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Nitrite diffusivity in calcium nitrite-admixed hardened concrete

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Abstract

The apparent diffusivities (D_{app}) of nitrite in concrete were estimated by monitoring time-dependent concentrations of nitrite leached into water from calcium nitrite-admixed hardened concrete specimens. Experiments were conducted with five different concrete mixes and with deionized water (DI), limewater, or synthetic seawater as the leaching agents. The D_{app} in Type II Portland cement concrete for long curing times and a w/c ratio of 0.40 was $\sim 1.7 \times 10^{-8}$ cm^2/s when leached at 22 °C with limewater. The D_{app} was relatively insensitive to nitrite dosage and to DI or limewater as the leaching agent, but an increase in the w/c ratio to 0.49, or an increase in temperature by ~ 14 °C, increased D_{app} by $\sim 50\%$. A 20% Type F fly ash cement replacement reduced the apparent diffusivity by $\sim 60\%$. The D_{app} decreased with concrete curing time. The magnitude of the D_{app} and its dependence on concrete and exposure parameters were comparable to those observed in the transport of chloride ions in concrete.

Keywords: Nitrite; Diffusion; Corrosion; Pozzolanic; Concrete

1. Introduction

Chloride-induced corrosion of reinforcing steel in concrete can be mitigated with an admixed calcium nitrite corrosion inhibitor. When present in concrete, nitrite significantly increases the critical chloride threshold for corrosion initiation [1–5]. This inhibiting species has been used extensively and in-service experience extends over 20 years. Long design service life requirements (e.g., 75 years or more) are increasingly more common, however, and the ability of the inhibitor to remain in concrete in sufficient amounts over extended periods is an important performance issue. Leaching by rainwater or from marine exposure is a potentially important mechanism of escape of nitrite from concrete during the long corrosion initiation stage while steel is in the passive condition (further nitrite depletion by reaction with iron ions [2] is not expected to be significant until later, during the corrosion propagation stage). As is the case for chloride ions, the kinetics of nitrite leaching are expected to be dominated by transport within the concrete, which can be considered to proceed mainly by diffusion [6,7].

The purpose of this investigation was to assess the transport of nitrite ions in concrete using leaching experiments that were interpreted to obtain values of apparent diffusivity (D_{app}) assuming applicability of Fick's first and second laws [8]. Concrete variables examined were w/c, pozzolanic addition, curing time, and inhibitor dosage. Environmental variables included leaching medium (deionized water, limewater, synthetic seawater) and temperature. The tests were exploratory in nature and coverage of some of those variables was limited.

2. Experimental

2.1. Materials

The investigation was conducted using concrete admixed with DCI®-S, a commercial corrosion inhibitor marketed by W.R. Grace & Co.-Conn. This product is supplied as a

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Table 1
Mix design and concrete properties of specimens used in leaching experiments

	Concrete type				
	C1H	C1	C2	P1	NR
Cement, kg/m^3	390	390	390	310	382
Water, kg/m^3	160	160	195	160	139
Fine aggregate, kg/m^3	700	694	600	674	679
Coarse aggregate, kg/m^3	986	986	986	986	967
Class F fly ash, kg/m^3	0	0	0	78	0
DCI-S, kg/m^3 (DCI-S, l/m^3)	14 (11)	28 (22)	28 (22)	28 (22)	28 (22)
Water/binder ratio[a]	0.41	0.43	0.49	0.40	0.40
Unit weight, kg/m^3	2237	2235	2178	2216	2195
Cylinder dimensions[b], cm	10.1 × 20.3	7.6 × 15.2	15.2 × 30	7.6 × 15.2	7.6 × 15.2
Curing time, days	100	160	60	180	50, 100, 270
Curing medium	limewater	limewater	limewater	limewater	100% RH

[a] Adjusted for water in inhibitor and moisture content of aggregates.
[b] Cylinder diameter × height.

liquid of density ∼1.3 g/cm^3 containing ∼30% (w/w) calcium nitrite and a set retardant; typical recommended dosages are between 15 and 30 l/m^3.

Five different concrete mixes were used (see Table 1 for nomenclature and details). Four of those mixes (C1H, C1, C2, and P1) were limited to available specimens made for a long-term test program. Mixes C1, C2, P1, and NR contained a full inhibitor dosage of 22 l/m^3 specified by the Florida Department of Transportation for aggressive marine service applications, whereas mix C1H only contained one-half of that amount. Mix P1 had 20% Type F fly ash as a cement replacement. All mixes used Type II cement. One of the mixes (C2 designation) was prepared with a significantly higher w/c than those of the rest. The concrete of all mixtures except NR was cast in cylinders that were demolded after 1 day and then immersed in a limewater tank for curing for 60–180 days (see Table 1). After curing, the cylinders were stored at ∼22 °C in a plastic enclosure at moderate to high humidity for at least 1 year before the leaching tests were performed. As some inhibitor leached from those cylinders during the initial tank curing, an additional batch of cylinders, named NR, was prepared with proportions approximating those of mix C1 but placed directly in an ∼100% RH and ∼22 °C air curing chamber after 1 day in the mold. For NR cylinders, nitrite loss from leaching during curing was expected to be negligible. Specimens from this batch were subject to leaching tests after controlled times of 50, 100, and 270 days of curing.

2.2. Leaching experiments

The test specimens were whole as-cast cylinders, or slices cut from the cylinders, with the dimensions indicated in Table 2, which also shows the test solutions and temperatures at which the tests were conducted. The test methodology generally followed the specifications of ANSI/ANS-16.1-1986 [9]. The specimen was placed, supported by a plastic stand, inside a lidded plastic container with enough solution to maintain a uniform thickness around the specimen and a ratio of liquid solution volume to specimen surface area of at least 10 cm. Some exploratory variations in procedure (e.g., changes in solution renewal interval and liquid volume) were used for specimens of concrete mix C1H, which were tested early in the program.

The leaching solutions were deionized water (DI), limewater (DI saturated by 2 g/l addition of calcium hydroxide), or synthetic seawater (DI with 41.95 g/l of synthetic "sea salt" per ASTM D-1141-52 Formula A, Table 1, Section 4). Leaching test temperatures were either ambient (∼22 °C) or 35–37 °C, which was achieved by placing the leaching containers inside a temperature-controlled chamber. The solution was sampled and completely replaced by fresh solution at regular intervals during cumulative leaching times ranging from 2 to 2160 h (a total of 90 days). Leaching tests on a few selected specimens were extended for another 90 days. The sampled solution was tested for nitrite with the spectrophotometric method described by Li et al. [6]. The D_{app} of nitrite in water-saturated concrete was

Table 2
Specimen specifications and testing conditions for leaching experiments

Concrete type	Specimen dimensions[a], cm	Leaching solution volume, ml	Specimen surface/volume, l/cm	Leaching solution type	Temperature, °C
P1 (cylinder)	7.6 × 15.2	4558	0.066	limewater, DI	22
NR (cylinder)	7.6 × 15.2	4558	0.066	limewater, DI, synthetic seawater	22
C1 (cylinder)	7.6 × 15.2	4558	0.066	limewater	22
P1(slice)	7.6 × 2.5	1500	1.31	synthetic seawater, DI	22
NR (slice)	7.6 × 2.5	1500	1.31	limewater, DI, synthetic seawater	22, 35
C2 (slice)	15.2 × 4.6	5834	0.70	limewater	22
C1H (slice)	10.2 × 2.5	375 and 1000	1.18	limewater	22, 37

[a] Specimen diameter × height.

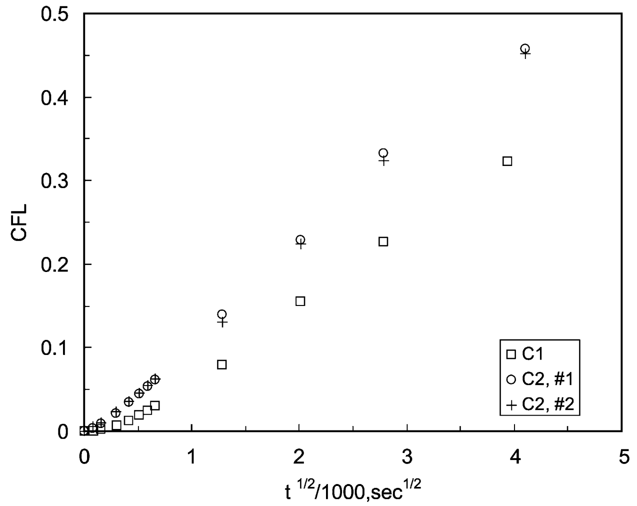

Fig. 1. The CFL as a function of the square root of leaching time ($t^{1/2}$) for concrete specimens of C1 and C2 in limewater at room temperature. Legend keyed to the D_{app} value for each specimen as listed in Table 3.

calculated from the recorded nitrite concentrations in the leaching solution as function of time, as described below.

2.3. Diffusion coefficient estimates

The apparent nitrite diffusivity D_{app} in concrete (with units of cm^2/s) is defined by Eq. (1), where J is the flux of nitrite ions along the direction x (in mg/cm^2/s) and C is the concentration of nitrite in concrete (in mg/cm^3).

$$D_{app} = -J\left(\frac{\partial C}{\partial x}\right)^{-1}. \tag{1}$$

Internal bulk diffusion of nitrite in concrete is likely to be the rate-determining mechanism during much of the leaching process. A semi-infinite one-dimensional model can approximate the leaching behavior during the early stages of leaching so that D_{app} can be estimated from solutions to the time-dependent diffusion problem [8,9]. From the measured nitrite amount a_n in the solution at the end of the n-th liquid replenishment interval, a cumulative fraction leached (CFL) can be defined as CFL$=\sum a_n/A_o$, where A_o is the total amount of nitrite inside the specimen at the beginning of the leaching experiment. In the leaching experiments, the nitrite concentration in the solution was always kept at a very low level by renewing the solution frequently, and the CFL was expected to be linearly proportional to the square root of the leaching time during the early stages of leaching (when CFL$<\sim$20%) [9]. Thus, if k is the proportionality slope (s$^{-1/2}$), V is volume of specimen (cm^3), and S is the geometric surface area of specimen (cm^2) [8,9]:

$$D_{app} = \pi\left(\frac{k}{2}\right)^2\left(\frac{V}{S}\right)^2. \tag{2}$$

When the CFL exceeds $\sim$20%, significant deviation from one-dimensional behavior takes place [9]. Under those circumstances, the apparent diffusivity can be obtained instead by

$$D_{app} = \frac{Gd^2}{t} \tag{3}$$

where t is the cumulative leaching time since the beginning of the first leaching interval (s), d is the diameter of the cylinder (cm), and G is a dimensionless time factor for the cylinder, which is dependent upon CFL and the specimen height-to-diameter (h/d) ratio [9].

For presenting results, it was desirable to indicate which equation was used to calculate D_{app}. Thus, the value of D_{app} calculated from Eq. (2) was named D_1 and the value calculated using Eq. (3) was named D_2 (if there was more than one datum with a CFL>20%, then D_2 was reported as the average for those data). The general designation D_{app} was used when discussing the significance of the findings.

3. Results

The CFL was calculated for every experiment assuming that the nitrite content of each specimen type was the same as the nominal admixed amount per Table 1. Nitrite measurements of powdered concrete samples from specimens of C1, C2, and P1 using the method described by Powers et al. [5] confirmed that the actual nitrite content near the center of the cylinder was close to the nominal nitrite content.

Typical behavior during the leaching tests was exemplified by the curves shown in Fig. 1. These curves illustrate the CFL evolution as function of $t^{1/2}$ for a specimen of C1 concrete (full cylinder, 7.6 × 15.2 cm) and two specimens of C2 concrete (4.6-cm thick slices with freshly cut faces, sliced

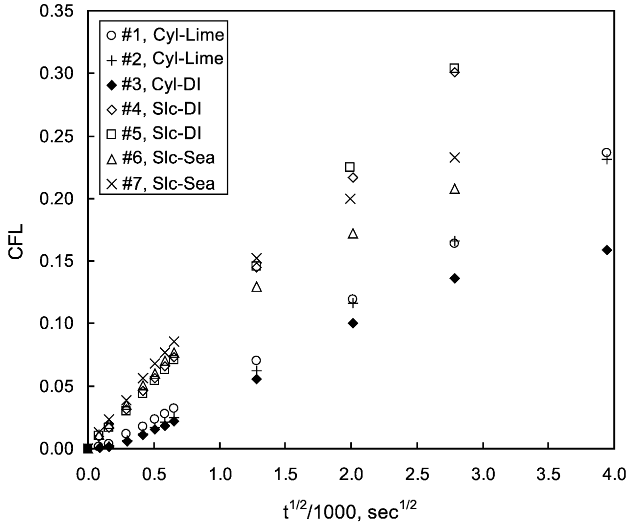

Fig. 2. The CFL as a function of the square root of leaching time ($t^{1/2}$) for specimens of P1 in limewater (Lime), deionized water (DI), and synthetic seawater (Sea) at room temperature. Cyl and Slc designated cylindrical and slice specimens, respectively. Legend keyed to the D_{app} value for each specimen as listed in Table 5.

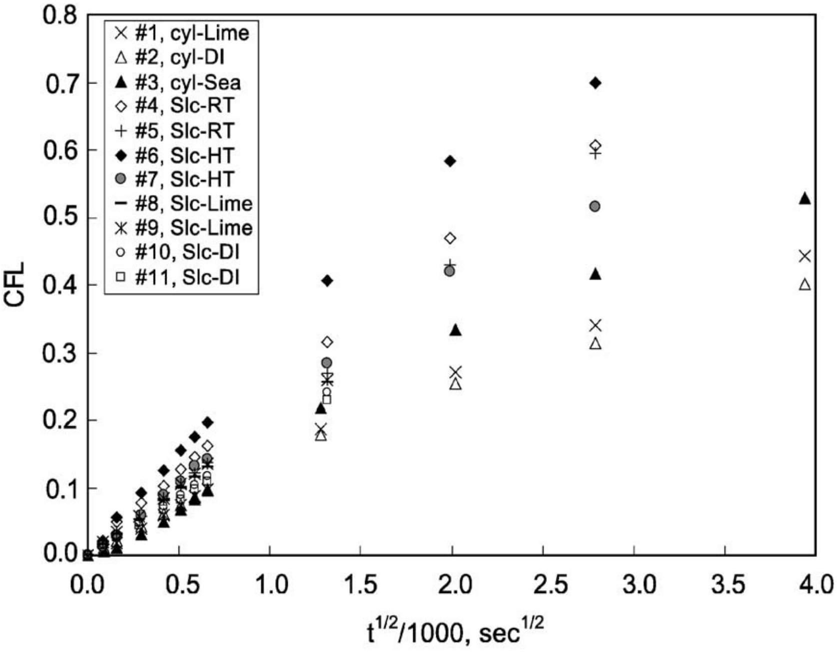

Fig. 3. CFL as a function of the square root of leaching time ($t^{1/2}$) for NR concrete specimens in limewater (Lime), deionized water (DI), and synthetic seawater (Sea) at room temperature (RT) and at ~35 °C (HT). Cyl and Slc designated cylindrical and slice specimens, respectively. Legend keyed to the D_{app} value for each specimen as listed in Table 6.

from a 15.2-cm diameter cylinder) in limewater at 22 °C. Except for an initial transient region, an approximately linear correlation between the CFL and $t^{1/2}$ is evident for each specimen, which indicates transport by diffusion. Calculating D_{app} (as D_1) in the presence of an initial transient is explained in Appendix A. The CFL versus $t^{1/2}$ slopes were smaller at earlier times, especially for the cylinder specimen of C1. This phenomenon may be attributed to earlier loss of the nitrite to limewater during curing, which would cause the nitrite concentration near the concrete surface to be lower than that of the bulk concrete. Since Eq. (2) was derived by assuming that the diffusive species are uniformly distributed before the leaching experiment is started, a lower surface concentration should yield a slower leaching rate at the beginning of the test. Compared with the cylinder of C1, the slices of C2 had 100 days shorter curing time in limewater and two freshly cut surfaces. These two freshly cut surfaces should have had a higher nitrite concentration than that of the previously exposed surface and accounted for more than 70% of the total slice surface area. Hence, the linearity of the curves for the slices of C2 should extend, as observed, to an earlier leaching time.

Table 3
Slope (k) and apparent diffusivity (evaluated as D_1 and D_2), obtained for specimens of C1 and C2 leached in limewater at 22 °C

Concrete type	k, $s^{-1/2}$	D_1, cm^2/s	D_2, cm^2/s
C1[a]	0.91×10^{-4}	1.5×10^{-8}	1.5×10^{-8}
Specimen 1, C2[b]	1.28×10^{-4}	2.6×10^{-8}	2.7×10^{-8}
Specimen 2, C2[b]	1.17×10^{-4}	2.2×10^{-8}	2.6×10^{-8}

[a] Full cylinder.
[b] Slice.

Fig. 2 illustrates the results of a series of experiments with the pozzolanic concrete P1 in various leaching media at 22 °C, while Fig. 3 shows the behavior for the NR concrete in various leaching media and at the two test temperatures. For the NR concrete, the straight-line behavior of the data extending in most cases to very short leaching times confirmed the absence of significant leaching during curing.

As illustrated in Figs. 1–3, there was generally good reproducibility in the CFL values from duplicate tests with specimens of the same type. Tables 3–5 show the slope (k) and apparent diffusivities (evaluated as D_1 and D_2) calculated from the data for all the experiments. For any given experiment and between replicates, the values of D_1 and D_2 typically agreed within ~20%, with the exception of a relatively large difference between D_1 and D_2 for P1 in synthetic seawater (Table 5, Specimens 6 and 7). The D_1 values were consistently derived from a larger number of data than for D_2, for which sometimes only one or two data points existed and relatively large shape corrections were needed. Consequently, the D_2 values were regarded only as supple-

Table 4
Slope (k) and apparent diffusivity (evaluated as D_1), obtained for specimens of C1H leached in limewater

Slice	k, $s^{-1/2}$	D_1[a], cm^2/s	Temperature, °C
1	1.76×10^{-4}	1.7×10^{-8}	22
2	1.76×10^{-4}	1.7×10^{-8}	22
3	1.76×10^{-4}	1.7×10^{-8}	22
4	1.65×10^{-4}	1.5×10^{-8}	22
5	1.55×10^{-4}	1.4×10^{-8}	22
6	2.33×10^{-4}	3.0×10^{-8}	37

[a] No D_2 evaluations were conducted for these experiments.

Table 5
Slope (k) and apparent diffusivity (evaluated as D_1 and D_2), obtained for P1 at room temperature

Specimen[a]	Leaching solution	k, $s^{-1/2}$	D_1, cm^2/s	D_2, cm^2/s
1	limewater	0.61×10^{-4}	6.8×10^{-9}	7.2×10^{-9}
2	limewater	0.59×10^{-4}	6.4×10^{-9}	7.4×10^{-9}
3	DI	0.57×10^{-4}	6.0×10^{-9}	–
4	DI	1.15×10^{-4}	6.1×10^{-9}	6.5×10^{-9}
5	DI	1.14×10^{-4}	6.0×10^{-9}	6.1×10^{-9}
6	synthetic seawater	1.15×10^{-4}	6.1×10^{-9}	2.8×10^{-9}
7	synthetic seawater	1.26×10^{-4}	7.3×10^{-9}	4.3×10^{-9}

[a] Specimens 1–3 were cylinders 7.6 × 15.2 cm. Specimens 4–7 were slices 7.6 × 2.5 cm.

mental evidence and all quantitative comparisons in the discussion were made based on D_{app} values evaluated as D_1 only.

Tests with specimens of P1 under the same conditions but using specimens of different shape (i.e., cylinder versus slice, Table 5, Specimens 3 and 4) yielded similar diffusion coefficients. The results appeared to be little affected by whether a cut or a cast concrete surface was in contact with the leaching solution.

4. Discussion

The available data set represents largely exploratory measurements and, as such, was limited in coverage of conditions and quantity of specimens. Nevertheless, the results provide useful preliminary information on how the diffusion of nitrite in concrete is affected by key material and exposure variables, which may serve as a guide to detailed future investigations. The trends examined are detailed below.

4.1. Magnitude of D_{app}

The experiments yielded D_{app} values for nitrite ion in concrete ranging from $\sim 6 \times 10^{-9}$ to $\sim 6 \times 10^{-8}$ cm^2/s (based on calculations of D_1). These values are on the same order as those reported for chloride ions in concretes comparable to those tested here [10–13]. This behavior was to be expected as both chloride and nitrite anions are univalent, have comparable diffusivities in water, and experience binding in the concrete matrix [14]. We must emphasize that the D_{app} values calculated from these leaching experiments reflect the assumption of simple diffusional behavior. Detailed descriptions of transport processes, including among others the effect of binding, would be required for more accurate evaluation of the distribution of the species in concrete and escape to the external environment.

4.2. Dosage

From the limited experiments performed, no significant dosage effect on D_{app} was detected. For leaching in limewater at 22 °C, the results from tests of specimens of C1H (half dosage) were compared with those of a group composed of the single available specimen of C1 and the specimens of the NR mix that had the longest curing period. That group had full inhibitor dosage, but shared approximately the same mix proportions as C1H and an extended curing history as well. The average D_{app} for the half- and full-dosage groups were $\sim 1.6 \times 10^{-8}$ and $\sim 1.7 \times 10^{-8}$ cm^2/s, respectively, and were within the experimental uncertainty, indicating little dependence on dosage.

4.3. Leaching medium

The P1 and the NR concrete were tested in different leaching media under otherwise comparable conditions. The results for P1 tested at 22 °C (Table 5) show average D_{app} of 6.6×10^{-9}, 6.0×10^{-9}, and 6.7×10^{-9} cm^2/s for tests in limewater, DI, and synthetic seawater, respectively. Tests at 22 °C for NR concrete cured 270 days (Table 6) indicated average D_{app} of 1.9×10^{-8} and 1.4×10^{-8} cm^2/s for leaching in limewater and DI, respectively. For the same concrete cured for 50 days, the results (only available for single specimens) were 3.9×10^{-8}, 3.5×10^{-8}, and 6.1×10^{-8} cm^2/s for limewater, DI, and synthetic seawater, respectively.

Table 6
Slope (k) and apparent diffusivity (evaluated as D_1 and D_2), obtained for specimens of NR concrete

Specimen[a]	Curing time, days	Leaching solution (temperature)	k, $s^{-1/2}$	D_1, cm^2/s	D_2, cm^2/s
1	50	limewater (22 °C)	1.47×10^{-4}	3.9×10^{-8}	3.5×10^{-8}
2	50	DI (22 °C)	1.40×10^{-4}	3.5×10^{-8}	3.0×10^{-8}
3	50	synthetic seawater (22 °C)	1.84×10^{-4}	6.1×10^{-8}	4.6×10^{-8}
4	100	synthetic seawater (22 °C)	2.38×10^{-4}	2.6×10^{-8}	2.9×10^{-8}
5	100	synthetic seawater (22 °C)	2.15×10^{-4}	2.1×10^{-8}	2.5×10^{-8}
6	100	synthetic seawater (35 °C)	2.97×10^{-4}	4.0×10^{-8}	3.7×10^{-8}
7	100	synthetic seawater (35 °C)	2.31×10^{-4}	2.4×10^{-8}	2.8×10^{-8}
8	270	limewater (22 °C)	2.00×10^{-4}	1.8×10^{-8}	2.9×10^{-8}
9	270	limewater (22 °C)	2.03×10^{-4}	1.9×10^{-8}	2.0×10^{-8}
10	270	DI (22 °C)	1.78×10^{-4}	1.5×10^{-8}	1.7×10^{-8}
11	270	DI (22 °C)	1.67×10^{-4}	1.3×10^{-8}	1.6×10^{-8}

[a] Specimens 1–3 were cylinders 7.6 × 15.2 cm. Specimens 4–11 were slices 7.6 × 2.5 cm.

The pH of DI in contact with concrete typically reached the range ~9 to ~10 after a few days, while that of the limewater stayed at ~12.6. The small difference between the results of DI and limewater tests suggests that those variations in pH of the leaching solution affected little the nitrite transport inside the concrete. The few available comparative data suggest that leaching in synthetic seawater resulted also in similar (but not always close) D_{app} values to those obtained with the other two leaching agents. The synthetic seawater tests with P1 showed anomalous behavior at large CFL values, which resulted in significant difference between D_{app} results when evaluated as D_1 and D_2. Since chloride ions tend to affect the partition between free and bound nitrite [6,14] in concrete, these observations may be a manifestation of the penetration during the test of chloride ions from the leaching solution into the concrete. In summary, the present results showed some, but not necessarily dramatic dependence of D_{app} on the leaching medium. However, the results from synthetic seawater tests underscore the needs for further investigation.

4.4. Concrete mix proportions and curing

The results of 22 °C tests in limewater of C1 and C1H (average w/c = 0.42), which may be considered together if the dosage effect is not important, yielded an average $D_{app} \sim 1.6 \times 10^{-8}$ cm^2/s. Mixture C2 was comparable to the other two except that it has w/c = 0.49 and the average D_{app} under the same conditions was 2.4×10^{-8} cm^2/s, or about 150% that of the lower w/c mixes.

The average D_{app} of P1 specimens (w/c = 0.40, 20% fly ash) tested under the same conditions as the C1 and C1H specimens was 6.4×10^{-9} cm^2/s, or about 40% that of the other concretes, which had only modestly higher w/c but no fly ash.

Tests at 22 °C with the NR concrete (Table 6) also indicate a consistent reduction of D_{app} with curing time. Assuming that diffusion is not a strong function of leaching medium, the average of the results for each of the curing times suggest that D_{app} was reduced by 50% by extending the curing time from 50 to 270 days.

These results indicate that curing time, w/c, and pozzolanic presence influence the D_{app} of nitrite in a manner consistent with the generally observed effect of those variables on transport of chloride species in concrete. As it has been well documented, variations in those parameters that decrease the interconnectivity of the pore network (i.e., increasing curing time, introducing pozzolanic admixtures, and reducing w/c) tend to substantially reduce the diffusivity of chloride ions in concrete [11–15].

4.5. Temperature

Increasing the temperature from 22 to 35 °C in synthetic seawater (Table 6) as much as doubled the average D_{app} in the NR concrete. A roughly comparable increase was indicated by the single available test with C1H in limewater. The change with temperature is consistent with that expected from thermally controlled diffusion. Assuming a simple Arrhenius dependence, these results suggest an activation energy on the order of ~10 kcal/mol, which is comparable with values reported by Goñi et al. [16] for leaching of calcium from concrete in DI.

5. Conclusions

- The apparent nitrite diffusion coefficient, D_{app}, at 22 °C in well-cured concrete with ~390 kg/m^3 of Type II Portland cement and w/c ~ 0.41 was on the order of 1.7×10^{-8} cm^2/s, as determined from leaching experiments. The results showed no strong sensitivity to the leaching medium or dosage, but the effect of seawater needs further investigation.
- An increase in the w/c ratio to 0.49, or an increase in temperature by ~14 °C, increased D_{app} by ~50%, whereas a 20% Type F fly ash cement replacement reduced instead the apparent diffusivity by ~60%.
- Extended curing of the concrete significantly reduced D_{app}.
- The magnitude of the observed D_{app} and the dependence of these values on test parameters were similar to the values and trends observed for transport of chloride ions in concrete under comparable circumstances.

Acknowledgements

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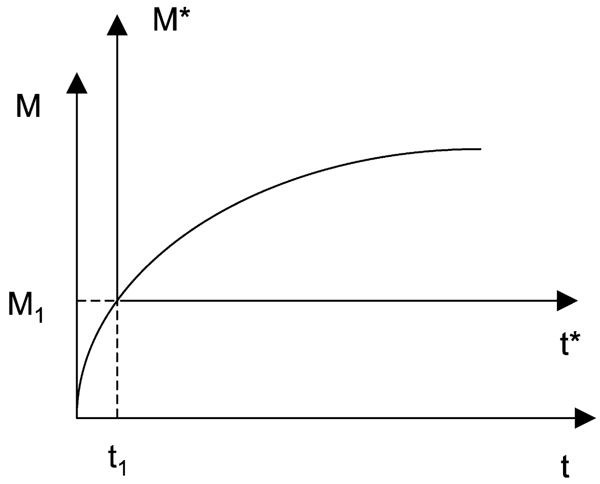

Fig. 4. Relationship between the cumulative amounts of nitrite leached and leaching times used in the derivation.

Appendix A. Analysis of leaching experiments with specimens having experienced prior leaching during the curing process

Some of the concrete cylinders used in this investigation had been cured in a limewater tank starting 1 day after casting. A certain amount of nitrite originally present in the cylinder was leached out into the tank during the curing stage. The nitrite concentration in the cylinder became therefore not uniformly distributed. When the actual leaching experiments started, the specimens presented a lower initial leaching rate than that which would have been observed in the absence of significant prior leaching during the curing processes. As a result, the dependence of the cumulative amount of nitrite leached with time deviated appreciably from square root dependence during the first few points, as can be seen in Figs. 1 and 2.

The relationship between prior leaching taking place during the curing process and that during the leaching experiment itself (assumed for simplicity to have occurred immediately after the end of the curing stage) can be expressed by:

$$M = M^* + M_1 \text{ and } t = t^* + t_1 \text{ (see Fig. 4)} \tag{A1}$$

where M and t are the cumulative amount of nitrite leached at any time and the cumulative time duration counting from the beginning of the curing stage, respectively; M_1 and t_1 are the cumulative amount of nitrite leached during the curing stage and the duration of the curing stage, respectively; and M^* and t^* are the cumulative amount of nitrite leached from the beginning of the actual leaching experiment and the time counting from the beginning of the actual leaching experiment, respectively.

It will be assumed that simple diffusion is the most likely rate-determining mechanism during the initial phase of the leaching process, and that leaching behavior approximates that in a semi-infinite medium. Then the cumulative amount of nitrite leached approaches a linear correlation with the square root of the leaching time, i.e.,

$$M = k\sqrt{t} \text{ and } M_1 = k\sqrt{t_1} \tag{A2}$$

then

$$M^* = M - M_1 = k(\sqrt{t} - \sqrt{t_1}) = k(\sqrt{t^* + t_1} - \sqrt{t_1})$$

since

$$(a+b)^n \approx a^n + a^{n-1}bn \; [\text{when } a >> b] \tag{A3}$$

and if it is assumed that $t_1 \ll t^*$, then $\frac{1}{\sqrt{t^*}}t_1 \Rightarrow 0$ and therefore:

$$M^* \approx k\left[\left(\sqrt{t^*} + \frac{1}{\sqrt{t^*}}t_1\frac{1}{2}\right) - \sqrt{t_1}\right] \approx k(\sqrt{t^*} - \sqrt{t_1}) \tag{A4}$$

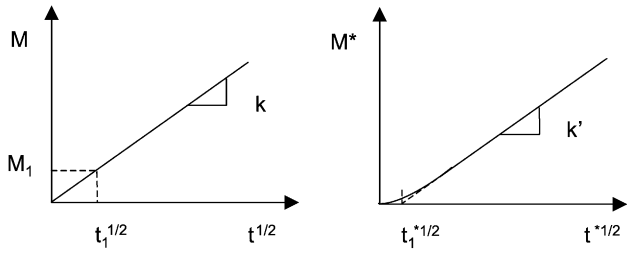

Fig. 5. Relationship between the cumulative amounts of nitrite leached and the square root of leaching time.

calling $\sqrt{t'} = \sqrt{t^*} - \sqrt{t_1}$, then

$$M^* \approx k\sqrt{t'}. \tag{A5}$$

Therefore, if the axis M^* is displaced from $t^{*\,1/2}=0$ to $t^{*\,1/2}=t_1^{*\,1/2}=t_1^{1/2}$ (the intersection of the extension line of the linear part of the curve with the $t^{*\,1/2}$ axis, as shown in Figure 5), the cumulative amount of nitrite leached during the actual leaching experiment becomes approximately proportional to $t'^{1/2}$. More importantly, the slope k' of the line $M^* \approx k\sqrt{t^*}$ at large value of t^* is the same as k. Therefore, under these conditions, the slope k' can be used to calculate D_{app} when the assumptions leading to Eq. (2) are satisfied. This approach was taken for interpreting the experimental results.

In the above derivation, it was assumed the curing and leaching test periods were consecutive, but in fact there was a lengthy interim period with some attendant relaxation of the nitrite profile developed during the curing stage. The approach used is nevertheless reasonably justified, as the relaxed profile could be considered, on first approximation, as being equivalent to that generated during a correspondingly shorter effective curing period. Improved analyses should further examine this issue, along with the possible effects of other complicating factors (e.g., carbonation at the concrete surface during the interim).

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