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Durable Concrete for a Waste Repository - Measurement of Ionic Ingress

by R.F. Feldman, J.J. Beaudoin and K.E. Philipose

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Résumé

L'aménagement d'un site d'enfouissement souterrain de déchets faiblement radioactifs est prévu aux Laboratoires nucléaires de Chalk River. Son succès dépend en grande partie de la durabilité du béton, pour lequel on exige une vie utile de 500 ans. Un programme de recherche visant à concevoir un béton durable et à prévoir sa durée utile est en cours.

La dégradation du béton est fonction de la vitesse de pénétration des agents de corrosion. La pénétration des chlorures et des sulfates est particulièrement critique. Vingt-six formules ont été élaborées pour créer plusieurs types et qualités de béton, et étudier leur comportement sous les diverses conditions environnementales auxquelles le béton est exposé, y compris l'effet du CO₂. Les facteurs relatifs à la durabilité ont été pris en compte. Les bétons chlorurés et sulfurés sont étudiés par rapport aux paramètres de porosité.

DURABLE CONCRETE FOR A WASTE REPOSITORY - MEASUREMENT OF IONIC INGRESS

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ABSTRACT

A waste repository for the below ground disposal of low level radioactive waste is planned at Chalk River Nuclear Laboratories. It relies greatly on the durability of concrete for the required 500 year service life. A research program to design durable concrete and predict its service life is in progress.

The degradation of the concrete depends to a large extent on the rate of ingress of corrosive agents. Penetration of chloride and sulphate ions are particularly relevant. Twenty mix formulations were developed to create various types and qualities of concrete, and to study their behaviour in different site environmental conditions. A total of 1000 concrete specimens are being exposed at 20°C and 45°C to 25 different combinations of the corrosive agents including CO₂. Procedures to measure the ionic profiles and to determine the factors controlling diffusion of the ions in the various concretes have been developed. Results of selected concrete systems exposed to chloride and sulphate solutions for 1 year are presented and discussed in terms of pore structure and permeability parameters of the concrete.

INTRODUCTION

A joint research program designed to predict the durability and service life of concrete required for the construction of low level radioactive waste repositories was initiated by Atomic Energy of Canada Ltd. and the National Research Council [1]. The primary objective was to obtain data needed to design concrete to perform in a known aggressive environment for a predetermined period of time. Different approaches have been considered [2]. The focus in this study was not on the development of a single highly durable concrete but a methodology which would assess the durability aspects of a wide variety of concrete types and quality subjected to different exposure conditions. Environmental factors considered included sulphate and chloride ion concentration in the groundwater, carbonation effects, long term phase changes of hydrated cement components, leaching of concrete constituents, freeze-thaw resistance and susceptibility of aggregates to alkali-aggregate reaction. Interactions between concrete and both chloride and sulphate ion, singly and in combination, were considered of major importance and this paper will concentrate on their effect. It was also deemed necessary to explore the possibility of synergistic effects due to combined action of these ions.

Durability prediction generally involves the appropriate selection of a suitable rate determining parameter. This will be achieved by determining the time dependent depth of penetration of chloride and sulphate ion into test

concretes exposed to chloride and sulphate solutions having a range of concentrations. The slow rate of ingress of Cl^- and SO_4^{2-} into some concrete types eg. 1 - 2 mm/year was instrumental in the decision to use energy dispersive x-ray analysis (EDXA) to establish depth of penetration profiles [3]. The challenge was to develop a consistent procedure for application to concrete as use has been limited to studies with pastes and mortars [4]. Drilling cores and saw cutting specimen slices for subsequent wet chemical analysis does not provide the required precision and accuracy for determining the rate parameter especially for low w/c ratio mixes [5,6]. Milling specimens for wet chemical analysis is suitable for cement paste specimens only [7].

Selection of corrosive agents and procedures for analysis were followed by implementation of a plan which included the following: mix designs for five concrete systems incorporating portland cement, fly ash, silica fume, slag and other additives; characterization of aggregates and concretes through a series of microstructural chemical and physical tests; casting of 1500 concrete test beams; preparation of 25 baths containing salt solutions of various concentrations; exposure of specimens and EDXA at various times of exposure.

Selected results obtained for up to one year exposure to two different corrosive solutions are presented for three concrete systems. Factors affecting durability processes and service life prediction are discussed. Synergistic effects due to combinations of aggressive ions are addressed.

EXPERIMENTAL

Method

- (1) **Binders:** portland cement types 10 and 50, silica fume and blast furnace slag were used for the three concrete systems described in this paper. The oxide analysis is given in Table I.

Table I Oxide Analysis of Cements, Silica Fume and Slag

	<u>Portland Cement Type</u>		Slag	Silica Fume
	10	50		
SiO_2	19.43	20.71	35.30	95.17
Al_2O_3	4.18	3.77	10.62	0.21
Fe_2O_3	3.20	4.36	0.58	0.13
CaO	61.21	62.46	36.94	0.23
MgO	4.09	3.35	13.32	0.15
Na_2O	.45	0.35	---	0.10
K_2O	0.89	0.87	---	0.27
C				1.56
L-O-I	1.53	0.88	1.16	2.30
SO_3	3.93	2.46	1.41	0.12
Free lime	1.15	0.70	---	---

- (2) **Aggregates:** An unblended sand consisting mainly of quartz and feldspar was used. The following tests were carried out: accelerated mortar bar test for alkali-aggregate reactivity where samples are placed in 1 M NaOH solution at 80°C, magnesium sulphate soundness test, freeze-thaw cycling and petrographic evaluation. All testing indicated the sand was satisfactory.

A limestone coarse aggregate of somewhat variable composition was used. The dominant rock type is a pelitic pelmicrite with fossil debris. Tests conducted were similar to those for the fine aggregate and the results were satisfactory.

- (3) **Concrete:** Three types designated system 1, 2 and 5 (S1, S2, S5) were each prepared at 4 different water-cement ratios, 0.35, 0.42, 0.5 and 0.60 denoted as mix 1, 2, 3 and 4 (M1, M2, M3, M4).

The cement contents for S1, S2 and S5 are as follows: S1 (M (1-4)): 485, 370, 335 and 280 kg/m³; S2 (M (1-4)): 383, 338, 338 and 275 kg/m³; S5 (M (1-4)): 437, 359, 325 and 259 kg/m³. S1 contains type 10 portland cement, S2 - 90% type 50 portland cement and 10% silica fume, S5 - 75% blast furnace slag, 22% type 50 portland cement and 3% silica fume. A target slump of 125-150 mm was maintained for all mixes by suitable addition of a naphthalene based superplasticizer.

Concrete Specimens

Two concrete prisms, 75 x 75 x 280 mm, were cast for each mix and each exposure condition. S1, S2 and S5 were moist cured for 7, 14 and 28 days respectively. Prior to immersion in the test solutions the prisms were coated with wax on all sides but one to allow unidirectional ingress of chloride or sulphate ions.

Solution Baths

In the test program the concentration range of NaCl and Na₂SO₄ solutions in the experimental baths varied from 1.98 - 49.47 g/L and 7.40 - 88.75 g/L respectively. Results obtained from exposure to two solutions - a solution containing 49.47 g/L of NaCl at 22°C (designated Bath 15) and a solution containing 88.75 g/L Na₂SO₄ and 49.47 g/L NaCl at 45°C (Bath 25) - are reported in this paper.

Depth of Penetration Profiles - Cl⁻ and SO₄⁼

- (1) **Sample Preparation:** Specimens for EDXA were prepared according to the following procedure. A 12.5 mm slice was cut from the concrete prism taken from the test solution. This slice is farther cut about 25 mm from the exposed surface and then immediately surface dried. The sample is then sliced perpendicular to the exposed surface (5-10 mm thick) using isopropanol as the

cutting fluid. The sample is then polished in 2 stages using a 62 μm and 15 μm diamond embedded polishing wheel and mineral oil polishing medium. After polishing the oil is removed with toluene and the samples are dried and mounted on stubs for SEM examination.

- (2) **Profile Determination:** A Cambridge Stereoscan S-250 was used for the examination and a Tracor Northern TN 5500 Energy Dispersive X-ray Analyser was used for the quantitative analysis employing the SSQ software. The ZAF corrections are incorporated in the SSQ package. The operating conditions include the following characteristics: 20 KV, W.O. = 30 mm, ROI-O (2.000 - 2.170 Kev); ROI-1 (2.930 - 3.080 Kev), Ca pk. ht. @ 2000 counts. The analysis was performed at 500 $\times$ magnification in a reduced raster mode which resulted in an area 70 μm $\times$ 60 μm being analyzed. Calibrations were performed with an obsidian standard containing 0.36% Cl. EDAX analysis on several pieces gave 0.38%, a difference of 5.5%. Analyses were performed in 0.5 mm steps and 3 profiles for each concrete sample were determined. Care was taken to only analyze the paste area in the sample resulting in deviations from path linearity due to presence of aggregate. At each position along the profile ion concentrations were expressed as mass percent of the paste. The oxide sum of the assigned elements is computed and used for calculation of ionic concentration. A value of 0.3% Cl was used to determine the position of the reaction front. This chloride concentration is considered a practical limitation for maintaining passivity of steel in concrete. A value of 3% $\text{SO}_4^{=}$ was used to locate the reaction front. The base amount of $\text{SO}_4^{=}$ found in all concrete systems was $2.5 \pm 0.5\%$.

Characterization of Concrete

- (1) **Pore Size Distribution:** Pore size data was obtained on mortars extracted from the concretes. An Autoscan 33 Quantachrome mercury intrusion porosimeter was used at pressures up to 227 MPa.
- (2) **Freeze-Thaw Cycling:** Frost resistance was evaluated by ASTM Procedure C666-A.
- (3) **Air Content:** Air void parameters were determined by the linear traverse method.
- (4) **Non-evaporable Water and $\text{Ca}(\text{OH})_2$ Content:** These determinations were performed on the mortar phase. Non-evaporable water was taken as the weight loss on heating between 100-550°C assuming the weight loss between 550-1000°C to be negligible. This avoided problems with aggregate decomposition around 650°C. Calcium hydroxide content was determined by estimating the weight loss associated with its decomposition at around 450°C.
- (5) **Permeability:** High pressure water permeation of the concrete mixes was determined using a Hassler system. Specimens were generally 76 mm diameter $\times$ 25 mm thick. De-ionized and de-aired water was used and a pressure of 6.7 MPa was applied using N_2 gas.

RESULTS

- (1) Mercury Intrusion Porosimetry: The results for total porosity and the median pore diameter obtained using the mercury porosimeter are presented in rows 1 and 2 of Table II.

Table II Physical and Chemical Properties of Concretes and Mortars

Property	Mix 1 System			Mix 2 System			Mix 3 System			Mix 4 System		
	1	2	5	1	2	5	1	2	5	1	2	5
Total Porosity, %	12.69	10.20	9.84	13.34	11.33	14.14	16.61	16.19	14.97	16.83	18.97	16.08
Median Pore Diameter, μm	0.026	0.020	0.014	0.031	0.020	0.016	0.033	0.026	0.016	0.040	0.034	0.023
Permeability, m/sec	$<1 \times 10^{-13}$	$<1 \times 10^{-13}$	$<1 \times 10^{-13}$	2×10^{-13}	$<1 \times 10^{-13}$	1.8×10^{-12}	4×10^{-12}	3.5×10^{-12}	19×10^{-12}	9×10^{-12}	8×10^{-12}	32×10^{-12}
Non-evaporable Water, %	12.4	12.5	12.5	12.3	15.8	15.4	14.4	14.9	15.2	15.5	15.0	16.3
Ca(OH)_2 Content, %	8.5	4.1	0.0	7.8	7.3	0.0	10.0	6.0	0.0	10.9	7.9	0.0

In general, for each water-cement ratio (Mixes 1 - 4), both the total porosity and median porosity decrease in the order $S1 > S2 > S5$. The higher the water-cement ratio, the greater the porosity and median porosity for all systems. The lowest porosity and median-pore diameter occurs with System 5 (blast furnace slag composite) Mix 1 (water-cement ratio of 0.35) while the highest porosity occurs with System 2, Mix 4 and the highest median pore diameter with System 1, Mix 4.

- (2) Permeability: These results are presented in row 3 of Table II. The values do not correlate well with porosity or median pore diameter. For Mix 1, the permeabilities for all three systems are $< 1 \times 10^{-13}$ m/sec. In the other mixes (systems 1 and 2) permeability values increase with water-cement ratio and are fairly similar except for system 5 where they are greater by a factor of 4 to 10.
- (3) Non-evaporable Water and Ca(OH)_2 Content: These data are presented in rows 4 and 5 of Table III. The non-evaporable water results indicate no great difference in the levels of degree of hydration for the three systems even though systems 1, 2 and 5 were cured for periods of 7, 14 and 28 days respectively. The Ca(OH)_2 content, in all mixes is considerably greater for system 1, intermediate for system 2, and very low for system 5 in all mixes.
- (4) Ion - Depth Profiles: Chloride and sulphate profiles were determined by EDXA for the three systems, each at 4 water-cement ratios after exposure in

FIG. 1. Ionic profiles

FIG. 2. Penetration depths of chloride ion versus time^{1/2} of immersion in Bath 15

two different baths (15 and 25). Typical results are presented in Fig. 1 for exposure periods 3, 6, 9 and 12 months. Profiles for chloride ion in system 1, mix 1 (S1, M1) due to exposure in bath 15 are shown in Fig. 1 A. The weight of chloride as a percent of the cement paste content. At low depths of

Table III Chloride Ion Ingress (mm) in Concretes as a Function of Time of Immersion in Bath 15

Square Root of Time (months) ^{1/2}	Mix 1 System			Mix 2 System			Mix 3 System			Mix 4 System		
	1	2	5	1	2	5	1	2	5	1	2	5
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.73	11.9	5.2	3.6	13.6	5.5	1.7	13.8	8.6	3.6	13.8	9.8	4.1
2.45	15.8	7.3	4.1	20.4	4.1	2.0	24.3	10.7	4.3	28.0	11.3	6.0
3.00	17.9	9.9	6.3	23.8	4.0	5.1	25.9	11.6	5.8	27.0	20.4	7.0
3.46	20.8	11.4	5.3	33.1	8.7	5.2	31.3	17.6	3.8	30.9	13.9	7.3
77.46	462	255	132	697	151	119	704.1	355	107	722	382	171
Corr. Coeff. Linear Regression Analysis	1.00	1.00	0.96	0.99	0.84	0.92	0.99	0.97	0.87	0.97	0.90	0.99

penetration the concentration is almost 3.0 percent after 3 months. The full profile for longer exposure was not measured, but it appears that it would be higher. The movement of the front was taken by monitoring the penetration depth at 0.3 percent.

Profiles for chloride ion due to exposure of system 5, mix 1 (S5, M1) in bath 15 are shown in Fig. 1 B. Values for chloride at low depths are in the 3 percent range, similar to System 1, but penetration at greater depths for this profile is considerably less than for System 1.

A profile for the sulphate ion is presented in Fig. 1 C for S5, M1. At low penetration depths after 9 months exposure a value for $\text{SO}_4^{=}$ as high as 4.4% of cement content was recorded for S1, M1 (not in figure) and a value of 6.8% for S5, M1, also after 9 months exposure was measured. The value of 3.0% $\text{SO}_4^{=}$ ion was used as the measure of the front penetration. This was based on measurements that showed that the sulphate threshold value for all systems was 2.5 ± 0.5 percent. It may be observed that in most cases the front value will not be changed much by the use of 3.0 percent compared to 2.5 percent due to the steepness of the concentration vs penetration depth curve. The depth of penetration of the $\text{SO}_4^{=}$ ion was observed to be considerably greater in S1, M1 than S5, M1.

- (5) Ionic Ingress as a Function of Immersion Time: Depth of chloride and sulphate ion penetration obtained from ionic profile data was plotted versus square root of time of exposure. The results for exposure in Bath 15 are presented in Figs. 2 (A) for S1 M (1-4), 2 (B) for S2 M (1-4) and 2 (C) for S5 M (1-4).

The data for the four experimental points up to 12 months are also presented in Table 3. A linear regression analysis was carried out on each set of data,

FIG. 3. Penetration depths of chloride ion versus time^{1/2} of immersion in Bath 25

FIG. 4. Penetration depths of sulphate ion versus time^{1/2} of immersion in Bath 25

using the starting time and zero ingress as the fifth point. Correlation coefficients and depth of ingress values after 500 years computed from the regression line are included in the table.

Curves for S1 M1 and S1 M2 in Fig. 2 (A) show reasonable linearity and indeed the correlation coefficients are 1.00 and 0.99 respectively. Extrapolated values for ionic ingress after 500 years exposure are 462, 697, 704 and 722 mm for S1 M1, S1 M2, S1 M3 and S1 M4 respectively. The correlation coefficients for S2 are all 0.90 or above except M2, which is 0.84. The ingress values extrapolated to 500 years are 255, 151, 355 and 382 mm for Mixes 1 to 4 respectively but Mix 2 has some relatively low experimental points (Fig. 2 (B)) and the extrapolated values are probably too low. The ingress values for S2 however are approximately half those of S1 for most mixes.

The correlation coefficients for S5 are all 0.92 or above except for Mix 3. The extrapolated values of the ingress at 500 years exposure however are 132, 119, 107 and 171 mm for Mixes (1 - 4) respectively, an average factor of about 5 times lower than S1.

The results for chloride ion ingress during exposure in Bath 25 (containing both chloride and sulphate) are presented in Fig. 3 (A)) for S1 M (1-4), (B) for S2 M (1-4), (C) for S5 M (1-4). The data and the results of linear regression analysis are presented in Table IV. The rate of ingress for S1 increases from

Table IV Chloride Ion Ingress (mm) in Concretes as a Function of Time of Immersion in Bath 25

Square Root of Time (months) ^{1/2}	Mix 1 System			Mix 2 System			Mix 3 System			Mix 4 System		
	1	2	5	1	2	5	1	2	5	1	2	5
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.73	11.3	7.9	1.2	10.1	4.6	1.8	13.8	7.1	1.7	13.8	9.2	5.0
2.45	9.0	7.1	4.4	9.3	8.1	3.3	16.3	9.4	4.4	20.0	10.9	4.6
3.00	14.6	9.1	6.2	14.6	11.7	5.9	32.7	16.6	5.5	38.0	17.9	9.2
3.46	13.5	10.4	4.0	15.8	11.3	2.7	26.8	13.6	4.1	36.8	15.8	6.3
77.46	309	222	123	347	275	96	675.8	347	116	876	386	169
Corr. Coeff.												
Linear Regression Analysis	0.92	0.95	0.86	0.97	0.98	0.78	0.94	0.95	0.91	0.96	0.97	0.88

M1 to M4. The correlation coefficients for S1 are all 0.92 or above, and the extrapolated values of the ingress for 500 years exposure are 309, 311, 676, 876 mm for Mixes (1 - 4) respectively which are on a similar level to those for S1 exposed in Bath 15. The correlation coefficients for S2 are all 0.95 or above and the extrapolated values of the ingress for 500 years exposure increase with water-cement ratio and are 222, 275, 347 and 386 mm for M (1 to 4) respectively. Except for Mix 2, these are close to those for S2 exposed to chloride alone in Bath 15. The correlation coefficients for S5 (0.86, 0.78, 0.91, 0.88) are the lowest for the chloride ion ingress (Fig. 3 (C)), and there is significant scatter in the data. The extrapolated values for 500 years ingress however are 123, 96, 116 and 169 mm for Mix 1-4, respectively, which as for

the other systems, are very similar to the values obtained for exposure in Bath 15.

The results for sulphate ion ingress during exposure in Bath 25, are presented in Fig. 4 (A) for S1 M (1-4), (B) for S2 M (1-4), (C) for S5 M (1-4). The data and the results of linear regression analysis are presented in Table V. The correlation coefficients for S1 M (2-4) are low, 0.74, 0.63 and 0.78 respectively, due primarily to the measurement made at 3 months exposure (Fig. 4 (A)).

Table V Sulphate Ion Ingress (mm) in Concretes as a Function of Time of Immersion in Bath 25

Square Root of Time (months) ^{1/2}	Mix 1 System			Mix 2 System			Mix 3 System			Mix 4 System		
	1	2	5	1	2	5	1	2	5	1	2	5
0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.73	1.8	0.6	0.5	4.3	0.6	0.4	8.1	1.3	0.5	6.1	1.3	1.4
2.45	1.3	1.4	0.5	1.7	1.2	1.0	3.5	1.7	1.0	3.9	1.8	1.8
3.00	3.2	1.8	1.6	3.8	2.5	1.0	4.3	2.7	1.4	4.1	2.7	1.6
3.46	4.3	2.7	1.0	3.9	2.9	0.8	6.9	2.5	1.3	6.1	2.5	2.8
77.46	86.7	57	28	78	65	22	116.1	60	32	112	61	54
Corr. Coeff.												
Linear Regression Analysis	0.91	0.95	0.82	0.74	0.93	0.89	0.63	0.98	0.97	0.78	0.98	0.96

However, extrapolations of ingress after 500 years are reasonably consistent for the four mixes (1-4), being 87, 78, 116, and 112 mm respectively.

Correlation coefficients for S2 (Fig. 4 (B)) are considerably better, values being 0.95, 0.93, 0.98 and 0.98 respectively, with extrapolated depths of ingress for 500 years exposure being 57, 65, 60 and 61 mm for M (1-4) respectively. Correlation coefficients for S5 (Fig. 4 (C)) are also better than S1, values being 0.82, 0.89, 0.97 and 0.96 for M (1-4) respectively. The extrapolated values of ion ingress after 500 years exposure follow a consistent trend, 28, 22, 32 and 54 mm for M (1-4) respectively.

DISCUSSION

Ionic profiles and kinetics of the reaction or diffusion front (determined by EDXA) in concrete show that reasonably accurate results can be obtained and predictions of ingress made. Profiles are particularly difficult to determine in dense concrete because the rate of movement of the front is very low (in some cases fractions of a millimetre in 3 months) and the path of ionic ingress in concrete due to the aggregate can be very tortuous leading to inconsistent results. In addition, the rate of movement of the front can be speeded up by rapid diffusion of ions in interfacial regions and in cracks. The procedure adopted here in following the diffusion path around the fine and coarse aggregate particles, using the SEM and electron-microprobe for analysis appears to be successful. It must be emphasized that results have been obtained after exposure in the baths for only 1 year.

The measurements of the chloride profiles yield relatively high chloride content values for all systems measured at the lower penetration depths. This is also true for the slag system, S5, which differs in this regard from the results of other authors [4]. The decrease of chloride content with depth of ingress is however more rapid with the slag system than the others, and this is consistent for all the water-cement ratios. The relatively high resistance of the slag system to chloride ion ingress may be partly explained by its lower median pore diameter and porosity values. This does not provide the full explanation. S5 M4 for example, with a total porosity of 16.11% and median pore diameter of $0.023\text{ }\mu\text{m}$ has a projected chloride ion ingress of 171 mm after 500 years in Bath 15, whereas S1 M1 with a total porosity of 12.71% and median pore diameter of $0.026\text{ }\mu\text{m}$ has a projected ingress of 462 mm. The calcium hydroxide contents for S5 M4 and S1 M1 are 0.0 and 8.5% respectively (Table 2) and it is possible that in systems with higher calcium hydroxide contents chloride ion diffusion is increased due to enhanced calcium hydroxide solubility or calcium hydroxide-chloride complex formation.

The chloride detected in the specimens during the measurements is both chemically and physically combined. Thus both chloro-aluminates and chlorides with different levels of attachment with C-S-H are present [7,8]. As a result the concentration of chloride measured is not related to the driving force of the diffusion process although it is clear from the correlation with square root of time that the process is diffusion controlled [9,10,11]. To calculate the diffusion constant, the point where the chloride ion concentration is zero should be known. This has not been accurately measured in this work.

The chloride ion concentration in baths 15 and 25 are at the same level ($\approx 30\text{ g/litre}$) but bath 25 also contains 60 g/litre of sulphate ions, and is at 45°C as opposed to 22°C for bath 15. The projected chloride ion ingress after 500 years exposure for the three systems generally does not differ greatly when comparing the two baths. Since the higher temperature should increase the rate of chloride ion ingress, it appears that the presence of sulphate ion reduces the rate of ingress of chloride ion in the three systems.

The profiles for the sulphate ion ingress show similar features to those of chloride ion. At low levels of penetration the sulphate ion concentration is especially high for the slag cement S5 M1, in the order of 7% as compared to 4.5% for S1 M1. The rate of ingress is again much higher for system 1 than systems 2 and 3 and as observed by other authors [12] much lower than the rate of ingress of the chloride ion. The projected ingress of sulphate ion in system 5 is 22 mm after 500 years. This data is only for 1 year and it is possible that the sulphate penetrated layer may be ruptured with further exposure, allowing the rates of ingress of both sulphate and chloride ions to increase.

CONCLUSIONS

1. The rate of ingress of chloride ion into the slag-cement system is approximately 20% of the rate into the Type 10 cement system and 50% of the rate into the silica fume cement system.
2. The rate of ionic ingress of sulphate into the slag cement system is approximately 30% of the rate into the Type 10 cement system and 50% of the rate into the silica fume cement system.
3. The rate of ingress of both ionic species generally increases with water-cement ratio for the three systems.
4. Rate of ingress of both ionic species into the three systems appears to be diffusion controlled.

5. The presence of sulphate ions in solution with chloride ions appears to decrease the rate of chloride ion ingress into the three systems.

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