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EVOLUTION OF pH DURING IN-SITU LEACHING IN SMALL CONCRETE CAVITIES

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ABSTRACT

Small amounts (0.4 cc) of neutral water placed in small cylindrical cavities (5 mm diameter) in concrete exposed to 100% relative humidity first developed a pH comparable to that of a saturated $Ca(OH)_2$ solution. The pH then increased over a period of days-weeks toward a higher terminal value. A micro pH electrode arrangement was used. This behavior was observed in samples of 12 different concrete mix designs, including some with pozzolanic additions. The average terminal cavity pH closely approached that of expressed pore water from the same concretes. A simplified mathematical model reproduced the experimentally observed behavior. The model assumed inward diffusional transport of the pH-determining species in the surrounding concrete pore solution. The experimental results were consistent with the model predictions when using diffusion parameters on the order of those previously reported for alkali cations in concrete. The cavity size, cavity water content, and exposure to atmospheric CO_2 should be minimized when attempting to obtain cavity pH values approaching those of the surrounding pore water. *© 1997 Elsevier Science Ltd*

Introduction

Considerable interest exists in evaluating the concrete pore water composition, especially in relation with the mechanism of chloride-induced corrosion of reinforcing steel. The most common procedure for analysis is the expression of the pore water by means of high pressures (1–3). This method is being used increasingly in spite of its limitations (4), including potential sample preparation artifacts and poor water yields when squeezing concrete. In spite of these difficulties, the results of this technique are often taken as a reference for other determinations. Another possibility for estimating the pore water com-

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position and in particular its pH value is indirectly by ex-situ leaching (5,6). This usually consists of allowing a crushed concrete sample to be in contact with a small volume of distilled water for a specified length of time, and determining the pH of the leachate afterwards. However, dilution effects cause the pH of the leachate to be significantly less than that of the pore solution and correction is difficult, as discussed below.

The main cations responsible for the high pore water pH of concrete are alkali metal ions (Na^+, K^+) and to a lesser extent Ca^{2+} (3). This occurrs even though the CaO content in cement (typically 20%) is much greater than that of alkali oxides Na_2O, K_2O (typically <1%), because at high pH the solubility of $Ca(OH)_2$ is much lower than that of the alkali hydroxides (7). Pore water expression experiments show that in water-saturated concrete a sizable fraction of the K and Na of the cement is present as dissolved ions in the pore solution (8,9). The ex-situ leaching experiment may be envisioned as one where a fully-hydrated water-saturated concrete sample of volume V_C, having pore water with alkali metal ion concentration C_{OM}, is allowed to completely equilibrate with a volume of water V_W. If all the alkali metal ions were in the pore water and simple dilution prevails, the concentration C_{DM} of those ions in the leachate would be:

$$C_{DM} = \frac{C_{OM}}{1 + V_W/\varepsilon V_C} \tag{1}$$

where ϵ is the volume porosity of the concrete. Conversely, the calcium ion content of the leachate would not be limited by dilution, because the large supply of $Ca(OH)_2$ simply allows for dissolution of additional Ca^{2+} and OH^- ions until reaching the solubility limit at the terminal pH of the leachate. Dilution in volumes of water on the order of V_C or larger is needed in practice to obtain good concrete-water contact and a manageable amount of liquid. Because ε is typically on the order of 0.1, the dilution then causes C_{DM} to be smaller than C_{OM} by a factor of approximately 10 or greater. This large reduction in alkali concentration tends to make Ca^{++} the pH-determinant cation. The terminal pH would then depend relatively little on the initial value of the concrete pore water solution before dilution, and approach instead that for the solubility limit of Ca $(OH)_2$ in nearly pure water (pH $\approx$ 12.6) (10). Leachate pH values nearing that limit are often reported (5,6,11), and are likely to severely underestimate the pH of the original pore solution. Conversely, attempts to correct for dilution by simple proportioning to the initial pore volume can lead to overestimation of the pore water pH because only a fraction of the OH^- ions in the leachate originated from the initial pore water volume (12).

The limitation of the ex-situ leaching technique indicated above led to examination of another alternative procedure based on in-situ leaching. In this procedure, a small hole is drilled in the concrete and less than 1 mL of water is introduced in the hole. The concrete has been previously saturated with water. The water in the cavity slowly evolves toward equilibrium with the surrounding pore water, and the pH in the hole is followed by means of a micro pH sensor until a terminal condition is reached. Because of the small volume of water in the cavity, dilution effects are minimized. The terminal pH in the cavity should then approximate that in the pore solution to a better extent than that obtained in the ex-situ technique. This investigation was conducted to test experimentally those expectations and to formulate an initial quantitative interpretation of the results.

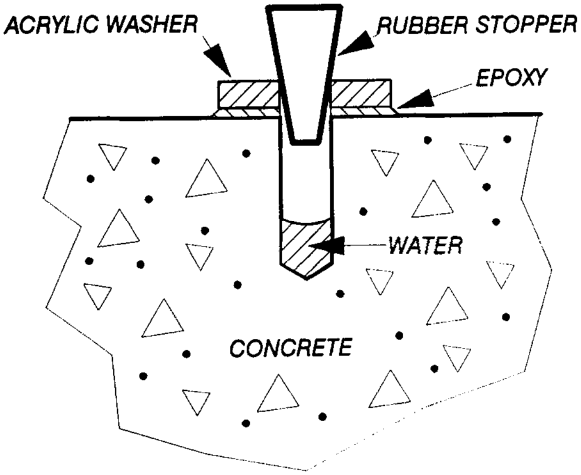

FIG. 1.
Schematic of the arrangement for the in-situ leaching.

Method

Cylindrical or cubic samples of hardened concrete with a mass of $\approx$0.5 kg were allowed to achieve constant weight at 22 ± 2°C inside a closed 100% relative humidity chamber with periodic distilled water mist-spray. A tray with fresh lime water was kept inside the chamber to minimize the partial pressure of CO_2. This preconditioning procedure typically involved two or more weeks. A hole, approximately 5 mm in diameter and 25 mm deep was then drilled on the upper surface of the sample using a masonry drill bit. Concrete dust was removed from the hole, and 0.4 mL of distilled water was pipetted into the hole. An acrylic washer was affixed around the mouth of the hole with fast-setting epoxy adhesive, and a tapered rubber stopper was pressed firmly into the washer (see Figure 1). The concrete sample was then returned to the humidity chamber and kept there for subsequent monitoring. One or two additional cavities >3 cm apart from the first one were made in the same concrete sample.

The pH of the water in the hole was monitored periodically by means of a MI-405 glass pH micro electrode (Microelectrodes, Inc.) with a 1.2-mm diameter bulb located at the end of a narrow stalk 75 mm long. The glass electrode was kept in a solution with a pH of approximately 7, and was exposed to environments of pH exceeding 12 for only a few minutes at a time. A silver-silver chloride (SSC) electrode with a 2-mm diameter bridge tube extension terminated by a glass frit was used as the reference electrode. The measurements were conducted by introducing the glass electrode and reference electrode extension into the hole until both touched the liquid at the bottom of the hole. The glass-SSC combination was previously calibrated with custom mixed nominal pH 12 and pH 13 buffer solutions (13), using the tabulated pH values for both solutions at the test temperature. The buffer solutions, concrete specimens, and electrode bodies were all typically within 1°C of laboratory air temperature, which was 22 ± 2°C throughout the investigation. The results are reported as measured, with no normalization to other temperature. The glass-SSC potential difference was measured with a pH/mV meter Corning model 140 that had 1-mV resolution. The

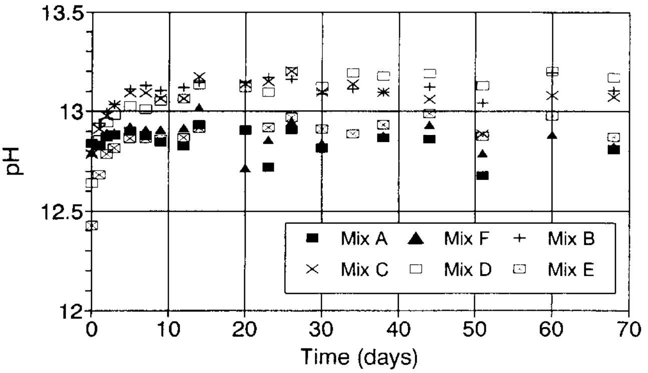

FIG. 2.
pH Evolution with time of concrete mixes A to F.

potential readings were converted to pH values using linear potential interpolation/extrapolation from the calibration points. Stabilization times for the electrode combination were in the order of 2 min.

In the pH range of interest, glass electrodes are subject to alkali ion error, which causes the potential/pH slope to be smaller than the ideal value expected in the absence of interference (14,15). The results reported in Figures 2 and 3 were obtained using the same individual glass electrode. Separate experiments using bulk test solutions with concentrations of K^+ and Na^+ representative of those encountered in concrete pore solutions (8,9) were made with that electrode. These tests showed that the alkali error was primarily related to the presence of Na^+ ions, and that calibration of the electrode with the buffers indicated above minimized systematic error (to 0.2 pH units) for test solutions with pH 13.5. Tests with duplicate electrodes with the same model number revealed significant unit-to-unit variation in response, indicating that the individual calibration of each electrode is important. In some instances, despite the >2-week exposure of the blocks to the 100% RH chamber environment, water inside the hole tended to be slowly absorbed into the surrounding internal concrete, especially in the concrete mixes with high water-to-cementitious (w/cm) ratios. In

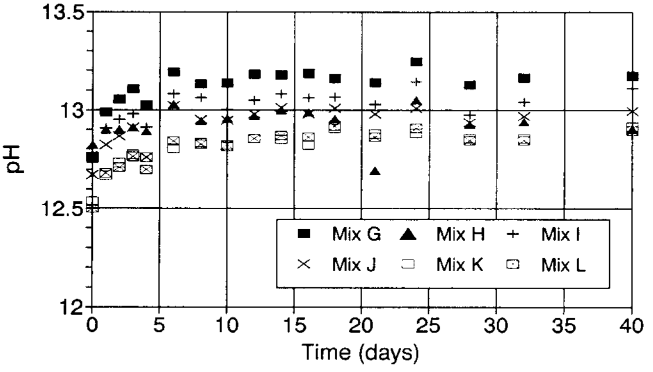

FIG. 3.
pH Evolution with time of concrete mixes G to L.

those cases, the solution inside the holes was periodically replenished by pipetting 0.2 mL of distilled water as needed.

For comparison, pore water expressions using the procedure outlined in (2,3) were performed. Coarse aggregate particles were removed as much as possible while concrete was crushed to obtain a particle size $\leq$3.5 mm. Then the sample was mist-sprayed with a fixed amount of water or, alternatively, was conditioned in a chamber with RH >95% at 20 ± 2°C during approximately 8 weeks. This treatment was necessary to have enough moisture content in the concrete for the expression. Much care was exercised to minimize excessive watering and the consequent dilution of the pore water. The squeezing of the concrete sample was effected by means of a device similar to that used in (3) and following all the procedures there described.

The concrete mix designs used are shown in Table 1. Florida limestone (maximum size approximately 10 mm) was used as coarse aggregate; each drilled hole typically intersected several aggregate particles. The fine aggregate was silica sand. The cementitious materials used were Portland cement type II, fly ash class F, and silica fume (microsilica). The Na_2O equivalent % was approximately 0.5 for the cement and approximately 0.7 for the fly ash. Mix designs B through E and G through L had a total cementitious content representative of current concretes for high performance marine substructure applications. Mixes A–F were 3 years old and Mixes G–L 2 years old at the time of the tests.

Results

Figure 2 shows the pH evolution with time for the first group of concrete samples (Mixes A–F). Each data point is normally an average of three measurements, corresponding to three different holes in the same specimen. The cavity pH in all mixes was between 12.4 and 12.8

TABLE 1
Concrete mix and properties.

Mix	Cementitious Material by weight	Cementitious Content (kg/m^3)	Water to Cementitious Ratio	Admixture to Cement Ratio
A	100% PC	33	0.55	—
B	80% PC + 20% FA	444	0.41	0.25
C	70% PC + 30% FA	444	0.43	0.43
D	72% PC + 20% FA + 8% SF	444	0.39	0.39
E	62% PC + 30% FA + 8% SF	444	0.39	0.61
F	100% PC	360	0.41	—
G	80% PC + 20% FA	444	0.37	0.25
H	100%	444	0.37	—
I	80% PC + 20% FA	444	0.50	0.25
J	80% PC + 20% FA (0.4%NaCl)*	444	0.50	0.25
K	72% PC + 20% FA + 8% SF	444	0.37	0.39
L	50% PC + 50% FA	444	0.37	1.00

PC, Portland Cement; FA, Fly Ash; SF, Silica Fume.
*NaCl% by weight of concrete.

TABLE 2
Apparent terminal pH values (averages of the last 30 days of testing)

Mix	A	B	C	D	E	F	G	H	I	J	K	L
pH	12.82	13.12	13.09	13.16	12.92	12.85	13.17	12.92	13.06	12.98	12.87	12.88

when measured a few hours after first introducing the water (Day 0). The pH increased rapidly and then more slowly during the next several days. An apparent terminal value (listed in Table 2) was reached for each mix after 2 weeks to 1 month of testing. The apparent terminal value is the average of the last 30 days of testing. To reveal possible relative trends, the values are shown with 0.01-pH resolution. However, some systematic glass electrode offset may exist as indicated earlier.

After the first 2 weeks, the pH was measured typically twice a week. When water replenishment was required in one of the cavities of a given specimen, the pH in that cavity was not determined until the next scheduled time. The value reported for the replenishment day is the average of the remaining cavities. Mixes A and F required replenishment of each cavity about twice a month, significantly more often than for the other mixes (cavities in mixes B and E were replenished once a month). Typically, pH values lower than the overall trend were recorded in a given cavity in the next scheduled test date after adding water.

After about 3 weeks of testing, consecutive pH measurements for mixes B–E showed variability on the order of 0.1 pH unit. Mixes A and F showed somewhat larger variability. Nevertheless, the apparent terminal values showed significant differentiation between groups of mixes. Mixes A and F, with unblended Portland cement, and mix E, with the highest combined pozzolanic addition (30% FA and 8% SF) showed apparent terminal pH values near 12.8–12.9. The remaining mixes (20% and 30% FA addition, and combined 20% FA + 8% SF) all showed apparent terminal pH of about 13.1.

The pH evolution with time for the second group of concrete samples is presented in Figure 3 (Mixes G–L). For this group, each data point is an average of two measurements (two holes per specimen). The pH behavior of these specimens followed the trend observed in the first group, with increasing values during the first week or two followed by small variations from test day to test day (typically less than 0.1 pH unit). Again, the highest apparent terminal value (Table 2) was recorded for a concrete mix with only fly ash as pozzolanic replacement (Mix G: 20%). The lower values were recorded for concrete mixes with high pozzolanic replacement (Mix L: 50% fly ash), or with ternary systems (Mix K: 20% fly ash, 8% silica fume). The value for the plain cement concrete was about 12.9.

A graphic comparison between the pH values from the pore water expression experiments (pH_{pwe}) and the apparent terminal pH values from in-situ leaching (pH_{ISL}) is presented in Figure 4. The solid diagonal line, shown as a reference, would represent ideal agreement. The pore water expression measurements with pH <12.6 may reflect some excess watering during sample preparation, despite precautions to the contrary. When considering all 12 specimens tested, the root mean square difference between the pH value obtained with both procedures is $(\Sigma((pH_{\mathrm{pwe}} - pH_{\mathrm{ISL}})^2/12))^{1/2} \sim 0.15$ pH units. The averages of all the measurements with each procedure ($\Sigma pH_{\mathrm{pwe}}/12$; $\Sigma pH_{\mathrm{ISL}}/12$) differs from each other by less than 0.08 pH units, suggesting little mutual bias.

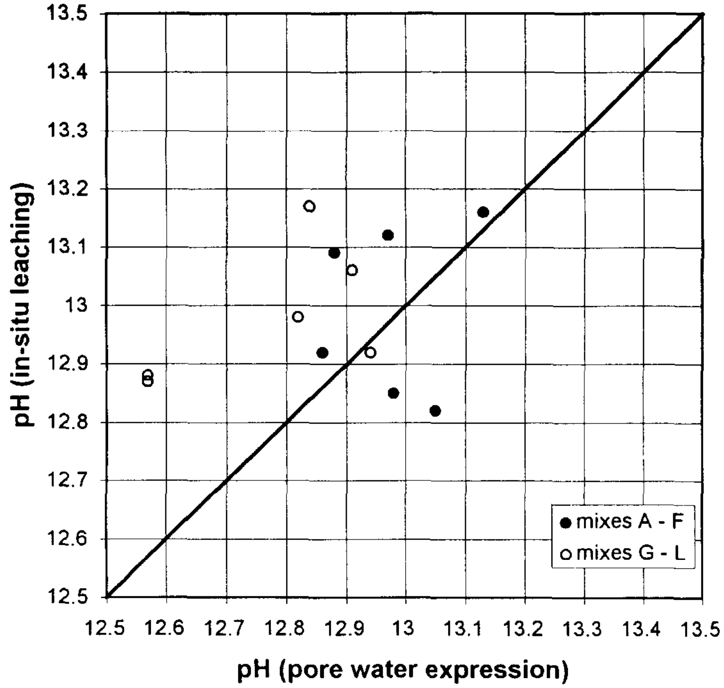

FIG. 4.

Results of measurements using pore water expression and in-situ leaching. The solid line represents ideal agreement.

Simplified Mathematical Model

To investigate which factors determined the evolution with time of pH inside the cavity, the system was subjected to simplified modeling as follows (Figure 5). The cavity was treated as

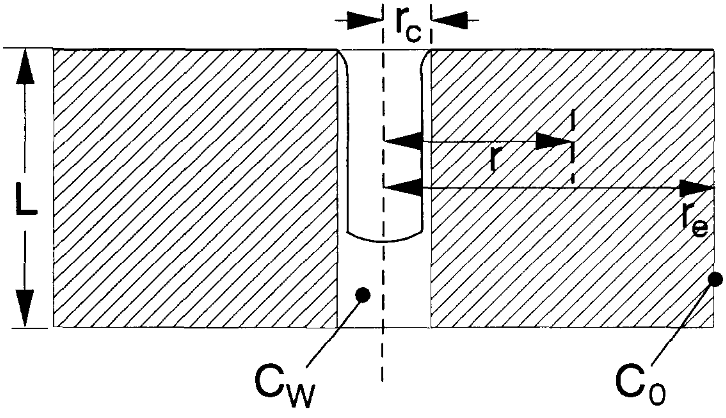

FIG. 5.

Schematic for the simplified modeling of the pH evolution inside the cavity.

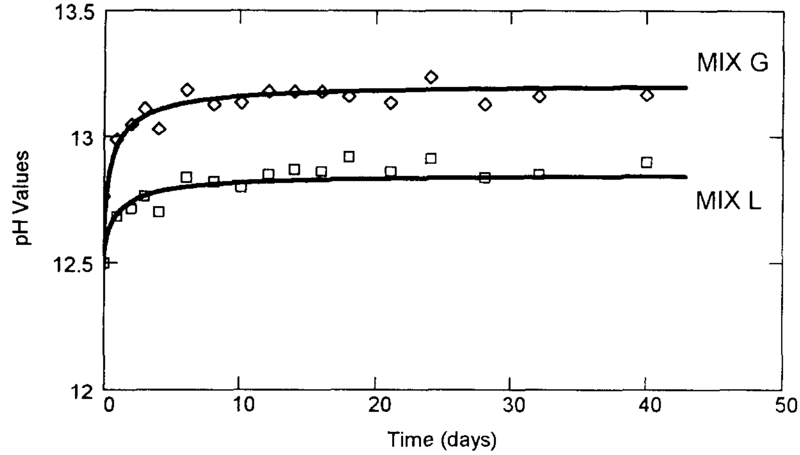

FIG. 6.

Model calculations (*solid lines*) and the experimental results (*symbols*) obtained from mixes G and L.

a cylinder with radius r_c and length L, surrounded by concrete in the form of a flat cylinder with radius $r_e \gg r_c$ and thickness L. The additional contribution of the concrete below the cavity was disregarded. The concrete was considered as a homogeneously porous medium with a total pore volume fraction ε. The pores were assumed to be always filled with water. As indicated in the Introduction, the liquid in the drilled cavity is expected to resemble a saturated $Ca(OH)_2$ solution shortly after placement of the water, and eventually evolve toward a terminal state where alkali ions are the predominant pH-determinant species. As a first approximation for these simplified calculations, the following assumptions were made:

1) The pH in the cavity water was related to the presence of a single pH-determinant species X, dissolved in the water to a concentration of C moles per cm^3, such that pH = $14 + \log_{10} (10^3\ C)$. Thus, X is a fictitious monovalent species representing the more complicated mix of alkali and Ca ions that determine pH in the actual system.
2) The species X resided only in solution at the concrete pores or in the cavity, and did not bind to the cement paste or aggregate.
3) The concentration of X in the cavity immediately after placing the water ($t = 0$) was $C_{W0} = 3\ 10^{-5}$ mol/cm^3 for an initial cavity pH of approximately 12.5. Also at $t = 0$, the concentration of X in the water in the pores immediately next to the cavity was C_{W0}, and C_0/ε everywhere else.
4) The species X was leached into the cavity from the surrounding concrete by diffusional transport.
5) The cavity was partially filled with water, but with walls efficiently wet by capillarity. Transport inside the cavity was fast enough so as to have the same concentration in the water at the bottom and on the moist cavity walls.
6) The water in the cavity was in equilibrium with the pore water at the walls at all times.

If the porosity ε is constant, then the concentration C_C of X in moles per cm^3 of concrete is given by:

$$C_C = \varepsilon C_P \tag{2}$$

where C_P denotes C for the pore water.

Defining D as the effective diffusion coefficient of X in the concrete, Fick's second law for the cylindrical problem considered here can be written as:

$$\partial C_C/\partial t = D[\partial^2 C_C/\partial r^2 + r^{-1}\partial C_C/\partial r] \tag{3}$$

where r is the distance from the center of the cavity as shown in Figure 5.

The number of moles of X flowing per unit time into the cavity, dm_X/dt, are given by Fick's first law as:

$$dm_X/dt = 2D\pi r_c L(\partial C_C/\partial r)_{r_c} \tag{4}$$

Calling the volume of the cavity $Vc = \pi r_c^2 L$, Vw_C the volume of the water in the cavity and defining $Vr = Vc/Vw_C$, then the value of C in the cavity water (denoted by C_W) varies with time as:

$$dC_W/dt = 2Dr_c^{-1}Vr(\partial C_C/\partial r)_{r_c} \tag{5}$$

Applying Eq. 2 and recalling that the water in the cavity is assumed to be in equilibrium with the pore water at the walls at all times:

$$(dC_C/dt)_{r_c} = 2\varepsilon Dr_c^{-1}Vr(\partial C_C/\partial r)_{r_c} \tag{6}$$

Eq. 3 can then be solved to obtain $C_C\ (r,t)$ for the boundary conditions in Eq. 6 as well as in the following:

$$C_C(r_c, 0) = \varepsilon C_{WO} \tag{7a}$$

$$C_C(r, 0) = C_O \qquad (r_e > r > r_c) \tag{7b}$$

$$C_C(r_c, t) = C_O \qquad \text{(Since } r_e \ll r_c,\ C_C \text{ at } r_e \text{ is considered to be unaffected by leaching within the time frame of the experiment)} \tag{7c}$$

The solution was obtained numerically by a finite difference technique in which the radial and time coordinates were divided into 30 intervals and ≥800 steps, respectively. The solutions showed little change when finer difference scaling was used.

Figure 6 shows again the measured evolution of the pH in the cavity with time for mixes G and L (*symbols*). The solid lines represent the solutions obtained with the model using $\varepsilon = 0.12$, $r_c = 0.25$ cm, $Vr = 3$, $C_0 = 1.9\ 10^{-5}$ mol/cm^3 for mix G, and $C_0 = 8.4\ 10^{-6}$ mol/cm^3 for mix L. The value chosen for D was $6\ 10^{-7}$ cm^2/sec. The cavity dimensions and its water content were representative of the those used in the experiments. The concrete porosity was typical of the concretes used. The C_0 values were chosen to match the terminal pH values observed. The chosen value of D was (after appropriate conversion) on the order of values reported in the literature for alkali ions in concrete (16–18). These choices provided a reasonable fit with the experimental trends, as shown in Figure 6.

The model equations can be stated in nondimensional terms by defining the generalized concentration $C_g = (C_w - C_{w0})/(C_0/\varepsilon - C_{w0})$ and the generalized time $T = t\ D/r_c^2$. The generalized results can then be represented by a single curve for each value of the product

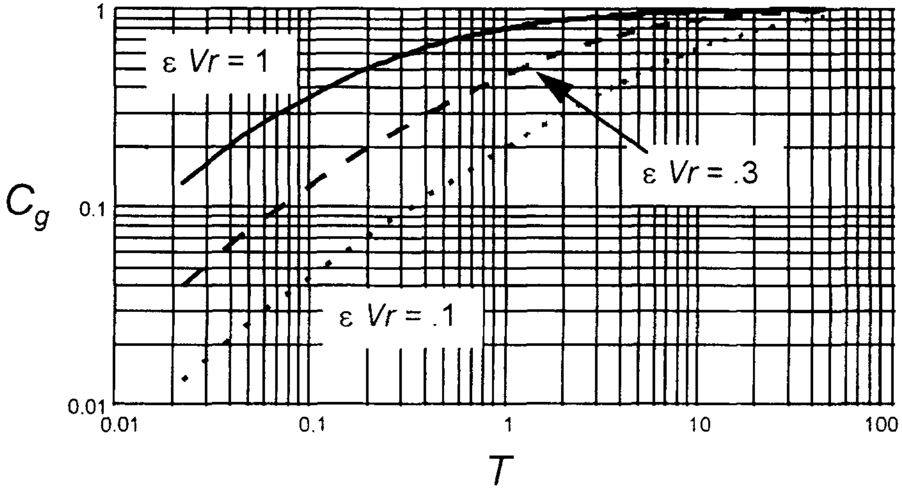

FIG. 7.
Nondimensional presentation of the model results. $C_g = (C_w - C_{w0})/(C_0/\varepsilon - C_{w0})$. $T = t\ D/r_c^2$.

ε Vr, as shown in Figure 7. The curves provide an indication of the influence of experimental conditions on the amount of time required to approximate the terminal pH to a given extent.

Discussion

The experimental results confirmed the expected behavior of pH inside the cavity starting at a value comparable to that of a saturated $Ca(OH)_2$ solution, and then increasing with time toward a higher terminal value. The average terminal value was quite close to the corresponding average from the pore water expression experiments. The time evolution of the cavity pH was also in agreement with the predictions of the simplified diffusional model when plausible parameter values where chosen for the simulation. The model was intended as an initial approximation to a complex phenomenon, to assist in identifying some of the more important transport variables in the problem. Because sweeping modeling simplifications were used (for example, the assumption of the virtual species X and neglect of transport from the lower specimen portion), the results should be considered as a rough indication of expected behavior. The nondimensional representation of results in Figure 7 serves to that end as will be discussed below.

Deviations between the pH in the cavity and that in the pores of the surrounding concrete may nevertheless stem from several causes. Of particular concern among those are: possible carbonation from interaction with the external atmosphere; slow equilibration and dilution from excessive volume of water in the cavity; and loss of cavity water into the surrounding concrete.

Carbonation of the fluid within the cavity and wetting its walls is not very likely when the stopper is in place and the entire assembly is placed in a closed humidity chamber with CO_2 traps. However, undesirable exposure to atmospheric CO_2 (including nearby human respiration) may result when removing the specimens from the chamber and removing the stopper for electrode insertion. Ideally, the pH measurements should be conducted within a mantle of decarbonated gas. Otherwise, the pH measurements should be conducted promptly while minimizing CO_2 contamination of the specimens from operator breathing or other sources.

Excessively slow equilibration of the cavity with the surrounding concrete may lead to underestimation of the terminal pH, and may aggravate errors introduced by carbonation. The results of the nondimensional formulation of the simplified model (Figure 7) indicated that once given Vr and the concrete properties, the time required to approximate the terminal pH to a desired extent was proportional to r_c^2. It is then desirable to make the radius of the cavity as small as possible. Figure 7 indicates also that once given the concrete properties and cavity dimensions, the time required to approach the terminal pH decreases markedly as Vr increases, so it is advantageous to use as little water in the cavity as practicable. A certain amount of dilution of the pore solution is inevitable at finite times and with finite concrete block dimensions. Nevertheless, the procedures indicated in the Method section represent a workable compromise between the size of the cavity, size of available electrodes, and use of a manageable amount of water.

The concrete pore network is not easily saturated with water in macroscopic specimens, even when the external surface is in direct contact with water (19). Thus, the cavity tends to lose water into the surrounding concrete and requires occasional replenishment, especially during the beginning of the experiment. As the surrounding concrete approaches saturation, the rate of water loss becomes smaller. The outward water motion acts against the inward diffusional transport of the pH-increasing species and delays the approach to a terminal pH. In most cases, the need for water replenishment was infrequent and appears not to have introduced significant adverse effects. However, in concretes mixes A and F, water replenishment was needed more often and the apparent terminal pH values were among the lowest observed, suggesting possible measurement artifacts. Future modeling work should quantitatively examine this effect by introducing the appropriate convective terms in Eqs. 3–6.

Measurements of pH were conducted in the cavity itself because of the small amount of liquid. The measurements were complicated by the alkaline error inherent to the glass-electrode (which applies also to extracted pore water and related techniques). Careful calibration and knowledge of the approximate alkali ion concentration expected was required to minimize systematic error. Deviations may be minimized also by selecting electrodes with glass formulations customized for high pH (14). Alternatively, the cavity liquid can be micropippeted and characterized externally with conventional analytical techniques to determine the concentration of dissolved species. This approach has been used successfully in an ongoing investigation on the behavior of nitrite inhibitors in concrete (20).

In-situ leaching may provide a desirable alternative method to study the composition of pore water solutions. In contrast with pore water extraction, this procedure is inexpensive and simple to implement, and not limited by low water yields in concrete. Mechanical disturbance of the sample is limited to the hole drilling, whereas pore water extraction involves massive crushing, which may expose much larger amounts of unhydrated cement and fresh aggregate surface with consequent changes in the composition of expressed water. Some of the potential limitations of in-situ leaching were discussed above. Various other issues need further investigation to establish the potential usefulness of this technique. Among those issues are the equilibrium partitioning of dissolved species between the macrocavity and the surrounding micropores and concrete bulk; the distribution of water and dissolved species between the cavity bottom and the walls; and the desirable size of the cavity vs. that of the coarse aggregates to obtain a representative indication of the average conditions in the concrete.

Conclusions

Neutral water placed in small cylindrical cavities in concrete first develops a pH comparable to that of a saturated $Ca(OH)_2$ solution. The pH then increases toward a higher terminal value.

The behavior indicated above was observed in samples of 12 different concrete mix designs, including some with pozzolanic additions. The average terminal cavity pH closely approached that of expressed pore water from the same concretes.

A simplified mathematical model reproduced the experimentally observed behavior. The model assumed inward diffusional transport of the pH-determining species in the surrounding concrete pore solution. The experimental results were consistent with the model predictions when using diffusion parameters comparable to those previously reported for alkali cations in concrete.

The model results indicated that approach to a terminal pH was faster for smaller cavity diameters and smaller amounts of water in the cavity. The procedure presented here is a potential alternative for probing the composition of pore water in concrete.

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