Investigations of reinforcement corrosion. 1. The pore electrolyte phase in chloride-contaminated concrete*

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A sampling procedure, which avoids the need for wet cutting, has been developed for determination of compositional profiles of the pore liquid phase within concrete exposed to chloride ingress. The technique has been used to assess the effects on various concrete specimens of exposure to different regimes of chloride penetration and to compare them with those of salt, introduced as a constituent of the mix materials. The implications regarding *corrosion risk to embedded steel are provisionally evaluated in terms of the ratio of chloride to hydroxyl ion concentrations in the pore solution. The significance of this parameter is to be considered in Part 2.*

1. INTRODUCTION

Chloride ions may enter concrete structures prior to hydration as admixtures and contaminants or, after hydration, from external sources such as sea-water and de-icing salts. Once they are within the concrete matrix they tend to depassivate embedded steel by locally breaking down the protective layer of oxide, which is normally formed in the highly alkaline environment produced during hydration [1]. The intense anodic sites so created develop into characteristic pits which may continue to grow provided the chloride ion concentration exceeds a critical level. It is believed from evidence of the behaviour of steel in aqueous solutions that this threshold value will be dependent upon the hydroxyl ion concentration of the pore electrolyte phase of the concrete $[2,3]$.

It is possible to determine the total chloride content of concrete samples by standard analytical procedures and to assess the alkalinity of the material by measuring the depth of carbonation with indicators such as phenolphthalein. Such methods give imprecise criteria for determining corrosion risk, however, as a variable proportion of chloride may exist in an insoluble form such as calcium chloroaluminate hydrate, and the pH of concrete classed as alkaline by the standard phenolphthalein test may vary considerably.

To obtain a more reliable indication of the corrosiveness of concrete specimens exposed to chloride-laden or carbonating environments it is necessary to undertake detailed analysis of the pore electrolyte composition as a function of distance from the exposed surface [4]. This

paper describes an experimental approach to the problem, which was intended to minimize risks of sample contamination and leaching arising from sectioning of the material to yield specimens for pore solution expression. The technique developed for this purpose avoids the need for use of a lubricated cutting wheel and has been termed 'crush-sectioning'.

In the present contribution it is shown that crushsectioning and pore solution expression can be used to obtain samples of pore liquid from cement paste and concrete specimens of various kinds. Analysis of pore solution samples for chloride and hydroxyl ions has been undertaken to yield concentration profiles of these species with distance from the concrete surface for a variety of mix compositions and conditions of exposure to salt ingress. Pseudo-diffusion coefficients for chloride ions have been calculated and the suitability of wet/dry cycling as a method for accelerating the penetration of chloride into concrete is discussed. The effects are compared with those of chloride salts introduced as mix contaminants.

2. EXPERIMENTAL PROCEDURE

2.1 External sources of chloride

In order to examine the effects of various external sources of chloride ions on the pore solution chemistry of concrete, a series of slabs, 200mm by 300mm with 100 mm depths, were produced. A 25 mm pond was cast on to the upper surface of each slab to allow the application of sodium chloride solution. A series of grooves were cast into the base so that after exposure the concrete could be broken into six roughly equal 100 mm cubes prior to sectioning. The vertical sides of the slabs were clad with 2 mm polypropylene sheeting so that only

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Table 1 Composition of cements

the top and bottom surfaces were exposed to the atmosphere.

The compositions of the two cements and four mixes are given in Tables 1 and 2. When tested according to procedures specified in BS 1881:1983 [5], the concretes had slumps of about 40 mm and Vebe times of approximately 4 s. The average 28-day compressive strengths of cubes were approximately 45MPa for the limestone concrete and 50 MPa for the two quartzite concretes. The aggregates were washed and surface-dried prior to use and deionized water was employed for mixing. Each specimen was vibrated during casting, demoulded after 48 h and cured under water for 7 days before preparation for exposure to chloride at 14 days.

Three methods for the introduction of chloride ions were utilized, all involving 5wt% sodium chloride solution. One set of slabs was exposed to a nominally constant solution of sodium chloride, which was maintained in a covered pond. This solution (a volume of 11) was replaced weekly as, after that time, the chloride ion concentration was becoming significantly reduced and the pH value was approaching 12.5 owing to the leaching of alkalis from the hydrated cement. A second set of slabs received a weekly wet/dry cycle in which 100 ml of salt solution was applied and allowed to dry in the uncovered pond for three to four days. After this 100 ml of water was applied and left to evaporate for the remainder of the week. The final method of exposure consisted of drying the slabs for one week at 35° C after which 11 of 5% sodium chloride solution was placed in the pond and maintained for three weeks. The remaining solution was then siphoned off and the cycle repeated.

2.2 Crush-sectioning and pore solution analysis

Chemical analysis of the above specimens was undertaken after exposure for 6, 12 and 24 months and consisted of free and total chloride ion and free hydroxyl ion determination at $10, 20, 30$ and 40 mm depths. Once each slab had been divided into six 100 mm cubes, the latter were wrapped in flexible polyethylene jackets and individually loaded slightly beyond the point of failure in a standard compression testing machine. At this point the shattered cube, held together by its jacket, was removed and successive layers of material, each 10 mm in thickness about the mean required depth (e.g. 20 ± 5 mm), were taken from the surface downwards. The coarse aggregates were separated from the crush-sectioned layers, to leave samples of mortar that were of suitable form for pore solution expression.

The method of sampling pore liquid was based on the technique devised by Longuet *et al.* [6]. This has been used in several recent studies of pore solution chemistry and its relationship with chloride-induced corrosion of steel in hardened cement pastes, mortars and concretes [7-16]. The apparatus was of the same design as that described in an earlier paper [9].

Samples of crush-sectioned material were placed into the pore liquid expression device and the pressure was gradually increased to a maximum value of about 350MPa, causing the mortar fragments to become consolidated and then to exude samples of pore solution. These were collected in plastic syringes and stored in airtight plastic vials prior to analysis. The hydroxyl ion concentration was determined by titration with nitric acid while the chloride ion concentration was measured by a standard spectrophotometric technique [17]. A small sample of every specimen of crush-sectioned material was retained for the determination by a standard procedure of the total chloride content as a proportion by weight of the cement [18].

2.3 Internal chloride additions

A further set of experiments was carried out with 100 mm cubes made with the OPC-quartzite and SRPC-quartzite

Table 2 Composition of mixes

concretes, containing various levels of chloride ion (as sodium chloride added during mixing) and exposed to laboratory air at 100% relative humidity. These cubes were simply crushed and subjected to pore solution analysis for chloride and hydroxyl ions after 6, 12 and 24 months.

3. RESULTS AND DISCUSSION

The analytical data obtained for specimens exposed to external sources of chloride are presented in Tables 3-6, whilst those for specimens containing admixed chloride are shown in Table 7.

3.1 Effects of external chlorides

Inspection of the results for external chlorides provides the following information regarding the influence of exposure condition and specimen composition on the evolution of pore solution chemistry as a function of depth and time.

(i) As expected, the chloride profiles recorded depended on the nature of the exposure regime. In specimens exposed to constantly maintained solutions of 5% sodium chloride, the increase in chloride level at the exposed surface was limited by the chloride concentration of the external medium (855 mmol1^{-1}) , though occasional anomalies arose in the results for concrete made from OPC and quartzite aggregate (see Table 4), suggesting that measures for preventing evaporation were not wholly effective. For specimens exposed to cyclic wetting and drying, however, substantially higher rates of ingress and ultimate concentrations of free chloride were found. This is consistent with evidence obtained from some real structures exposed to intermittent treatment

Table 3 Analytical data for specimens of OPC paste

Exposure condition	Time (months)	Depth (mm)	Total chloride (mg per g cement)	Free chloride $(mmol1^{-1})$	pH	log[Cl]/[OH]
Constant solution	$\overline{6}$	$10\,$	$11-3$	225	13.35	0.00
		20	7.1	51	13.51	-0.80
		30	5.3	33	13.54	-1.02
		40	3.7	14	13.58	-1.43
	12	10	13.0	230	13.24	0.12
		20	11.9	125	13.37	-0.28
		30	9.0	35	13.53	-0.98
		40	8.3	30	13.56	-1.08
	24	10	21.0	623	13.04	0.75
		20	16.7	484	13.24	0.44
		30	13.9	323	13.40	0.11
		40	12.1	235	13.47	-0.10
Weekly cycle	$\boldsymbol{6}$	10	12.6	650	13.46	0.35
		20	7.9	145	13.58	-0.42
		30	5.6	85	13.61	-0.68
		40	4.8	$\bf 48$	13.61	-0.93
	12	10	16.6	900	13.45	0.50
		20	16.0	580	13.51	0.25
		30	10.4	280	13.59	-0.14
		40	8.7	140	13.61	-0.46
	24	10	32.6	2196	13.28	1.06
		20	24.7	1478	13.51	0.66
		30	21.3	1368	13.58	0.56
		40	19.8	1094	13.58	0.46
Monthly cycle	6	$10\,$	17.9	750	13.32	0.56
		20	11.5	430	13.56	0.07
		30	9.2	310	13.61	-0.12
		40	7.0	280	13.58	-0.13
	12	10	21.9	1080	13.22	0.81
		20	18.4	840	13.39	0.53
		30	15.4	635	13.48	0.32
		40	12.8	530	13.57	0.15
	24	10	35.9	2306	12.81	1.55
		20	35.1	2267	13.03	1.33
		30	32.4	2261	13.23	1.12
		40	30.3	2215	13.34	1.01

Table 4 Analytical data for specimens of OPC-quartzite concrete

Exposure condition	Time (months)	Depth mm	Total chloride (mg per g cement)	Free chloride $(mmol1^{-1})$	pH	log[Cl]/[OH]
Constant solution	$\boldsymbol{6}$	10	15.2	375	12.85	0.72
		20	14.6	125	13.25	-0.15
		30	12.2	50	13.34	-0.64
		40	8.4	15	13.35	-1.17
	12	10	25.7	1055	12.78	1.24
		20	19.1	595	13.01	0.76
		30	14.8	202	13.18	0.13
		40	11.2	137	13.21	-0.07
	24	10	26.4	1270	12.65	1.45
		20	23.6	940	12.78	1.19
		30	21.9	795	12.98	0.92
		40	20.6	773	13.11	0.78
Weekly cycle	$\boldsymbol{6}$	10	23.8	1605	13.07	1.14
		20	23.8	1120	13.42	0.63
		30	13.3	265	13.46	-0.04
		40	6.4	50	13.40	-0.70
	12	10	31.1	1800	13.05	1.21
		20	24.8	1075	13.31	0.72
		30	18.2	422	13.39	0.24
		40	11.5	343	13.39	0.15
	24	10	40.2	2720	12.79	1.64
		20	37.2	2250	13.02	1.33
		30	25.1	1400	13.22	0.93
		40	23.6	1350	13.39	0.74
Monthly cycle	$\boldsymbol{6}$	10	31.7	1750	12.98	1.26
		20	29.9	1415	13.26	0.89
		30	18.9	645	13.40	0.41
		40	10.2	315	13.48	0.02
	12	10	34.9	1350	12.85	1.28
		20	32.7	1300	13.08	1.03
		30	20.4	730	13.24	0.62
		40	20.2	578	13.23	0.53
	24	10	46.3	3250	12.72	1.79
		20	39.7	2550	12.85	1.56
		30	30.3	1850	13.09	1.18
		40	29.9	1850	13.11	1.16

with de-icing salts where high concentrations of chloride have been found to develop [19].

(ii) Linear relationships between total chloride and free chloride concentration in the pore solution phase were observed for all four types of specimen. These are illustrated in Figs 1-4, which show the straight lines of best fit obtained by regression analysis. Very high correlation coefficients $(R>0.94)$ were obtained in all cases (see Table 8). The fact that the lines were all characterized by positive intercepts on the horizontal axis, corresponding to total chloride contents in the range $0.6-1.0\%$, is in contrast with the findings of Tuutti [7] who reported that free chloride concentrations show rectilinear dependence on total chloride from the origin. The results of the present study imply that, at total chloride contents below about 1.0%, the cement hydrates bind a substantial proportion of the chloride in an

Fig. 1 Relation between free and total chloride for OPC paste exposed to salt ingress.

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Fig. 2 Relation between free and total chloride for OPC-quartzite concrete exposed to salt ingress.

Fig. 3 Relation between free and total chloride for OPC-limestone concrete exposed to salt ingress.

Table 6 Analytical data for specimens of SRPC-quartzite concrete

Exposure condition	Time (months)	Depth (mm)	Total chloride (mg per g cement)	Free chloride $(mmol1^{-1})$	pН	log[Cl]/[OH]
Constant solution	6	10	15.2	500	12.64	1.06
		20	14.6	230	13.03	0.33
		30	9.0	175	13.12	0.12
		40	8.4	58	13.23	-0.47
	12	10	18.6	798	12.58	1.32
		20	15.2	593	12.95	0.82
		30	11.9	388	13.08	0.51
		40	10.0	155	13.11	$0.08\,$
	24	10	21.1	850	12.41	1.52
		20	17.3	700	12.48	1.37
		30	16.4	650	12.68	1.13
		40	14.3	590	12.75	1.02
Weekly cycle	6	10	32.7	2150	13.10	1.23
		20	19.5	915	13.29	0.67
		30	13.8	330	13.31	0.21
		40	11.5	270	13.32	0.11
	12	10	35.3	2200	13.00	1.34
		20	20.7	900	13.08	0.87
		30	16.1	640	13.20	0.61
		40	16.1	600	13.21	0.57
	24	10	38.7	2500	12.61	1.79
		20	38.3	2300	12.92	1.44
		30	29.8	1800	12.97	1.29
		40	25.1	1365	13.07	1.07
Monthly cycle	6	10	35.9	2550	12.73	1.68
		20	29.1	2400	13.02	1.36
		30	22.9	1185	13.24	0.83
		40	13.3	555	13.28	0.46
	12	10	36.3	2550	12.71	1.70
		20	34.8	2400	12.97	1.41
		30	29.9	1450	13.11	1.05
		40	20.6	750	13.14	0.74
	24	10	38.3	2570	12.38	2.03
		$20\,$	38.1	2550	12.38	2.03
		30	38.0	2540	12.38	2.02
		40	37.3	2460	12.75	1.64

Fig. 4 Relation between free and total chloride for SRPC-quartzite concrete exposed to salt ingress.

insoluble form but beyond this point the binding capacity is largely exhausted. If it is assumed that further binding of chloride is negligible, the slopes (m) of the lines in Figs I-4 may be related to the available pore water content (W_p) of the concretes concerned by

$$
W_{\rm p} = \frac{10^4}{35.5m} \,\text{g per g cement}
$$

Calculated values of $W_{\rm p}$ are presented in Table 8, from which it would appear that the available pore water was relatively constant, and of reasonable value for wellhydrated concrete of water/cement = 0.5 [20], except in the case of specimens containing limestone aggregate. For the latter, the porosity of the aggregate had significantly enhanced the available pore water. In confirmation of this, it was shown by initial testing that both the quartzite

and limestone aggregates originally contained negligible amounts of chloride, but alter ponding with 5% sodium chloride solution, analysis of particles removed from the crush-sectioned concretes showed that the limestone contained up to 2% chloride by weight whereas the quartzite contained less than 0.1%. Thus in limestone concrete it appears that chlorides can be transported through the aggregate as well as the surrounding cement paste, but this is not so for quartzite concrete.

(iii) The pH values of the pore solution within the exposed specimens tended to decrease with time owing to the influence of leaching and/or carbonation. This was a marked effect for specimens exposed to the monthly cycle of wetting and drying and for those in contact with a constantly applied solution of sodium chloride. It was relatively moderate for the materials exposed to the weekly cycle. The overall effect of changes in pH and free chloride concentration on the corrosive nature of the pore solution may be judged in terms of the ratio

 $[Cl^-]/[OH^-]$. The logarithms of this index are given in Tables 3-6 for the various regimes. On the basis of this criterion, it would appear that the most severe of the three testing regimes was consistently the monthly cycle, followed by the weekly cycle, with the constantly maintained solution tests the least aggressive. This finding is of practical interest in relation to accelerated corrosion testing.

(iv) Viewed from a similar standpoint of the level of [CI-]/[OH-] corresponding to given exposure conditions, it is possible to rank the various types of specimen studied in order of the protection they might be expected to afford to embedded steel. Comparison of the $log [Cl^-]/[OH^-]$ data in Tables 3–6 indicates that the SRPC concrete was somewhat less protective than the two OPC concretes, which were marginally less protective than the OPC paste specimens. The reduced level of protection afforded by the SRPC concrete appeared to be due to a combination of factors, amongst which were the

Table 8 Parameters derived from linear regression (Figs I-4)

Specimen type	Slope, m	Correlation coefficient,	Pore water content. $W_{\rm p}$
OPC paste	798.4	0.97	0.35
OPC-quartzite concrete	804.9	0.95	0.35
OPC-limestone concrete	659.9	0.94	0.43
SRPC-quartzite concrete	864.3	0.98	0.33

Specimen type	Time	$D \times 10^{13}$ (m ² s ⁻¹)			
	(months)	Constant solution	Weekly cycle	Monthly cycle	
OPC paste	6	101	125	160	
	12	98	120	131	
	24	104	129	177	
OPC-quartzite concrete	6	135	181	357	
	12	140	168	405	
	24	145	177	353	
OPC-limestone concrete	6	108	145	269	
	12	102	157	265	
	24	112	146	277	
SRPC-quartzite concrete	6	254	313	431	
	12	245	310	444	
	24	260	284	377	

Table 9 Pseudo-diffusion coefficients from free chloride profiles

relatively high mobility of chloride and hydroxyl ions, the low natural alkalinity of the cement and its low capacity to bind chloride as calcium chloroaluminate hydrate (SRPC, C_3A content $\sim 2\%$, cf. OPC, C_3A content $\sim 15\%$).

(v) As a further indicator of the relative rates of chloride ingress for the various specimens and exposure conditions, the free chloride concentration profiles have been extrapolated to yield surface values (C_s) and then used to estimate pseudo-diffusion coefficients (D) from a standard solution of Fick's second law, which applies to unidirectional diffusion into a semi-infinite medium of constant D

$$
\frac{C}{C_s} = 1 - \text{erf}\left(\frac{x}{2(Dt)^{1/2}}\right)
$$

where $C =$ concentration at distance x from the exposed surface after time t . The assumptions involved in applying this equation [21] clearly cannot be rigorously justified for specimens exposed under the various conditions employed in the present investigations. Nevertheless the results of the calculations, which are presented in Table 9, provide a useful means of classifying the effects of specimen type and exposure condition. The values of D obtained for those specimens exposed to constantly maintained solutions are of similar magnitude to diffusion coefficients obtained previously for chloride ions in concrete and related materials by alternative methods [22,23].

3.2 Effects of internal chlorides

The results in Table 7 indicate that relatively stable concentrations of chloride and hydroxyl ions were found in the pore solutions of all specimens which were stored in air at 100% RH for 6 months or more.

At the lowest level of addition of sodium chloride (0.4% chloride ion by weight of cement) there was a substantial difference between the concentrations of free chloride present in the concretes made from OPC and SRPC. This confirms the well-known importance of C_3A content of cements in relation to their chloride binding capacity [24]. At higher levels of addition of sodium chloride, the differences between the two cements became proportionately less significant though the trend was still observable at chloride levels of 2.0% by weight of cement,

A secondary effect of sodium chloride was to enhance the natural pH value of the pore solutions, as has been noted in previous studies where effects of salt contamination on the risk of alkali-silica reaction have been discussed [25]. The net effect of changes in free chloride levels and pH in the various specimens is shown in Fig. 5, which illustrates that conditions within the SRPC concretes were consistently more aggressive than those in the OPC concretes at the same levels of total chloride.

Comparison of the data for log [Cl-]/[OH-] in Table 7 with those obtained for external chlorides (Tables 4 and 6) suggests that the effects of the latter at a given level of total chloride are likely to be the more severe, owing to the reduced pH values of concretes exposed to external solutions. It should be noted, however, that such a

Fig. 5 Relation between ratio of free chloride to hydroxyl ion concentration and total chloride for OPC and SRPC-quartzite concretes with salt as an admixture.

generalization clearly cannot be expected to apply to specimens at early stages of curing and this may have an important bearing on the behaviour of embedded steel as will be discussed in Part 2 [26].

4. CONCLUSIONS

The main conclusions arising from this part of the investigation were as follows.

(i) The method of crush-sectioning provided a convenient means of preparing concrete samples for pore solution expression. It avoided the disadvantages of wet cutting procedures that are often employed for sectioning concrete prior to analysis.

(ii) The three methods used for introducing externally applied chlorides into concrete produced substantially differing effects on the pore solution chemistry, monthly wetting and drying cycles being the most severe regime in terms of their influence on [Cl^{-}]/ [OH^{-}] ratios.

(iii) For specimens into which relatively high concentrations of chloride had penetrated ($> 1\%$ chloride by weight of cement), the relationship between free and total chloride concentrations was roughly linear with a slope that appeared to depend on the available porosity of the concrete; this was in turn influenced by the type of aggregate.

(iv) Concrete made from SRPC was found to exhibit higher ratios of free \lceil Cl⁻⁻ \rceil / \lceil OH⁻⁻ \rceil than that made from OPC, when exposed under identical conditions to external chlorides and when made with chlorides in the original mix. The differences between the two cements studied were most significant when the total chloride content of the concretes was low.

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REFERENCES

- I. Page, C. L. and Treadaway, K. W. J., 'Aspects of the electrochemistry of steel in concrete', *Nature* 297 (5862) (1982) 109-115.
- 2. Hausmann, D. A., 'Steel corrosion in concrete', *Mater. Protection* 6 (November 1967) 19-23.
- 3. Gouda, V. K., 'Corrosion and corrosion inhibition of reinforcing steel: 1. Immersed in alkaline solution', *Br. Corrosion* J. 5 (1970) 198-203.
- 4. Page, C. L. and Lambert, P., 'Analytical and electrochemical investigations of reinforcement corrosion', TRRL Contractor Report CR 30 (Transport and Road Research Laboratory, 1986).
- 5. British Standards Institution, 'The testing of hardened concrete', BS 1881 (1983).
- 6. Longuet, P., Burglen, L. and Zelwer, A., 'La phase liquide du

ciment hydraté', *Rev. Matér. Constr. Trav. Publics* 676 (1973) 35-41.

- 7. Tuutti, K., 'Corrosion of steel in concrete', Research Report FO 4 (Swedish Cement and Concrete Institute, Stockholm, 1982).
- 8. Sorensen, B. and Maahn, E., 'Penetration rate of chloride in marine concrete structures', *Nordic Concr. Res.* 1 (1982) 24.1-24.18.
- 9. Page, C. L. and Vennesland, O., 'Pore solution composition and chloride binding capacity of silica-fume cement pastes', *Mater. Struet.* 16 (1983) 19-25.
- 10. Holden, W. R., Page, C. L. and Short, N. R., 'The influence of chlorides and sulphates on durability', in 'Corrosion of Reinforcement in Concrete Construction', edited by A. P. Crane (Ellis Horwood, Chichester, 1983) pp. 143-150.
- 11. Andrade, C. and Page, C. L., 'Pore solution chemistry and corrosion in hydrated cement systems containing chloride salts: a study of cation specific effects', *Br. Corrosion J.* 21 (1) 1986) 49-53.
- 12. Page, C. L., Short, N. R. and Holden, W. R.,'The influence of different cements on chloride-induced corrosion of steel in concrete, *Cement Concr. Res.* 16 (1) (1986) 79-86.
- 13. Byfors, K., Hansson, C. M. and Tritthart, J., 'Pore solution expression as a method to determine the influence of mineral additives on chloride binding', *ibid.* 16 (5) (1986) 760-770.
- 14. Diamond, S., 'Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures'. *Cement Concr. Aggreg.* **8** (2) (1986) 97-102.
- 15. Mangat, P. and Gurusamy, K., 'Pore fluid composition under marine exposure of steel fibre reinforced concrete'. *Cement Concr. Res.* 17 (5) (1987) 734-742.
- 16. Kayyali, O. A. and Haque, M. N., 'Chloride penetration and the ratio of Cl^-/OH^- in the pores of cement paste', *ibid.* 18 (6) (1988) 895-901.
- 17. Vogel, A. I., "A Text-book of Quantitative Inorganic Analysis', 4th Edn (Longman, Harlow, 1978) pp. 753-755.
- 18. Berman, H. A., "Determination of chloride in hardened portland cement paste, mortar and concrete', *J. Mater. 7* (1972) 330-335.
- 19. Wallbank, E. J., "The performance of concrete in bridges: a survey of 200 highway bridges' (Department of Transport, HMSO, London, 1989).
- 20. Neville, A. M. and Brooks, J. J., 'Concrete Technology' (Longman, Harlow, 1987) pp. 101-108.
- 21. Crank, J., 'The Mathematics of Diffusion' (Oxford University Press, 1975).
- 22. Collepardi, M., Marcialis, A. and Turriziani, R., 'Penetration of chloride ions into cement pastes and concretes', *J. Amer. Ceram. Soc.* 55 (1972) 534-535.
- 23. Page, C. L., Short, N. R. and El Tarras, A., 'Diffusion of chloride ions in hardened cement pastes', *Cement Concr. Res.* 11 (1981) 395~406.
- 24. Roberts, M. H., 'Effects of calcium chloride on the durability of pre-tensioned wire in prestressed concrete', *Mag. Concr. Res.* 14 (42) (1962) 143-154.
- 25. Nixon, P. J., Page, C. L., Canham, I. and Bollinghaus, R., 'Influence of sodium chloride on alkali-silica reaction', *A~h,. Cement Res.* 1 (2) (1988) 99-106.
- 26. Lambert, P., Page, C. L. and Vassie, P. R. W., 'Investigations of reinforcement corrosion. 2. Electrochemical monitoring of steel in chloride-contaminated concrete', *Mater. Struct.* in press.

RESUME

Etude de la corrosion des armatures: 1. La phase 'électrolyte interstitielle' dans le béton contaminé par des **chiorures**

On exprime généralement en termes de contenu total de *chlorure et de profondeur de carbonatation les critères qui déterminent le risque de corrosion dans le béton armé, On détermine par les procédures analytiques classiques la teneur totale en chlorure, et par les indications de pH telles que la phénolphtaléine, la profondeur de carbonatation. Ces* m éthodes sont imprécises du fait qu'une proportion variable *de la teneur totale en chlorure peut exister sous forme insoluble comme celle de l'hydrate de chloroaluminate de calcium et que, d'autre part, le pH de l'électrolyte présent* dans le béton que la phénolphtaléine indique comme étant *alcalin, peut varier d'environ 10-14.*

Afin d'obtenir une phts shre indication du risque de

corrosion à différentes profondeurs dans le béton exposé à des milieux riches en chlorures, on doit analyser la composition de l'électrolyte interstitielle en fonction de la distance de la surface exposée. Cet article, qui est le premier *d'une étude en deux parties, décrit une approche* expérimentale par laquelle on dispose d'échantillons de matériau avec solution interstitielle à différentes pro*fondeurs dans des spécimens de béton exposés sans qu'on ait* recours à un outil de coupe lubrifié. Cette technique appelée 'crush-section' élude par conséquent les risques p *>tentiels de contamination de l'échantillon et de lessivage. On a procédé* \dot{a} une estimation des effets de l'exposition sur plusieurs *types de béton à différents régimes de progression de sels. Les risques de corrosion en tant que fonction de la* profondeur de pénétration et de la durée d'exposition sont provisoirement évalués en termes de variation des con*centrations relatives de chlorure libre et d'ions hydroxyles dans la solution interstitielle.*