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Alkaline leaching method for the determination of the chloride content in the aqueous phase of hardened cementitious materials

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Abstract

The need of determining "free" chloride content in the aqueous phase of hardened cementitious materials arises from the fact that chloride is the responsible agent of the depassivation of the rebars in reinforced concrete. This paper presents a method of obtaining free chlorides by leaching in an alkaline solution during 24 h. The method is calibrated by comparison with the values obtained by means of the pore-pressing technique (PPT). The agreement found is reasonably good in spite of the risk of excessive leaching that aims to solve part of bound chlorides. The use of decarbonated water as extraction agent has resulted appropriately, perhaps due to the fact that the samples are not powdered, instead, pieces of around 2 mm in size are used. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The main aggressive factor regarding reinforcement corrosion is the chloride ion. The amount of chlorides inducing active corrosion of the steel is called the chloride threshold [1,2]. Up to now, a single value for this threshold has not been found, because it varies depending on concrete [2] and steel characteristics [3]. Although the expression of this threshold is usually made as total chloride content, either by weight of cement or concrete, it is also accepted that only free chlorides are able to depassivate the steel. In this respect, it was proposed, in the 1960s [1,2], to express the threshold in terms of the Cl^-/OH^- ratio, although there are other proposals [4] that justify the total chloride content as a better indication of the corrosion risk due to the variation of this threshold along the time. However, the expression as Cl^-/OH^- ratio seems to be more rigorous due to the competitive action of both ions and, additionally, it accounts for the different cement types and their evolution with time.

One of the main reasons of the preference towards the calculation of only the total chloride content lies in the difficulty of a reliable and cheap determination of the Cl^-/OH^- ratio. Up to now, the most accurate method of analyzing both Cl^- and OH^- seems to be, in spite of its limitations [5], the squeezing of the concrete in order to obtain its pore solution [6–9]. Other leaching methods also based on water extraction [10,11] may overestimate, depending on the mode of operation, the free chloride content by dissolving part of the bound chloride content [12]. However, recently, the AFREM method [13], also based on water extraction, has reported proper results. Sagüés et al. [14] have proposed an in situ leaching method based on making a small hole in the concrete surface and introducing in it some water drops, which reduce the dilution impact on the leached amount.

In the present paper, a method based on the use of an alkaline solution to extract the free chlorides is presented, wherein first attempts were made by Petterson [15]. The method has been optimized and compared with the results obtained from the same samples by the Pore Solution Expression Technique (squeezing or pore-pressing technique (PPT)). The present proposed method's results are more quick and cheap, enabling to test a great amount of

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samples in a short time. Another advantage is that the amount of sample needed is much smaller than in the case of the PPT.

2. Experimental

2.1. Materials and specimens

Two sets of mortar specimens were prepared:

1. The first set was cast with 1.38% total chloride by weight of sample, added to the mixing water as NaCl. This set was used to evaluate the influence of the contact time of the leaching solution in the determination of the free chloride content.
2. The second set consisted of a series of mortars with different concentrations of total admixed chloride (0.5%, 1.0%, 3.0% and 6% by weight of sample). This series was used to evaluate the influence of the chloride concentration in the extraction process.

The specimens were prepared with an Ordinary Portland Cement (OPC), standard sand (UNE 80 101-88), a cement/sand ratio of 1:3 and water/cement ratio of 0.5. The specimens were cured for 28 days in a chamber at 100% of RH. The cement composition is shown in Table 1.

2.2. Techniques and procedures

2.2.1. Basis of the method

The method aims to extract through leaching the aqueous phase from hardened cementitious materials. The determination of free chlorides is made from the leached liquid, and it is expressed regarding the dry material. This implies the need to calculate the free capillary water in the sample.

Two assumptions were made in calculating the free chlorides:

1. The volume of the free water determined (in a separate sample) represents the volume of the solution contained in the pores of the sample.
2. Equilibrium between the pore solution of the sample and the leaching solution is assumed to be reached. This means that after the settled time of the test, any difference between their chemical compositions is neglected.

Table 1
Portland cement composition of the Type I/45 A

Cement composition (%)									
RI	SiO_4	Al_2O_3	Na_2O_3	CaO	MgO	SO_3	PF	Na_2O	K_2O
1.92	18.32	5.43	3.28	61.34	1.51	3.08	3.13	0.15	1.04

According to these approaches, calculation of free chlorides is made through Eq. (1):

$$\%\mathrm{Cl} = 0.035\,\frac{(2+W)\mathrm{Cl}H}{W} \tag{1}$$

where %Cl is the percentage of free chloride (by weight of sample), H the percentage of evaporable water in the sample, W the evaporable water in the sample (ml) and Cl the chloride concentration in the leaching solution (M).

2.2.2. Description of the method

In order to extract free chlorides from the aqueous phase of the pores, the leaching solution used has been 0.3 M NaOH. The choice of this leaching solution was due to the fact that it provides a pH value of about 13.5, which is assumed to be an average of the pH of aqueous phase inside hardened cementitious materials. This pH value will minimize the alterations that a leaching process may provoke in the paste. As complement, leaching with decarbonated water have been also made in order to check the differences.

The expression of the free chloride values as percentage by weight of dry sample or by weight of cement is proposed. This will enable the comparison of samples that had been exposed to different environments and pore saturation degrees. In addition, this is the usual mode to express the total chloride content in concrete.

2.2.3. Sample conditioning

In order to reduce the testing time, the samples (mortar or concrete) have to be crushed to a particle size between 2.5 and 3.5 mm in a homogeneous form. Subsequent handling must avoid carbonation. The sample must be weighed only if the chloride content is going to be expressed as a concentration in the pore aqueous phase. Finally, it is held in a 100% RH in order to saturate it before the test and avoid carbonation.

2.2.4. Equipment

After the samples are adequately conditioned, they are placed in a glass device as shown in Fig. 1. It consists of a cylindrical body with a tube and a valve in its bottom to obtain the leached liquid. It has a porous glass in which the sample to be leached is placed. The apparatus has a hermetic cap, as well as three inlets (for inert gas (N_2), leaching solution and aeration).

A filter must be placed between the sample and the porous glass. The first step consists in the insulation of the device, circulating N_2 in order to avoid carbonation and draining it through the respective outlet. As a second step, it is necessary to add the leaching solution by the corresponding inlet. N_2 gas is then circulated again. In this way, an inert atmosphere is assured. Once filtered, the leached liquid is collected through the bottom valve, and chlorides in the collected liquid are then analyzed by $AgNO_3$ titration.

When a great number of tests have to be performed, a plastic tube with a hermetic cap or any other type of device

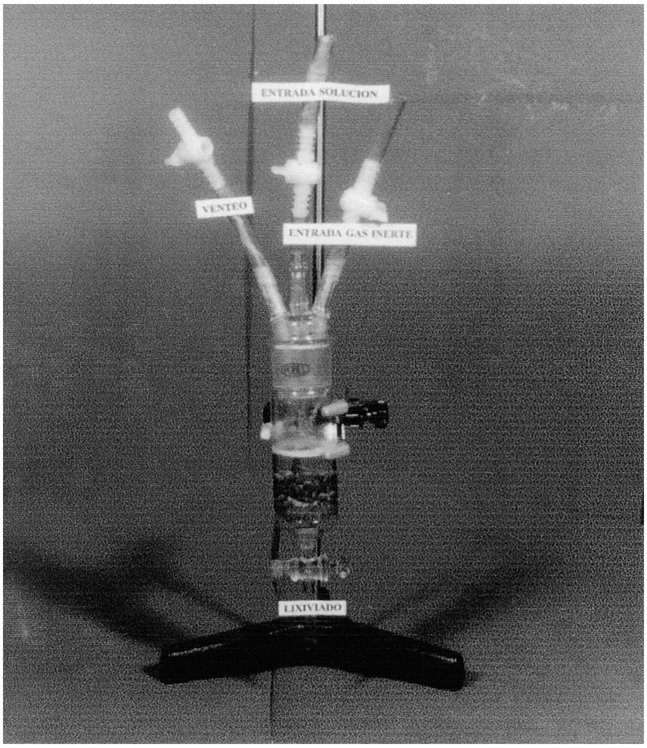

Fig. 1. Experimental device used to determine free chlorides by the proposed leaching method.

for the extraction procedure can be used, taking care to follow the same steps as described previously. Use of the special device is preferable because it was designed to allow the displacement of the air by passing N_2 through the sample, as can be seen in Fig. 1. When test tubes are used, the remaining air is also displaced with N_2 gas without stirring, the device is then hermetically closed in a quasi-inert atmosphere that, according to the obtained results, also avoids further carbonation.

2.2.5. Specimen preparation and extraction process

The sample to be analyzed is split into two parts: one of them weighing 3 g; the other is the rest of the sample. The 3-g sample is placed in the leaching device, and 2 ml of the leaching solution are added. This solution should be previously prepared with decarbonated water. From the leached solution, free chlorides will be determined.

After displacing the air with N_2 gas, the sample is stirred (magnetic stirrer in the case of the device, and manual stirring in the case of the tubes) for about 30 s, and left to rest for 24 h in the solution. After this time, it is stirred again and the leached liquid is obtained by filtration.

The second part of the sample is used to determine the capillary free water content. To carry out this determination, the sample is weighed and introduced for 24 h in a stove at 105°C. After this time, the sample is weighed again and the evaporable water percentage is dry-basis determined.

2.2.6. Performance of the tests

In order to determine the optimum duration of the test, the variable of the process that was first tested was the influence of the duration of the contact between the leaching solution and the sample. These tests were performed in

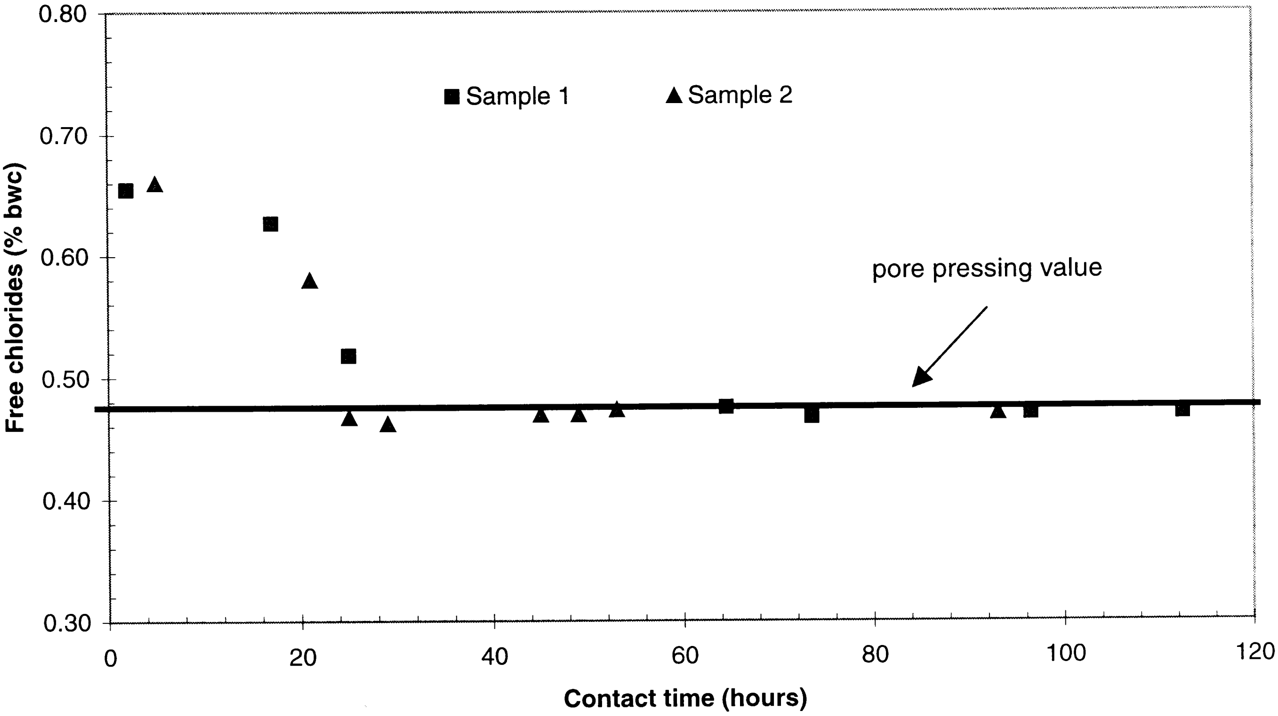

Fig. 2. Free chlorides in a function of the contact time of the sample having 1.38% of total chloride content and leached with 0.3 M NaOH solutions.

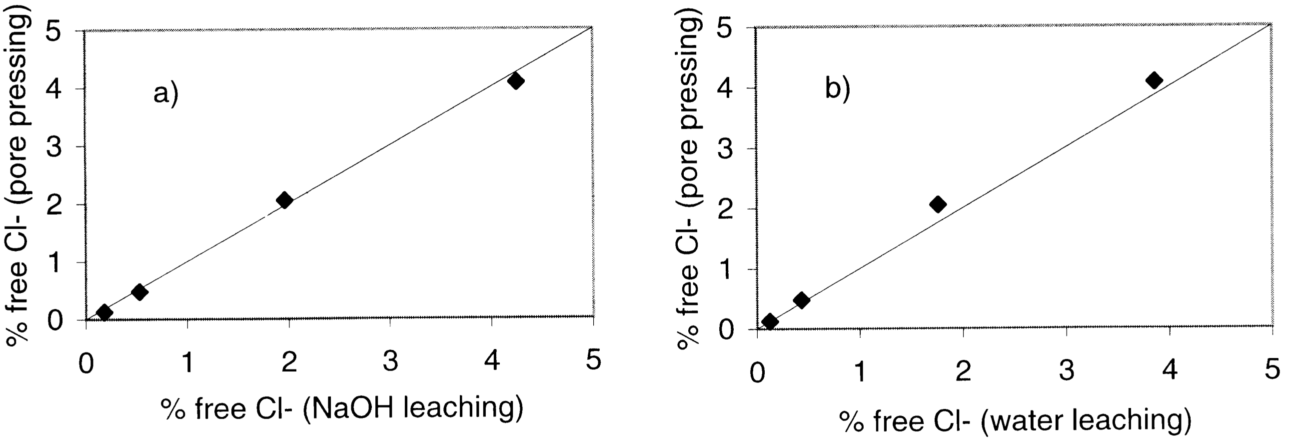

Fig. 3. Comparison between free chlorides obtained by the leaching methods: (a) alkaline solution and (b) decarbonated water, when compared with the PPT values.

duplicate specimens. The different values of the free chlorides so determined were compared with those of the PPT.

Then, the accuracy of the method has been evaluated for different chloride concentrations in the mortars. These experiments were carried out by leaching triplicate specimens in the alkaline solution, and also using decarbonated water as leaching agent (following exactly the same described procedure with the exception of the solution used). The results were also compared with those from the PPT [6–9] (duplicate specimens) for calibration purposes.

The analysis of the concentration of the chlorides in solution was made by potentiometric titration. For total chlorides, X-ray fluorescence (XRF) was used.

3. Results

3.1. Influence of the time of contact

Fig. 2 shows the amount of leached chlorides in a function of time of contact in the mortar containing 1.38% of total chloride by weight of sample. It can be seen that at the beginning of the leaching, the amount of chlorides is high, but after 24 h of contact, the chloride values were stabilised at a fixed value for the two samples tested. The PPT value, which was used as a reference, is also represented in Fig. 2 by a horizontal straight line and has a value of 0.48%, which is very close to the final value obtained by leaching.

3.2. Calibration with results from pore-pressing extraction: influence of the chloride content

Fig. 3a,b shows the percentages of free chlorides in the samples with different chloride contents, obtained by leaching in alkaline solution (a) and water (b), plotted vs. those obtained from PPT. For each concentration, an average of the values of the replicate specimens (three for leaching and two for pore-pressing tests) is shown. It can be seen that, again, there is a good agreement among the values obtained by the different methods in all the range of chloride concentrations studied.

Individual values obtained, as well as statistical analysis of the data, are given in Table 2, where the standard deviation and the percentage of deviation, from the corresponding pore-pressing mean value according to Eq. (2), are given (negative sign indicates underestimation).

Table 2
Comparison of data of free chlorides obtained through different methods with pore-pressing extraction and statistical analysis of the data

	Percentage of total Cl	Sample 1	Sample 2	Sample 3	Average	S.D.	Coefficient of variation (%)	Percent bias vs. pore press
Pore pressing	0.5	0.132	0.120	–	0.126	–	–	–
	1	0.476	0.480	–	0.478	–	–	–
	3	2.068	2.028	–	2.048	–	–	–
	6	4.072	4.092	–	4.082	–	–	–
NaOH leaching	0.5	0.188	0.184	0.18	0.184	0.004	2.2	46.03
	1	0.500	0.556	0.536	0.531	0.028	5.3	11.02
	3	1.828	2.020	2.024	1.957	0.112	5.7	– 4.43
	6	4.288	4.376	4.080	4.248	0.152	3.6	4.07
Water leaching	0.5	0.128	0.124	0.120	0.124	0.004	3.2	– 1.59
	1	0.452	0.460	0.384	0.432	0.042	9.7	– 9.62
	3	1.676	1.780	1.836	1.764	0.081	4.6	– 13.87
	6	3.704	3.904	3.964	3.857	0.136	3.5	– 5.50

$$\mathrm{DA} = \frac{(\text{leaching value}) - (\text{pore} - \text{pressing value})}{(\text{pore} - \text{pressing value})} \times 100 \qquad (2)$$

Table 2 shows that the standard deviation of the results is very small, being the coefficients of variation smaller than 10% in all the cases. Providing that the repeatability of the method of analysis is about 2%, the repeatability of the leaching methods is very good. Concerning the bias of data obtained from leaching methods taking the pore-pressing value as reference, it can be observed that alkaline leaching works better at higher concentrations and water leaching at lower ones. It is important to point out that in all the cases, leaching with water only underestimates the free chloride content.

4. Discussion

Regarding the influence of the contact time, from results of free chlorides at different times of contact, it can be deduced that, as expected, when the leaching solution is added to the sample, the initial equilibrium of the system gets broken, and it evolves in the sense of balancing the concentrations in and out of the sample. This evolution may induce that part of the combined/adsorbed chlorides passed into the solution. Following the assumption of a binding isotherm, the dilution produced when adding the leaching agent, should induce the corresponding dropping of bound chlorides in order to fit the equilibrium isotherm. However, as can be seen in Fig. 2, the original equilibrium is reached after approximately 24 h of contact time. This rearranging in the chloride concentration in the aqueous phase is attributed to the pH of the extracting alkaline solution and to the small liquid/solid sample ratio, which is kept at 2 ml/3 g, which might imply that the controlling factor is the number of active centres able to bound chlorides instead of the concentration in the liquid phase. Therefore, in this process, there is a mechanism that is not yet understood and must be clarified.

A contact time of 24 h was adopted as the optimum time from a practical point of view. Petterson [15] also found an optimum time around 20–30 h, with a simulated pore solution. Chaussadent and Arliguie [13] use shorter testing times when leaching with water and powdered samples.

With respect to the validity of the leaching procedure for application to a wide range of chloride concentrations, its comparison with the values of the PPT confirms its suitability. The statistical values from the obtained results (Table 2) show a good repeatability, better for the alkaline solution than for water, and a low scattering among the values when compared with the PPT. The alkaline extraction shows a better suitability at the highest chloride concentrations, because the highest deviation was found at the lowest chloride concentrations.

According to data from Table 2, the scatter of water extraction with respect to the PPT indicates a slight underestimation when leaching with water (not in agreement with other findings [12], which found the opposite), while in the case of the alkaline solution, the scatter is distributed around PPT values. It is necessary to mention that the results of other authors, which found overestimation when leaching with water, corresponded to powdered samples, while in the method proposed in the present work, samples are not crushed so finely. In addition, these authors have used different extraction periods.

5. Conclusions

The conclusions that can be drawn up are the following.

- An alkaline leaching procedure for extracting “free chlorides” from hardened cementitious materials has been developed. This method enables to obtain enough similar results than those obtained by the PPT, which until now is accepted as the unique reliable procedure for analyzing the concrete aqueous phase.
- Proposed leaching solution is 0.3 M NaOH, (simulating aqueous phase of concrete) in a ratio liquid (ml)/solid sample (g) of 2:3. Size of particle of the solid: 2.5–3.5 mm; optimum time of contact: 24 h in an inert environment.
- In the present study, by using nonpowdered samples, the extraction with decarbonated water has also given enough approximate results of soluble chlorides.

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