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Water extraction of chloride, hydroxide and other ions from hardened cement pastes

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Abstract

The extraction of OH^-, Cl^-, K^+ and Ca^{2+} ions from ground samples of hardened cement pastes by water was studied, as well as the conditions affecting it. Cement pastes from Portland cement containing various dosages of KCl and the addition of condensed silica fume (SF) were used in the test. The variable parameters adopted during the water extraction were the solid-to-water ratio, the fineness of a sample, and the extraction time. It was found that in cases where extraction was accomplished with the addition of small amounts of water, the quantity of the leached out Cl^- and OH^- ions within 24 h was almost independent of the fineness of the crushed samples. The quantity of extracted ions changes with each type of ion as well as with the sample-to-water ratio itself. The chemical composition of the water leachates reflects the composition of the hardened cement paste samples. A method for assessing the Cl^-/OH^- ratio in a pore solution of hardened cement paste based on extrapolation of the results obtained during the water extraction is proposed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: pH; Chloride; Cement paste; Silica fume; Leaching

1. Introduction

The mixing of crushed or granular materials such as concrete with water and the subsequent chemical analysis of the obtained leachate are essential steps used for the determination of water soluble substances in these materials. The technique is denoted as leaching, water extraction, eluation, or decantation; often the terms are used interchangeably. A variety of leaching conditions is generally used in the tests. This paper focuses on subject matter related to the corrosion of embedded steel in concrete.

In sound concrete, the embedded steel is covered by a thin, protective iron oxide film that, at a high pH of the pore solution in concrete, makes the steel passive to corrosion. Pore fluid in hardened cement pastes made of common cements principally represents a relatively concentrated solution of alkaline hydroxides (with concentrations varying from about 0.3 to 1 mol/l), which contains only a very small concentration of sulfates and about 1 mmol/l or less of calcium [1–7]. The passivity of the reinforcement can be destroyed in the event the pH value of the concrete is decreased, and also in the presence of chlorides or other substances.

Chlorides can be introduced into concrete at the time of mixing the concrete (“internal” or “primary” chlorides), or they may penetrate into hardened concrete from the outer environment (“external” or “secondary” chlorides). Out of the total amount of chlorides in the concrete, some remain free in the pore solution; some become bound to the hydration products. It is generally recognized that only the free (the unbound) chloride ions affect the corrosion of reinforced steel.

There are several ways that chlorides may bind with cement hydration products. The most important is chemical binding with the hydration products of the C_3A and C_4AF phases to form the chloro-aluminate complex of $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$ (Friedel’s salt). In addition to this phase, the formation of its ferrite-based analogue $3CaO{\cdot}Fe_2O_3{\cdot}CaCl_2{\cdot}10\ H_2O$ from the C_4AF is also possible [8]. According to Suryavanshi et al. [9], Friedel’s salt in cement pastes is formed by two separate mechanisms. One fraction of Cl^- ions is supposed to react by an anion-exchange mechanism leading to the release of an equivalent amount of OH^- ions into the pore solution; a majority of the

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Cl^- ions is expected to be bound by adsorption in the interlayers of the principal layer of the AFm structure. Chlorides may also bind more loosely with the C-S-H gel [10–13]. It has been suggested that chloride ions introduced as calcium chloride can be held by chemisorption on the surface of C-S-H, in the interlayer space or can be incorporated into the lattice of C-S-H. According to Lambert et al. [10], the hydrates of calcium silicate show no detectable capacity to bind $NaCl^-$ supplied chloride anions. Some general agreements on the binding of internal chlorides can be summarized as follows:

a. The amount of bound chlorides increases with the amount of C_3A in cement [14,16].
b. The stability of Friedel's salt is pH dependent. The solubility of Friedel's salt increases with the degree of atmospheric carbonation of the specimen [15].
c. An inhibiting effect of the addition of condensed silica fume (hereinafter referred to as "SF") on the chloride-bearing capacity of cement composites is also explained by a reduction in the pH of the pore fluid [14,17,25]. As a consequence, the Cl^-/OH^- ratio in the pore fluid increases [25].
d. There is controversial data about the effect of alkali content in cement. According to Arya et al. [14], a significantly higher level of binding was achieved with a high alkali than with normal OPC. On the other hand, Rasheduzzafar et al. [16] has reported that the alkali content of a cement appears to have an inhibiting effect on its chloride-bearing capacities.
e. The amount of bound chlorides depends on the associated cation; it is significantly higher (and the amount of Friedel's salt produced is greater) in the case of $CaCl_2$ than NaCl [9,18–21]. The binding of Cl^- ions from NaCl was reported to increase OH^- ion concentrations in the pore solution [9,16,18–22], reaching a maximum at the Cl^- content of about 0.8–1.5% by the weight of the cement [27]. On the other hand, chlorides from $CaCl_2$ seem to cause a reduction in the OH^- concentration [9,17–19,22]. Contrary results were reported by Al-Hussaini et al. [21].
f. The chloride binding capacity has a limit [14,16,18,20,21,23]. While in the case of NaCl additions, the percentage of bound chlorides seems to remain approximately constant; in the case of $CaCl_2$ the percentage of bound chlorides seems to increase with the amount of total chlorides [14].

Seven terms concerning chlorides in concrete can be distinguished as follows: (a) internal, (b) external, (c) free, (d) bound, (e) total, (f) acid soluble, and finally, (g) water soluble chlorides. The first four terms were mentioned in the previous paragraphs.

The term "total chloride" content covers all chlorides present in a sample. Total chlorides can be determined by a nitric acid extraction. However, the diluted nitric acid does not completely remove all the chlorides from the samples [26]. The term "water soluble chlorides" denotes those chlorides that can be released from a sample by water extraction [20,21,24,26,30]. It has been concluded that the only reliable method to determine the free chlorides in a cement composite is based on an analysis of the pore fluid expressed. Despite that, water extraction methods can also produce valuable information [20,24].

It is generally accepted that the Cl^-/OH^- ratio in a pore solution is an indicator for assessing the onset of the depassivation of steel in concrete. On the basis of corrosion tests undertaken with steel exposed to a model of a concrete-simulated electrolyte of Ca(OH) with a pH of about 12.5, Hausemann [27] suggested that corrosion is initiated only when the Cl^-/OH^- ratio in the pore solution at the iron–matrix interface exceeds a threshold level of 0.61. Diamond [22] suggested a value of the Cl^-/OH^- ratio of 0.3 for the depassivation threshold level, considering it to be more appropriate for concretes where the pore fluid usually exceeds a pH value of 13. Page and Vennesland [17] emphasized the unreliability of predicting the corrosion behavior of steel in concrete by such methods, since the experiments could not simulate actual conditions in concrete. Mangat and Gurusamy [28] also cite other authors, claiming that the critical value of the Cl^-/OH^- ratio is likely to be much higher than the value suggested by Hausemann.

2. Experimental

2.1. Materials used and preparation of test specimens

Neat Portland cement pastes and Portland cement pastes containing 10% of condensed SF were prepared with a water-to-cement ratio of 0.4. The composition of the Portland cement is given in Table 1. The condensed SF contained 91% SiO_2; its specific surface was 19,600 m^2/kg and its density was 2200 kg/m^3. Both types of cement pastes were prepared with various additions of analytically pure potassium chloride, which was dissolved in distilled water prior to mixing. The chloride concentration in both types of cement pastes is given in Table 2.

Batches consisting of 1 kg each of the cement pastes were prepared. After thorough mixing, the cement pastes were cast into cylindrical plastic molds and sealed. These samples were assigned for water extraction tests. (In addition to these, cubical specimens for determining their compressive strength were also cast. These results are not included in this paper.) The cylindrical specimens were demolded after 35 days of hardening, then crushed and

Table 1
Chemical composition of Portland cement

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Na_2O	K_2O	Ign. loss
62.2	2.9	20.8	5.1	2.9	2.7	0.3	0.7	1.8

Table 2
Composition of cement pastes and designation of samples (SF denotes the silica fume)

Designation of samples	A1	A2	A3	A4	B1	B2	B3
Cl^- content (% by weight of cement)	0	0.5	1	2	0	0.5	1
SF content (% by weight of cement)	–	–	–	–	10	10	10

sieved through 0.5, 1, and 2 mm sieves into three fineness ranges of 0–0.5, 0.5–1, and 1–2 mm. Samples of the finely crushed material were then transferred into small glass bottles, which were closed to avoid drying and carbonation until required. Evaporable water was determined by heating the samples to a constant weight at 105°C; the non-evaporable water and bound carbon dioxide were determined by heating the samples at 1050°C.

2.2. Leaching tests and analysis of leachates

The effect of various regimes of water extraction (water leaching) on the quantities of the OH^-, Cl^-, K^+, and Ca^{2+} ions leached out from the hardened cement pastes was investigated. The leaching test consisted of mixing a known quantity of the crushed sample, which was used in an undried state, with the distilled water. The mixture (suspension) obtained was then sealed in a Teflon vessel to avoid carbonation and water evaporation for various periods of time, with stirring at chosen intervals. The mixtures were stirred for 2 min immediately after being prepared, then after 10 and 30 min, and at 1, 2, 4, 8, 15, 20, and 24 h, depending on the duration of the test, each time for 30 s. The effects of the following three variable parameters were tested: (a) the particle size of the sample, (b) the solid-to-water ratio of the prepared mixture, and (c) the extraction (leaching) time. The solid-to-water ratios used in the tests were 1:2, 1:5, and 1:50; in some cases a ratio of 1:1 was also used. The mixtures were filtered after a selected period of time that was 1, 6, or 24 h, and in some cases, also after 2 and 10 min through a filter paper. Each filtrate (leachate) was prepared individually from the original leaching test. The leachates were used for determining the Cl^-, OH^-, Ca^{2+}, and K^+ ions, using the following chemical analysis methods.

The chlorides were determined by titration against standard mercury nitrate at a pH of 2.5 using bromphenol blue and diphenylcarbazid as indicators.

The OH^- ions were determined by titration against a standard hydrochloric acid of 0.2 mol/l using phenolphtalein as an indicator. The pH value of the leachates was calculated from a concentration of OH^- ions ($pH = 14 + \log[OH^-]$).

The calcium and magnesium ions were determined by titration at a pH of 10 against chelaton III using eriochrom black as the indicator. Because the pH of all the leachates was above 11.5 and the concentration of magnesium ions was insignificant, it was ignored. The consumption of the entire chelaton was thought to correspond only to Ca^{2+} ions.

Potassium ions were determined photometrically by measuring turbidity. The Potassium Cell Test supplied by Merck was used.

The rationale for choosing potassium chloride as the chloride source was that the concentration of the K^+ cation in the leachates could be easily monitored (by the mentioned method)—which was important in this work where numerous routine analyses were assumed; moreover, the effect of the K^+ cation on the chloride binding was studied.

3. Results and discussion

3.1. Extraction of OH^- and Cl^- ions: samples A1–A4

Figs. 1–4 present the results of the leaching tests of the samples A1, A3, and A4 containing an additional 0%, 1%, and 2% of Cl^- ions. Figs. 1 and 3 characterize the effect of the three variable parameters on the concentration of OH^- and Cl^- ions in the leachates. Figs. 2 and 4 show the

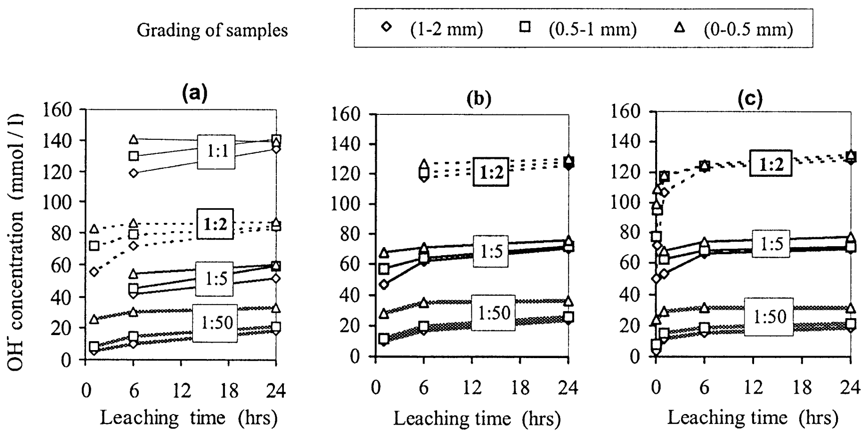

Fig. 1. Concentration of OH^- ions in the leachates obtained at various sample-to-water ratios in millimoles per liter: (a) sample A1 containing no addition of chlorides; (b) sample A3 containing 1% addition of chlorides by weight of cement; (c) sample A4 containing 2% addition of chlorides by weight of cement.

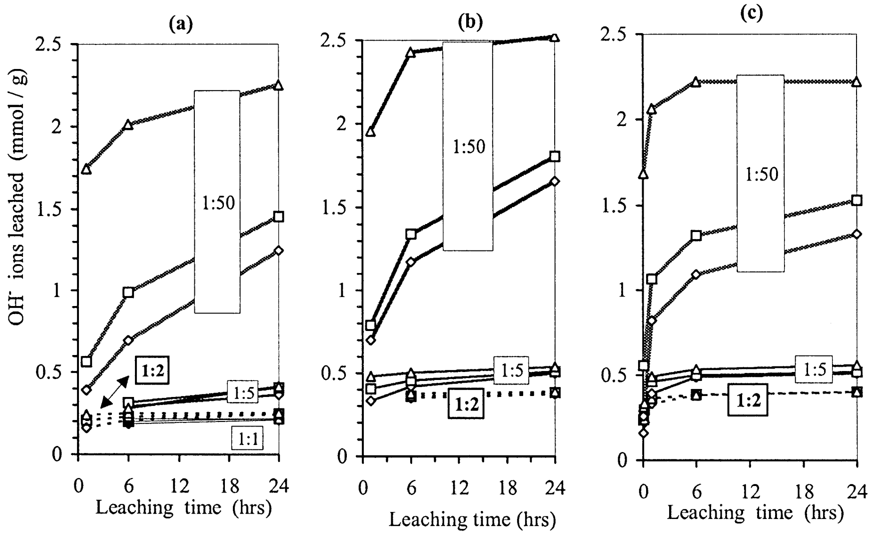

Fig. 2. The amount of OH^- ions leached from the A1 (a), A3 (b), and A4 (c) samples (containing 0%, 1%, and 2% of chlorides added by weight of cement) in millimoles per gram of cement.

quantity of the ions extracted from these samples (in millimoles per gram of cement).

The concentration of OH^- and Cl^- ions in the leachates chiefly increased during the first 6 h; later the increase was moderate or none (Figs. 1 and 3). The concentration of both of these ions was highest in the leachates obtained with the smallest addition of water, i.e., at a sample-to-water ratio of 1:1 or 1:2, as might be expected. The pH value in the leachates varied at a range from 12.3 to 13.1 after 24 h.

The effect of the particle size of the samples on the quantity of both ions which leached out within 24 h was very small, provided that the sample-to-water ratio was 1:1, 1:2, and 1:5, respectively (Figs. 2 and 4). However, if the leaching was accomplished at a sample-to-water ratio of 1:50, then the quantity of both of the leached ions was substantially higher and increased with the fineness of the samples. This was very significant in the case of the leaching of the OH^- ions. As seen in Fig. 2a,b,c, the quantity of the leached OH^- ions (in millimoles per gram of cement) significantly increased with the amount of water. Fig. 2a,b,c, and also Tables 4 and 5, further indicate that the quantity of the OH^- ions released into the solution at sample-to-water ratios of 1:2 and 1:5 also increased with the KCl content in the sample. These findings are in agreement with those that have been previously reported by other researchers [18–20].

Contrary to the OH^-, the chloride ions exhibit some differences in leaching behavior. Fig. 4b,c show that the

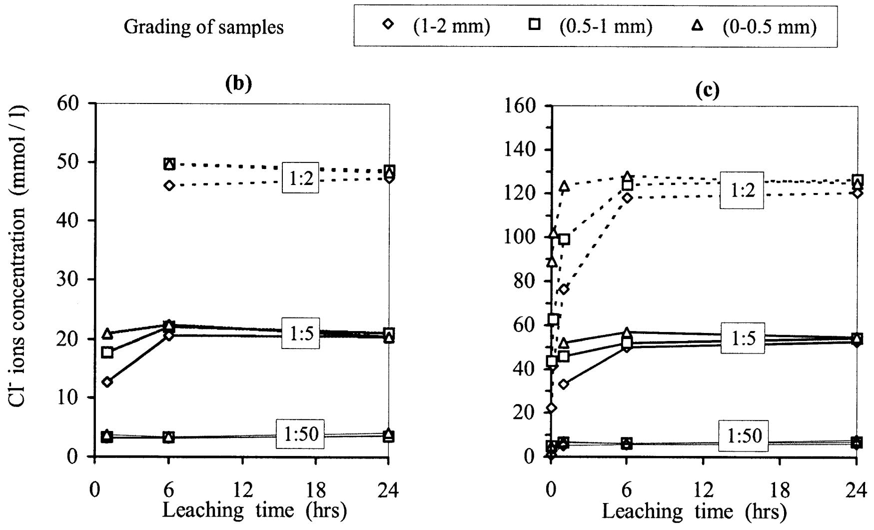

Fig. 3. Concentration of chloride ions in the leachates from the A2 (b) and A3 (c) samples with the Cl^- content of 1% and 2% by weight of cement, respectively.

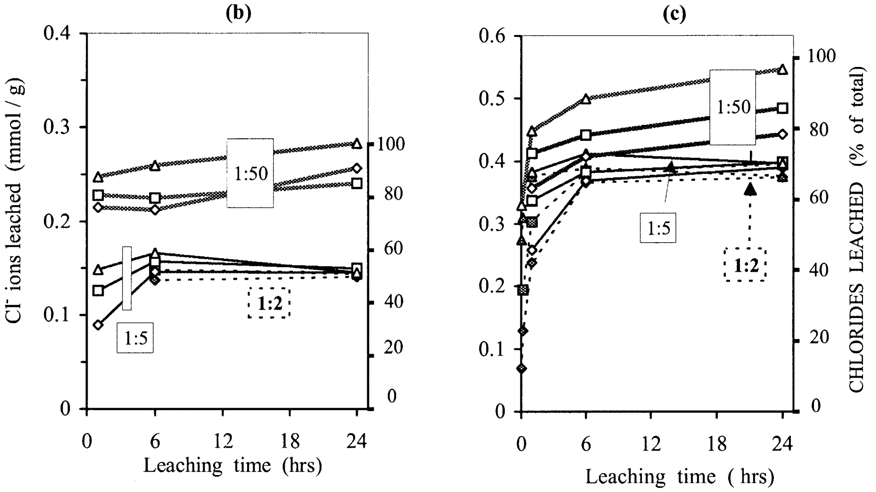

Fig. 4. The amount of chloride ions leached from the A3 (b) and A4 (c) samples in millimoles per gram of cement.

amount of the Cl^- ions extracted within a period of 24 h from samples A3 and A4 at sample-to-water ratios of 1:2 and 1:5 was nearly alike, being only slightly affected by the particle size and the sample-to-water ratio. For example, the amount of Cl^- ions released under different conditions from sample A4 within 24 h ranged from about 65% to 71% of the total chloride content in the sample (Fig. 4c). In other words, the particle size and sample-to-water ratio showed only a small effect on the leaching of the Cl^- ions under these conditions. These findings are basically in agreement with the conclusions of Arya et al. [24].

An evaluation of Fig. 4b,c has revealed that the quantity of the Cl^- ions released from samples A3 and A4 within the first hour of extraction increased significantly with the fineness of the samples at all values of the sample-to-water ratio. However, after 6 h of extraction with sample-to-water ratios of 1:2 and 1:5, the effect of the fineness was smaller, and after 24 h, it was close to zero. The concentration of chlorides chiefly increased during the first 6 h; later it increased only slightly or even decreased—as in the case of the finest samples. This indicates that after 6 h, the diffusion flow of the Cl^- ions from the particles of the sample (from the pore solution and/or the solid phases themselves) was ceasing or had stopped. We assume therefore that: (a) the concentration of the Cl^- and OH^- ions in the leachate and the pore solution at that time was close to equal; (b) the concentration of the Cl^- and OH^- ions in the leachate was close to equilibrium values with the solid

Table 3
Comparison of some water extraction techniques used by various authors and the results obtained

	Type of samples and extraction technique					
	Sample			Water extraction method at 20°C (25°C)		
Authors	Type	Cl^- content (percentage weight of cement)	Fineness (μm)	Sample-to-water-ratio	Extraction time, agitation	Percentage of Cl^- extracted
Arya et al. [24]	hardened cement paste[a] (W/C = 0.5) dried at 105°C	1% (NaCl)	<75	1:20	stirred 5 min, left standing for 55 min	21.1
			75–150			18.6
			150–300			17.9
			300–600			18.5
			<75		stirred 2 h	about 50
					stirred 4 h	about 60
					stirred 12 h	about 67
Al-Hussaini et al. [21]	cement mortars[a] (W/C = 0.5)	1% (NaCl) 2% (NaCl)	<150	sample containing 3 g of cement + 100 ml of water	stirred 1 min, left standing for 24 h	60 70
Dhir et al. [26]	concrete[a] (W/C = 0.57)	1% (NaCl) 2% (NaCl)	<150	1:20	extraction time from 24 to 48 h	67–70 76–77
Haque and Kayyali [20]	concrete of various composition[a]	1% (NaCl) 2% (NaCl)	<600	1–3.5 to 4	stirred for 5 min, left standing for 24 h	35–52 70–88

[a] Portland cement.

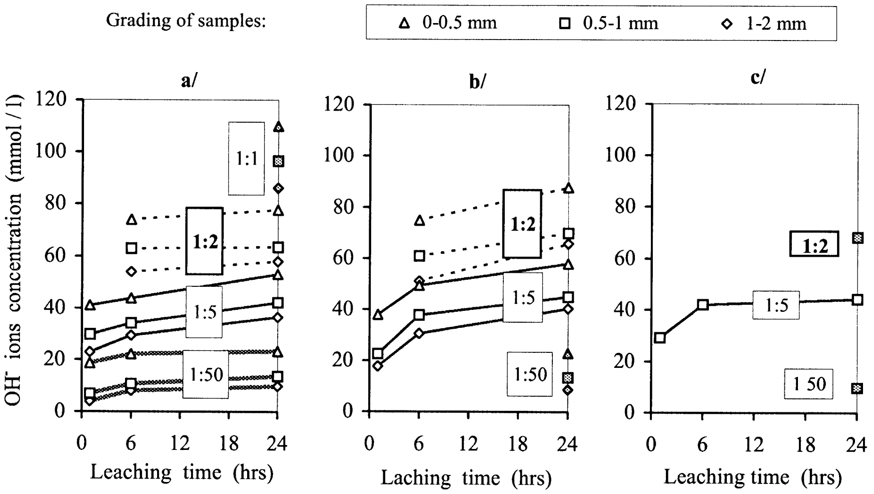

Fig. 5. Concentration of OH^- ions in the leachates obtained at various sample-to-water ratios. (a), (b), and (c) correspond to the B1, B2, and B3 samples, respectively, containing additional 0%, 0.5%, and 1% chloride ions by weight of cement.

chloride-bearing phases and thus sufficient to maintain their relative stability, and/or (c) decomposition (dissolution) of the chloride-bearing phases under these conditions was low. These assumptions might be supported by the findings of Wiens and Schiessl [29], who investigated the binding of external chlorides in hardened cement pastes. These authors have found that up to about 1.5 mg of Cl^- were bound per gram of the cement paste after it had been immersed in a 0.1 M solution of NaCl for 15 days; with the binding it still continued later. They also concluded that the chloride binding capacity of pure Portland cement mix was virtually independent of the grain size of the granulated materials, which were 0.063/0.125 and 0.5/1.0 mm.

We can further assume that within 6–24 h of the extraction, most of the free chlorides from the samples had passed into leachate. We can also expect that within 24 h, the quantity of the chlorides extracted with the addition of low amount of water was only slightly higher than the amount of the free chlorides in the sample (and that only a minute quantity of chlorides had been released from the solid chloride-bearing phases). This assumption can be supported by finding a significant proportion of chlorides unleached from the samples (Table 5).

However, when the extraction was accomplished at a sample-to-water ratio of 1:50, the quantity of the Cl^- ions leached out from the A3 and A4 samples was much higher. Under these conditions the concentration of Cl^- increased significantly even after 6 h and also rose with the fineness of the samples (Figs. 3 and 4). The quantity of the Cl^- ions released from the A4 sample after 24 h was in a range of about 78 to 98% by weight of cement (Fig. 4b,c). These facts indicate that with the addition of greater amounts of water, the chloride-bearing phases in the samples continuously decomposed, being in contact

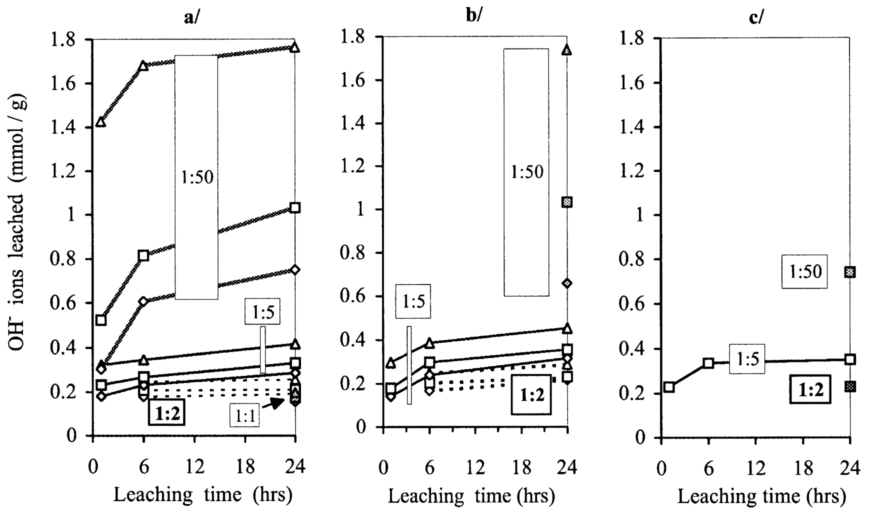

Fig. 6. The amount of OH^- ions leached from the B1 (a), B2 (b), and B3 (c) samples in millimoles per gram of cement.

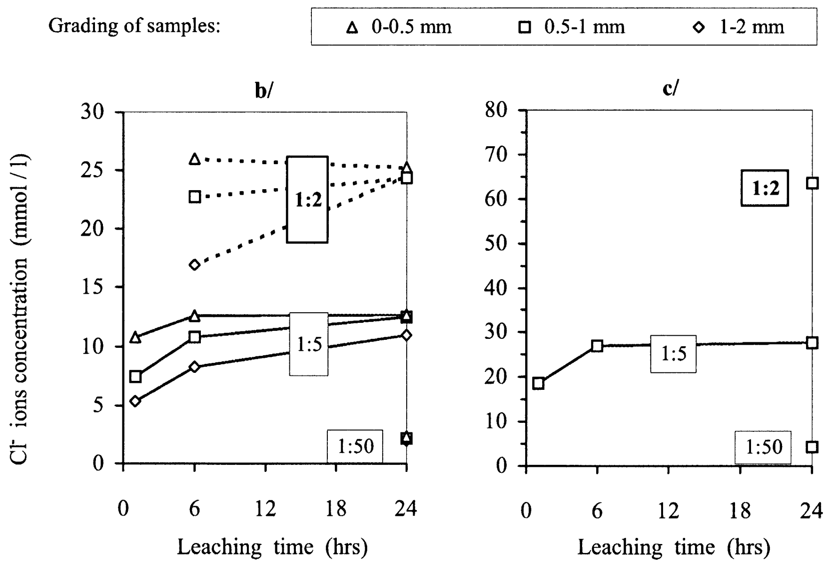

Fig. 7. Concentration of chloride ions in the leachates from the B2 (b) and B3 samples (c) with the Cl^- content 0.5% and 1% by the weight of cement, respectively.

with the leachates with a concentration of Cl^- (OH^-) ions far from the equilibrium.

3.1.1. Comparison of our results with those of other authors

A comparison of our results with those of other authors indicates difficulties arising from substantial differences in the extraction techniques adopted. According to Arya et al. [24], the amount of chloride ions released into a solution during water extraction depends upon the method adopted, which involves factors such as the fineness of the pulverized sample, the amount of water added, the temperature, the agitation method and the time allowed. However, the water-to-solid ratio and the fineness of the samples have been found to have only a small or negligible effect. Guenther [30], on the contrary, has reported that fineness was an important factor in the case of mortars. Agitation appears to be a factor that supports the leaching of chlorides. Because suspensions settle if they are not stirred, the leaching of Cl^- ions from an unagitated suspension of a sample is supposed to occur mostly in the local environment of a sediment [24]. The consequence of this is a decrease in the leaching rate of the Cl^- ions. According to Dhir et al. [26], the concentration of chlorides in the solution appears to be independent of the method of water extraction, providing the extraction time is equal to or greater than 24 h. A higher temperature (or the boiling of the suspensions) also belongs among the factors that are supposed to support the extraction of chlorides.

Some representative results on the water extraction of chlorides obtained by various authors are given in Table 3. The results in Table 3 relate only to the chlorides that were incorporated as NaCl and extracted by water at room temperature.

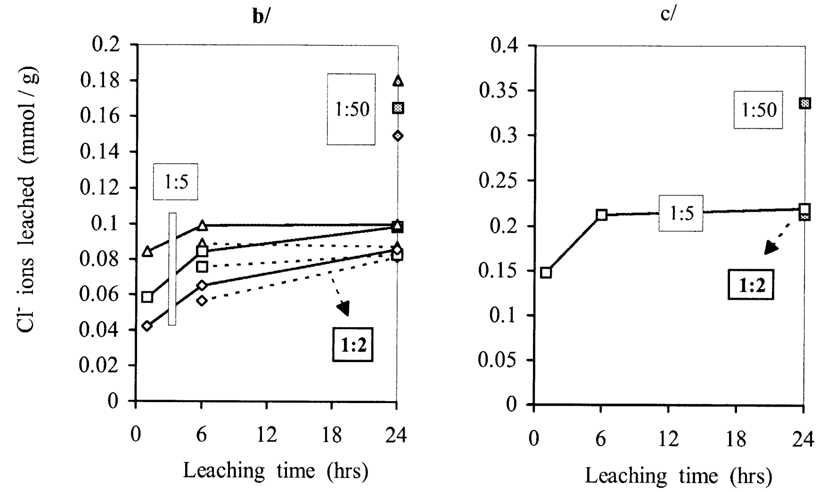

Fig. 8. The amount of chloride ions leached from the B2 (b) and B3 (c) samples in millimoles per gram of cement.

Table 4
Composition of water leachates after 24 h from samples with a particle size of 0.5–1 mm obtained under sample-to-water ratio of 1:5

Sample	Cl^- content (%)	Concentration of ions in leachates (mmol/1)				pH	Cl^-/OH^-	Total charge of ions (mmol/1)	
		OH^-	Cl^-	Ca^{2+}	K^+			$\sum (+)$	$\sum (-)$
A1	0	58.50	–	13.95	17.30	12.77	–	45.20	58.50
A2	0.5	60.60	10.98	12.08	42.43	12.78	0.18	66.59	71.58
A3	1.0	72.00	21.12	12.80	60.71	12.86	0.29	86.31	93.12
A4	2.0	70.60	54.20	12.725	92.69	12.85	0.77	118.14	124.80
B1	0	42.20	–	9.00	17.35	12.63	–	35.35	42.20
B2	0.5	45.00	12.54	8.90	28.54	12.65	0.28	46.34	57.54
B3	1.0	44.20	27.78	11.50	45.75	12.65	0.63	68.75	71.98

Some of the above-mentioned authors have determined both the water soluble and free chlorides in the samples and compared them. The method for determining free chlorides included the expression of a pore solution from the sample under high pressure and a chemical analysis of the pore solution obtained. As far as the free chlorides are concerned, their content in the samples has also been found to vary within a wide range of concentrations, as is shown, for example, in the papers of the authors in Refs. [14,16,20,24]. In cases where the chlorides had been introduced as NaCl, the amount of the free chlorides varied from about 11% to 77% of the total—at a Cl^- content of about 1% by the weight of the cement, and up to 81%—at a Cl^- content of about 2% [14,16,20,24]. Variations in the results were dependent on the composition of the Portland cement, the W/C, the mineral admixtures, and other factors. Haque and Kayyali [20] claim that the Cl^- determination in the water leachates gives an overestimation of the Cl^- ions in the pore solution.

As regards our results that are presented in this paper, it is difficult to compare them with those in Table 3, due to the differences in the conditions used in the water extraction tests. Nevertheless, we found a consistency in our results with those of the other authors mentioned, but only in cases where we performed the water extraction tests at a sample-to-water ratio of 1:2 and 1:5. However, when performing the extraction at a sample-to-water ratio of 1:50, we found the proportion of leached chlorides to be close to 100% for the finest sample after 24 h (Fig. 4b,c). These values were higher than those that most of the other authors have reported. The disproportion is difficult to explain unambiguously, but we think that the effect of the associated cation might also be responsible, since we incorporated the chlorides as KCl.

3.2. Extraction of OH^- and Cl^- ions: samples B1–B3 with the addition of SF

The results of the extraction of the OH^- and Cl^- ions from the B1, B2, and B3 samples with a 10% content of SF are presented in Figs. 5–8 and Tables 4 and 5. Tables 4 and 5 present the results of the leaching of the four monitored ions from the A1–A4 and B1–B3 samples under identical extraction conditions.

A comparison of the results of the OH^- extraction from the B1–B3 samples (Figs. 5 and 6) with those from the A1, A3, and A4 samples (Figs. 1 and 2) reveals that the addition of SF led to a significant reduction in the quantity of the OH^- ions leached. Figs. 5a,b,c and 6a,b,c further show that the incorporation of the KCl had no observable effect on the quantity of OH^- ions extracted from the pastes containing SF. This result contradicts the results obtained for the A1, A3, and A4 samples (Figs. 1 and 2), where the quantity of the extracted OH^- ions increased with the chloride content.

The leaching of the chlorides is presented in Figs. 7 and 8. Fig. 8b,c point to a very small effect of the sample-to-water ratio on the leaching of the Cl^-, providing it was in a range from 1:2 to 1:5. This is in agreement with the results obtained with the A3 and A4 samples (Fig. 4b,c). The

Table 5
Amount of ions leached in 24 h from samples with particles sizes of 0.5–1 mm when carrying out the extraction at a sample-to-water ratio of 1:5

Sample	Cl^- content (% by weight of cement)	Amount of leached ions (mmol/g cement)				Proportion of Cl^- ions leached (% of total)	
		OH^-	Cl^-	Ca^{2+}	K^+	Leached	Remaining in sample
A1	0	0.405	–	0.097	0.120	–	–
A2	0.5	0.428	0.078	0.085	0.300	54.99	45.01
A3	1.0	0.510	0.150	0.091	0.430	53.07	46.93
A4	2.0	0.518	0.398	0.093	0.680	70.52	29.48
B1	0	0.331	–	0.071	0.136	–	–
B2	0.5	0.355	0.099	0.070	0.225	69.84	30.16
B3	1.0	0.350	0.220	0.091	0.362	77.96	22.04

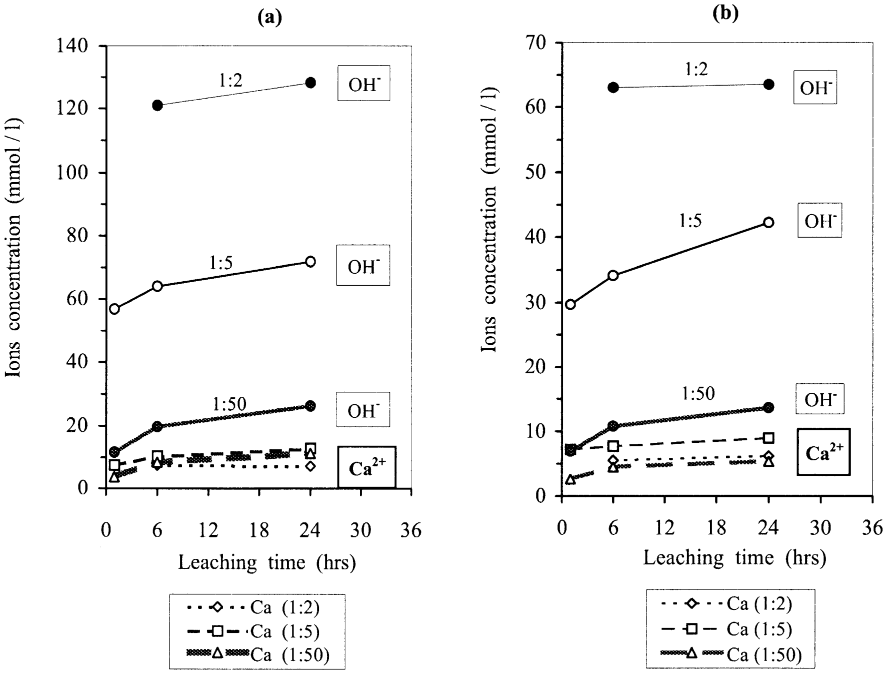

Fig. 9. Concentration of OH^- and Ca^{2+} ions in the leachates of the A3 (a) and B1 (b) samples with grading of 0.5–1 mm at various sample-to-water ratios.

addition of SF to cement pastes led to an increase in the amount and proportion of Cl^- ions released into the solution. This conclusion can be arrived at by comparing the results from the B2 and B3 samples with those from the A2 and A3 samples in Table 5 and Fig. 8c with Fig. 4b. These results correspond to the findings of other researchers in Refs. [14,17,25].

3.3. Leaching of the OH^-Cl^-, Ca^{2+}, and K^+ ions: all samples tested

Fig. 9a,b show a rise in the concentration of OH^- and Ca^{2+} ions in the leachates from samples A3 and B1 (chosen as examples) in relation to time. These results showed that changes in leaching conditions, especially those of the sample-to-water ratio, had a different effect on the leaching behavior of different type of ions. With the addition of higher amounts of water, the concentration of ions in the leachate is generally lower and therefore much further from the state of equilibrium with the solid phases. Trying to reach equilibrium again, the solid phases dissolve (congruently or incongruently) or release the adsorbed ions. As the dissolution of each compound (ion) is dependent on its solubility, the equilibrium conditions, rate of dissolution, stirring, etc., each ion is therefore affected individually.

Tables 4 and 5 confirmed our expectations on the relatively low amount of Ca^{2+} ions having passed into the solutions, bearing in mind the low solubility of calcium hydroxide in solutions of alkali metals and/or in pore solutions of hardened cement paste. Likewise, no surprise resulted from discovering a lower proportion of Ca^{2+} ions released from the B1–B3 samples containing SF than from the A1–A4 samples with no SF addition.

The results presented in Tables 4 and 5 illustrate the previously mentioned increase in the leached Cl^- ions with a chloride content in the samples. The proportions of Cl^- ions leached from the A2 and A3 samples containing 0.5 and 1% chlorides were both slightly above 50% of the total (Table 5). However, the proportion of Cl^- ions leached from the A4 sample with a chloride content of 2% was higher (60% of the total). This confirms the finding of Arya et al. [14] and other researchers on limits in the binding of chlorides.

The results presented in Tables 4 and 5 also reveal that the amount of leached K^+ ions exceeded the amount of Cl^-

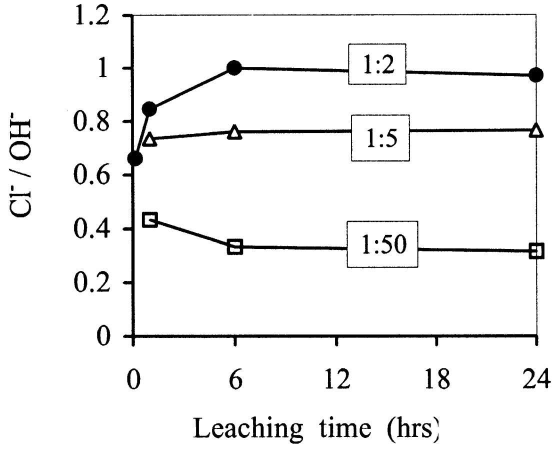

Fig. 10. Cl^-/OH^- ratio in the leachates of the sample A4 with grading of 0.5–1 mm related to leaching time.

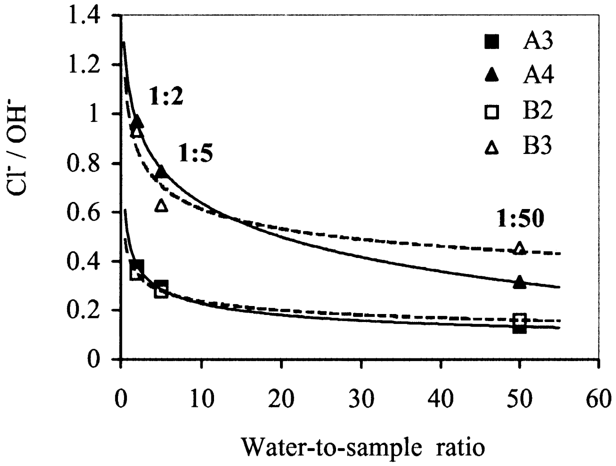

Fig. 11. Cl^-/OH^- ratio in the leachates of the samples A3, A4, B2, and B3 with grading of 0.5–1 mm after 24 h related to the sample-to-water ratio.

ions. Two factors can be responsible for this. Firstly, the binding of Cl^- ions in hardened cement paste phases is expected to be higher than that of the K^+ ions. Secondly, the higher content of the K^+ ions in the sample than of the Cl^- ions is due to the potassium content in the cement.

3.4. Cl^-/OH^- ratio in the leachates

The ratio of the molar concentration of Cl^- and OH^- ions in the leachates (Cl^-/OH^- ratio) increased with the chloride content in the samples (Table 4).

Figs. 10 and 11 show that the values of the Cl^-/OH^- ratio were significantly dependent on the leaching conditions before the others in the sample-to-water ratio (Fig. 11). This fact is not surprising, taking into account the differences in extracting Cl^- and OH^- ions. We recall here that Haque and Kayyali [20] have reported that the values of the Cl^-/OH^- ratio in the water extracts is manifestly lower than in the pore solutions expressed from the same samples. Haque and Kayyali [20] concluded that the "decantation" method cannot be reliably used to estimate the concentrations of OH^- ions in concrete. Finding their results to depend on the conditions of the leaching tests, the authors also concluded that assessment of the Cl^-/OH^- ratio in the pore solution of the concrete (and thus the corrosion risk of embedded steel) on the basis of results from the water extraction test is very questionable. We can only agree with this conclusion.

3.5. Assessment of the concentration of OH^- and Cl^- ions in the pore fluid

Figs. 12a,b and 13 show the hypothetical concentrations of OH^- and Cl^- ions in the pore fluid that were calculated from the following parameters: (a) the evaporable water content in a sample, (b) the sample-to-water ratio used during water extraction and, c/the final concentration of OH^- and Cl^- ions in the leachates after 24 h (we used specimens with 0.5–1 mm particle sizes). The calculations were based on a simple idea about the concentration of the ions in the leachate having been merely the result of the dilution of the pore solution contained in a sample with water added during the extraction test. We were conscious of the inaccuracy of the method, because it ignored the dissolution/decomposition of solid phases during extraction and the incomplete leaching of ions from the pore solution.

If assuming that the concentration of ions in the leachate is the result only of mixing the pore solution (in the sample) with water added during extraction, then the calculated hypothetical concentration of the pore solution should not be dependent on the sample-to-water ratio and should give the lines parallel with the *x*-coordinate in Figs. 12 and 13. However, Figs. 12 and 13 show that the hypothetical pore

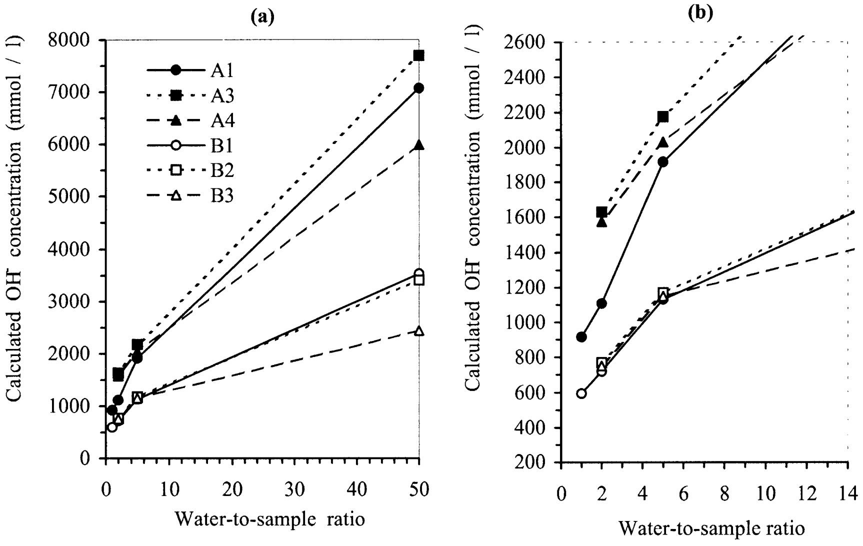

Fig. 12. (a) Calculated hypothetical concentration of the OH^- ions in the pore solution of the samples with particle sizes 0.5–1 mm related to the water-to-sample ratio. (b) This represents enlarged area of the figure at low values at both axes.

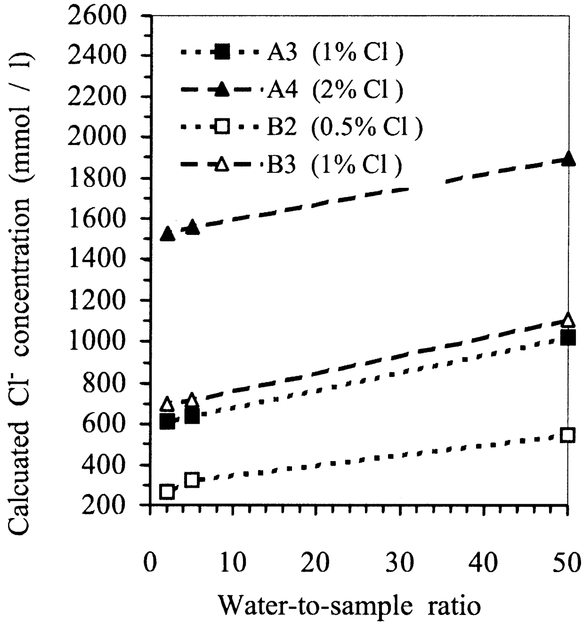

Fig. 13. Calculated hypothetical concentration of the Cl^- ions in the pore solution of the specimen related to the water-to-sample ratio.

solution concentration of both ions increases with the amount of water added. This tendency is very significant for OH^- ions and slight for Cl^- ions that show a linear dependence. These results suggest that both ions have also probably been released from the solid phases, especially with the addition of higher amounts of water where they were immersed in the diluted solutions. Observations about an enormous increase in the released OH^- ions in the diluted leachates were again in agreement with the findings of Haque and Kayyali [20].

The concentrations of OH^- and Cl^- ions in the pore solution can finally be estimated by extrapolating the hypothetical pore solution concentrations to a zero value of the sample-to-water ratio in Figs. 12 and 13. These are denoted as "extrapolated pore solution concentrations." The hypothetical Cl^-/OH^- ratios in the pore solutions, which were calculated from the "extrapolated pore solution concentrations" were 0.5 and 1.2 for the A3 and A4 samples, and 0.4 and 1.4 for the B2 and B3 samples, respectively. Even when we could not compare these results with the actual values in the pore solution, they seem to be close to, or in the range of, the Cl^-/OH^- ratios in the actual pore solutions of comparable samples, as was reported by other investigators [18,20,25]. The results are also in agreement with the findings of Rasheeduzzafar [25] about a significant increase in the Cl^-/OH^- ratio with the addition of SF.

4. Conclusions

1. Water extraction can provide valuable information about the chemical composition of hardened cement paste.
2. The results obtained depend on the conditions of the water extraction test. Changes in leaching conditions affect the leaching of various ions in different ways.
3. The effect of the particle size of the samples is relatively low if a low sample-to-water ratio is used during water extraction.
4. The addition of low amounts of water not exceeding the sample-to-water ratio of 1:5 is recommended for testing hardened cement pastes. This condition can bring about difficulties when testing samples of pulverized concrete, due to the high proportion of finely ground aggregate in the sample that dilutes it.
5. The Cl^-/OH^- ratio in the pore solution can be assessed from the results of a series of water extraction tests carried out at different sample-to-water ratios.

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