for the reactions on the anode.

2.2. pH variations

The pH decreases in the anodic compartment (Fig. 3) but increases in the cathodic compartment (Fig. 4). These variations are directly related to the nature of the reactions that occur during the test. As the potential is applied between the electrodes, the hydroxide ions migrate toward the anode, where they oxidise by giving oxygen and yielding electrons [Eq. (1)]:

$$2OH^- \rightarrow 1/2\ O_2 + H_2O + 2e^- . \tag{1}$$

Simultaneously, sodium ions migrate toward the cathode. They do not react directly but the surrounding molecules of water are electrolysed, giving directly hydroxide and hydrogen. The electrons provided by the cathode are those that come from the anodic reaction [Eq. (2)]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- . \tag{2}$$

The electrolysis phenomenon appears to be the main process that occurs during the accelerated test of concrete chloride permeability. The consumption of hydroxide on the surface of the anode causes the drop of pH in the anodic compartment, whereas the electrolyses of water molecules causes the increase of pH in the cathodic compartment. The

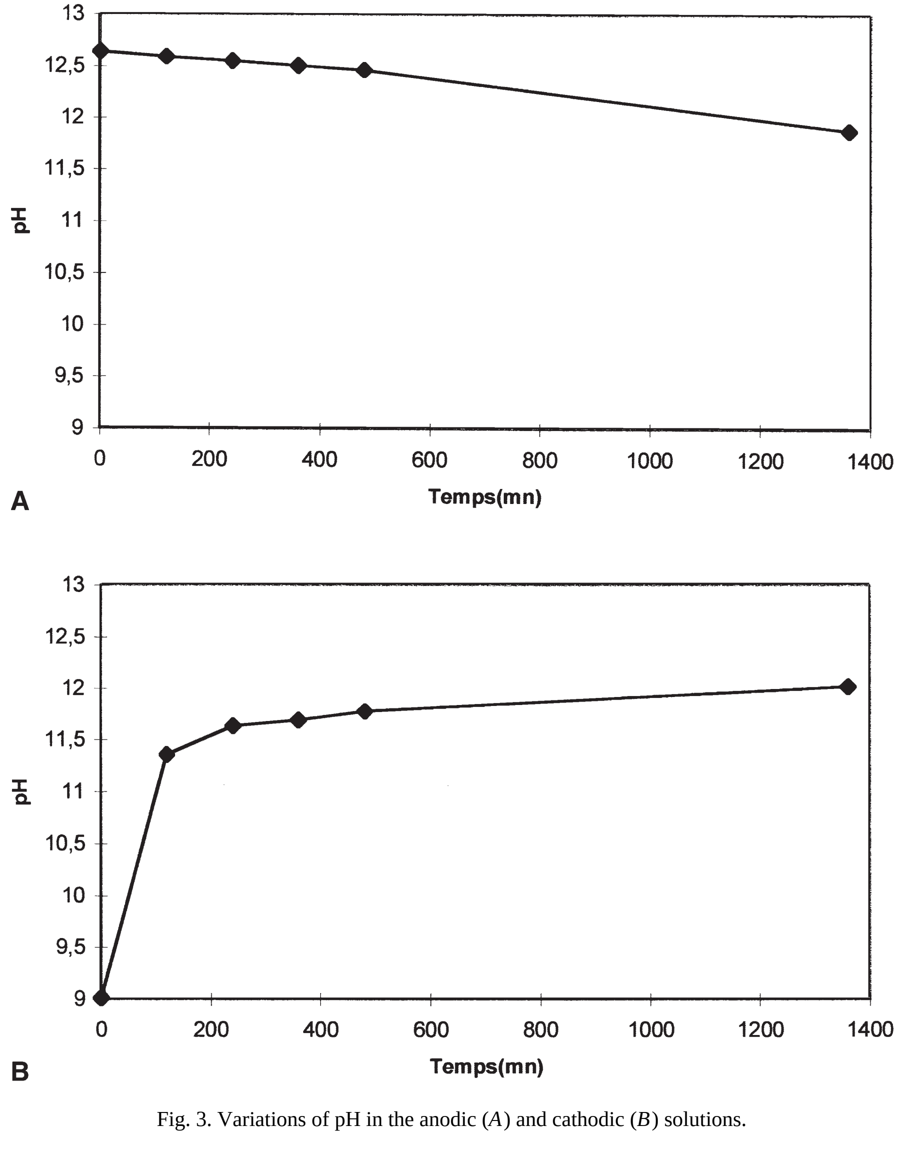

Fig. 3. Variations of pH in the anodic (*A*) and cathodic (*B*) solutions.

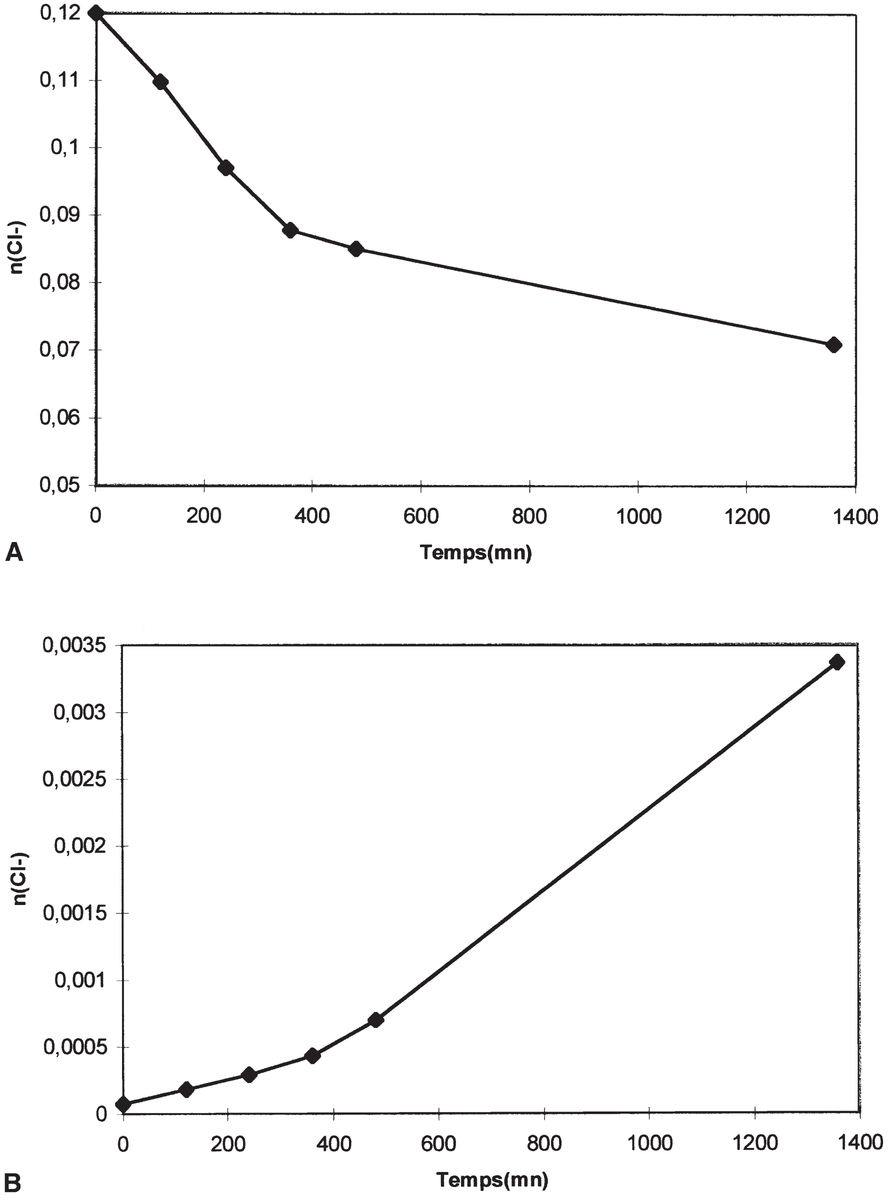

Fig. 4. Variations of chloride concentration in the cathodic (*A*) and anodic (*B*) solutions.

process continues as long as there is electrical charge transfer in the external circuit and ionic transport through the cell. Ionic transports are provided not only by sodium and chloride ions but also by all the different ions present in the concrete.

2.3. Chloride concentration variations

The electrical field established between the electrodes induces the chloride migration through the concrete toward the anode. On the anode, oxidation gives chlorine. However, because of the high pH of the anodic solution, chlorine reacts rapidly with hydroxide and gives hypochlorite and chloride [Eq. (3)]:

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O. \tag{3}$$

Consequently, the amount of chloride that emerges in the anodic compartment is twice as much as the amount of chloride currently assessed by potentiometric titration. In addition, special care should be taken with regard to the stability of hypochlorite ions. First, it is well known that light and temperature breaks hypochlorite ions and release oxygen and chlorine [Eq. (4)]:

$$ClO^- + H_2O \rightarrow Cl^- + O_2 + 2H^+ + 2e^-. \tag{4}$$

Second, in acidic conditions, hypochlorite reacts with chloride and gives chlorine [Eq. (5)]:

$$ClO^- + Cl^- + 2H^+ \rightarrow Cl_2 + H_2O. \tag{5}$$

The problem is that the acidification of the anodic solution is the direct consequence of the electrolysis that goes

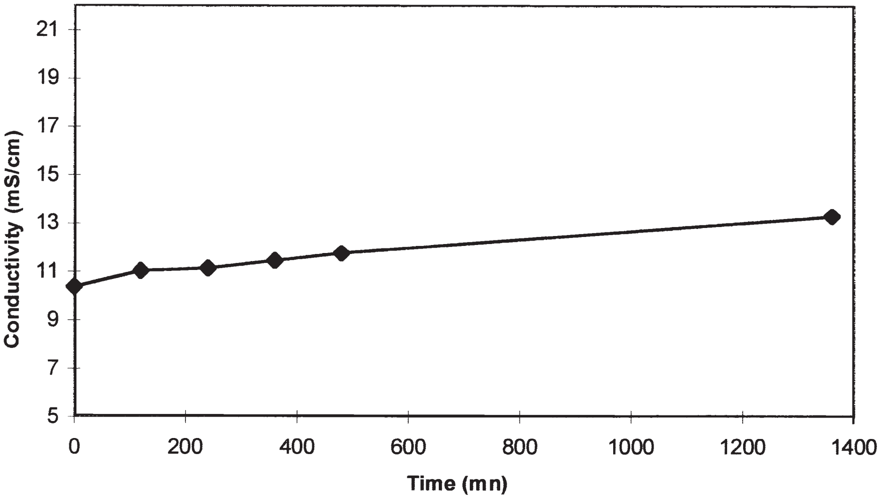

Fig. 5. Variations of conductivity of the cathodic solution.

on with the anode. Therefore, it is essential to keep count of these reactions if ion mass balance is considered. In particular, the renewal of the anodic solution is essential for long-term experiments.

2.4. Conductivity variations

Fig. 5 shows that the conductivity of the cathodic solution has increased during the test. This is due first to the release of hydroxide ions by the electrolysis reaction and second to the arrival of sodium ions coming from the anodic compartment through the sample

On the opposite side, the conductivity of the anodic compartment regularly decreases because of the important consumption of hydroxide ions by the anode probe (Fig. 6). Because the main ionic species in this anodic solution are Na^+, Cl^-, ClO^-, and OH^-, the electroneutrality condition could be written as $(Na^+) = (Cl^-) + (ClO^-) + (OH^-)$. During the test, Na^+ concentration decreases because of the migration toward the cathode while Cl^- and ClO^- increase due to the migration of chloride. Because the electroneutrality must be constantly satisfied, the evolution of the process would lead to an important reduction of OH^-. This means that the amount of hydroxide ions that reacts at the anode is much higher than the amount of chloride that reaches the anodic compartment. To highlight the role of OH^- ions, we carried out experiments with variable concentrations of OH^-.

2.5. Effect of hydroxide concentration in the anodic compartment

We modified the NaOH concentration in the anodic compartment and examined the effect of this modification on the current and the chloride migration. Results shown in Fig. 7 indicate that the increase of NaOH concentration

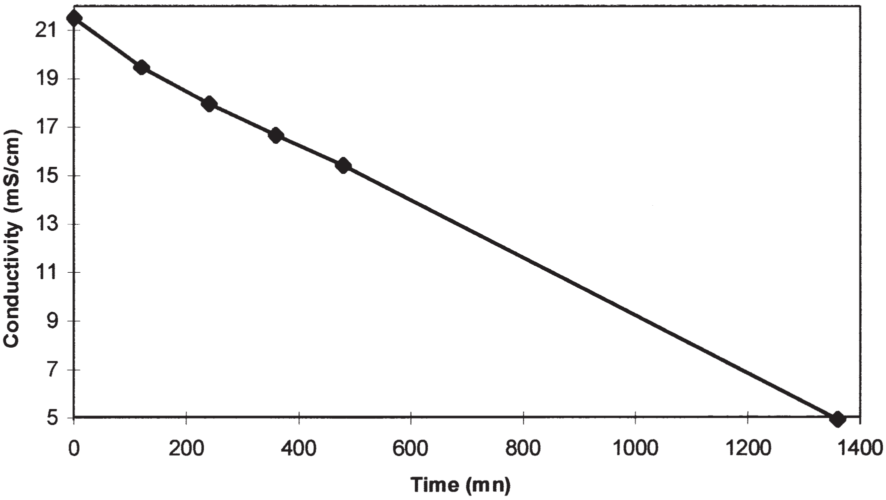

Fig. 6. Variations of conductivity of the anodic solution.

causes a correlated increase of the current but does not modify the chloride variations in both anodic and cathodic compartments (Fig. 8). This clearly shows that the current reflects not only the migration of chloride and sodium ions but also the migration of anodic solution hydroxide.

For each type of ion, the current due to migration is proportional to the transport number ≪t≫. The transport number is related to the concentration and the mobility by Eq. (6):

$$t_i = (\mu * z * c)/\Sigma(\mu_i * z_i * c_i). \tag{6}$$

As the mobility of $OH-$ ions is nearly twice as great as that of $Cl-$ and as their concentration in the anodic compartment is 10 times higher than that of the $Cl-$ ions, it follows that [Eq. (7)]:

$$tOH^{-} \gg tCl^{-}. \tag{7}$$

Consequently, the contribution of OH^- ions is dominating in the ionic transport between the electrodes of the cell of diffusion. However, OH^- ions are present not only in the anodic compartment but also in the internal liquid of the concrete. In the following experiment we tried to examine the incidence of these internal OH^- ions on the curve of intensity.

2.6. Experience

Three cores of identical size were taken in the same block of a high-performance concrete. The first sample was saturated in a vacuum chamber with demineralized water; the two other samples were saturated with a 0.1 M/L sodium hydroxide or a lime solution. The samples were cleaned superficially with a wet sponge. The three samples were subjected to the chloride permeability test according to the procedure described previously.

Fig. 9 shows the variations of intensity vs. time. It appears clearly that for the core saturated with soda or lime, the intensity is much higher than the intensity obtained with the sample saturated with demineralized water.

The composition of the internal liquid is essential. The hydroxide ions contained in the pores modify notably the intensity of the current. A determination based only on the electrical charge could lead, in many cases, to misinterpretation of the chloride permeability. Two concretes having the same w/c ratio could lead to very different measurements if their compositions are different. In particular, because silica fume causes a reduction of the hydroxide content in the internal solution, it should decrease the current. Several authors report that for the same w/c ratio, the introduction of silica fume decreases the current.

3. Conclusion

The cell used in this study enables a better understanding of the mechanisms involved in the accelerated test of chloride permeability. We showed that electrolysis is the main process that occurs during the test, and it is accompanied by a generalized migration of the ions through the concrete. Depending on the porosity and permeability of the concrete, the actual chloride flow remains limited during the first days whereas the hydroxide ions play the essential role. The accelerated chloride permeability test proves the existence of a connected poral network in which ions migrate or diffuse. The current not only reflects the migration of chloride ions; it constitutes a global criterion that must be interpreted with precaution if concrete samples of different compositions are to be compared. A good characterisation must be based on the actual chloride flow through the sample. The

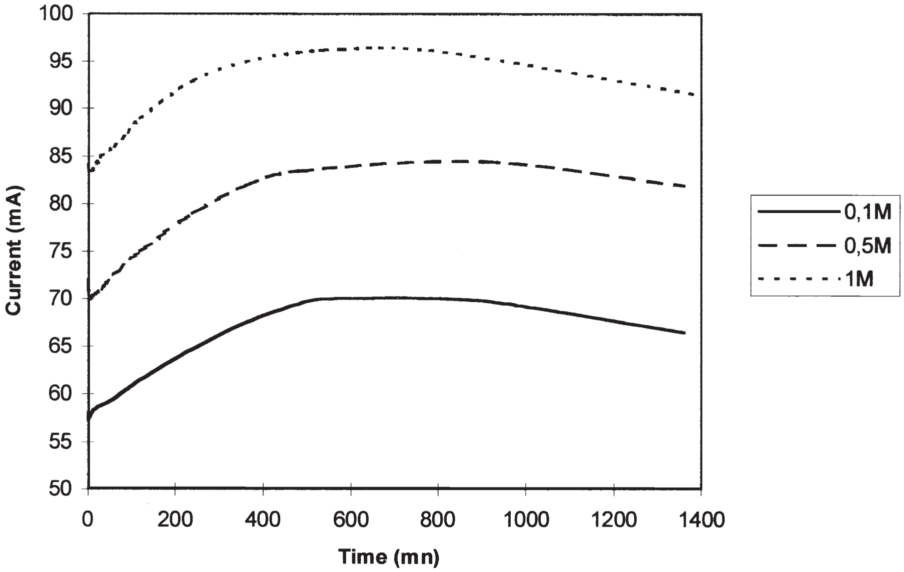

Fig. 7. Effect of variations of the initial concentration of NaOH on the intensity curve.

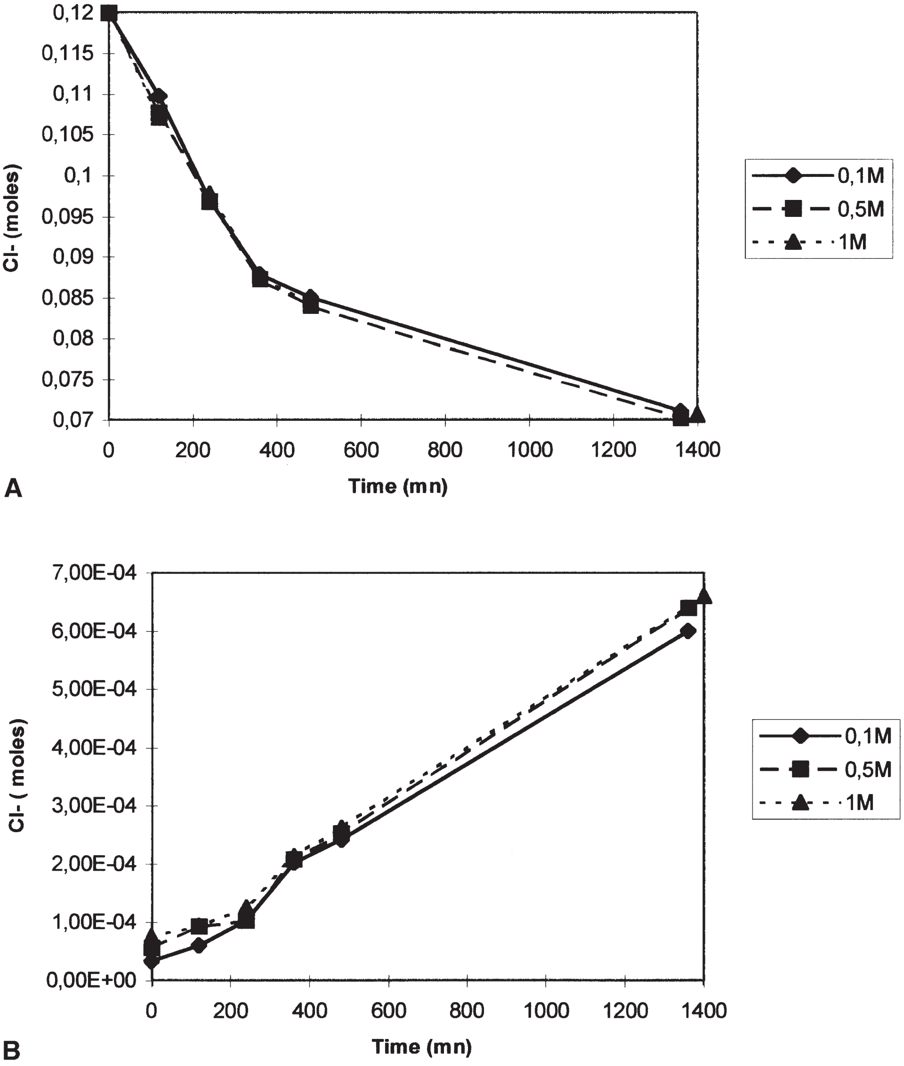

Fig. 8. Effect of initial concentration of NaOH on the chloride concentrations in the cathodic (*A*) and anodic (*B*) solutions.

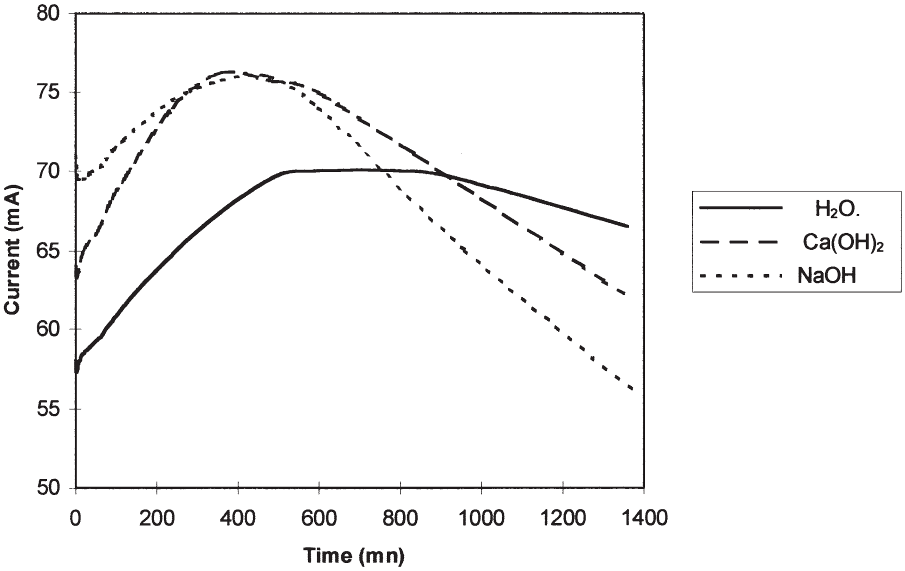

Fig. 9. Effect of internal hydroxide on the intensity curve.

special device described in this study allows such determination.

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