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Calculating Cement Paste and Mortar Diffusivity from Conductivity Measurements: Preliminary Results of a New Method

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ABSTRACT

A new method to determine the chloride diffusivity of concrete is being developed which is both expeditious and accurate. The method is based upon the Nernst-Einstein equation relating conductivity and diffusivity. Results from a single measurement can be used to calculate the diffusivity for any specified ion, given the "free" diffusivity of that ion. The experimental procedure, along with preliminary results, are reported.

Keywords: building technology, conductivity, diffusivity, impedance spectroscopy, service life.

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1 INTRODUCTION

The time-to-corrosion of steel reinforcement in concrete, induced by external chloride ions, depends upon the rate chloride ions penetrate the concrete. Theoretical models for predicting the effect of corrosion on the service life of reinforced concrete are based on the premise that diffusion is the predominant transport mechanism for the chloride ions [1]. Therefore, to obtain reliable predictions from the models, accurate measurements of the chloride ion diffusivity are needed.

The advent of high performance concretes places a greater demand upon the methods and equipment used to measure transport properties. Currently, concrete diffusivity is measured using the standard divided-cell technique which may require months, or possibly a year, to achieve an acceptable level of accuracy for extremely low diffusivity concretes [2]. The long duration of this test has initiated research towards developing a more rapid test with equal or better accuracy.

A new technique is proposed which provides an indirect measure of diffusivity from a conductivity measurement. The relationship between conductivity and diffusivity is given by the Nernst-Einstein equation [3]:

$$\frac{D}{D_o} = \frac{\sigma}{\sigma_o} \tag{1}$$

where D is the diffusivity of the specimen, D_o is the "free" diffusivity of the pore solution which can be obtained from chemical handbooks [4], σ is the conductivity of the specimen, and σ_o is the conductivity of the pore solution. The advantage of this approach is that specimen conductivity can be measured quickly and accurately.

Eq. 1 implicitly assumes that the specified ion is not absorbed by the material. For example, magnesium in concrete absorbs a small fraction of the diffusing chloride ions, effectively reducing the chloride diffusivity of the sample. Therefore, in the case of ion absorption, Eq. 1 is an upper limit for diffusivity. Also, Eq. 1 assumes the matrix is an insulator.

The conductivity of a solution is the linear sum of the contribution from each electrolyte. If there are N electrolytes in a solution, the conductivity of the solution, σ_o, is

$$\sigma_o = \sum_{i=1}^{N} z_i F c_i u_i \tag{2}$$

where z is the valence, F is Faraday's constant, c is concentration, and u is the conventional ion mobility.

There are two useful results of Eqs. 1 and 2. Since σ/σ_o is a constant for a given specimen, the ratio D/D_o is also a constant for a given material. Once the ratio is known, a specific value for D can be determined from the value of D_o for a specific ion. Secondly, the conductivity measurements can be made with any combination of ion type and concentration that yields the desired solution conductivity. Therefore, the specific ion for which the diffusivity is sought does not have to be present during the conductivity measurement.

To determine the diffusivity of a specimen, the pore solution conductivity must be known. Although the pore solution of cement paste is primarily saturated calcium hydroxide, the conductivity of the pore solution is dominated by the presence of the cations Na^+ and K^+,

typically at concentrations of a few tenths of a mole per liter, depending upon the value of the water:cement ratio (w/c). Since the concentrations of sodium and potassium ions varies among samples and cement types, the pore solution conductivity varies from sample to sample.

There exist three methods to determine the pore solution conductivity: measure the pore solution conductivity directly; replace the pore solution with a solution of known conductivity; or assume a value for the pore solution conductivity. Measuring the pore solution directly is only practical for young (< 28 days old) samples because pore water is consumed during hydration. Secondly, very low water-cement ratio concretes have extremely low quantities of pore solution initially, further complicating pore solution extraction from older specimens. As a general test for arbitrary samples, measuring the pore solution directly is not feasible.

Replacing the pore solution with a solution of known conductivity appears to be straightforward. However, to perform this would require high precision experimental apparatus. The specimen would have to be mounted into a sample holder and a displacing solution would have to be forced through the sample under very high pressure. The effluent would have to be monitored to determine when the sample had been flushed. The method is further complicated by an extremely low flow rate of effluent due to the low permeability ($\approx 10^{-20} m^2$) of low water:cement ratio pastes [5].

Using a constant value for the pore solution conductivity has practical advantages. Experiments performed at Northwestern University indicate that the pore solution conductivity of cement paste is linearly proportional to degree of hydration. After hundreds of hours of hydration the pore solution conductivity of Type I cement paste typically approached a value between 15 and 20 S/m [1] [6]. From an engineering perspective, this range of values may be insignificant with respect to acceptable errors in the final value of diffusivity. Since values of diffusivity can vary over orders of magnitude, assuming a typical value of 17 S/m induces a relatively small error. For simplicity, this method of assuming a value for the pore solution conductivity was used in this report.

2 IMPEDANCE SPECTROSCOPY

Impedance spectroscopy (IS) [7] is used to determine the bulk resistance of a specimen. For any porous material containing electrolyte, the complex impedance varies as a function of frequency, as depicted in Fig. 1. The figure shows the real, Z', and negative imaginary, $-Z''$, impedance response of a model sample. The free parameter is frequency and the logarithm (base 10) of the frequency is superposed on the data. The bulk and electrode each have an impedance response similar to a resistor and capacitor in parallel, as shown in Fig. 2; the subscripts 'b' and 'e' represent bulk and electrode components, respectively.

The impedance response of a single resistor-capacitor pair is a single semi-circle. At zero frequency the semi-circle originates at a real impedance value equal to the resistor value. At infinite frequency the semi-circle returns to the real axis at the origin because at infinite frequency an ideal capacitor acts as a 'short'. The characteristic frequency of the resistor-capacitor pair, $\frac{1}{2\pi RC}$, occurs at the "top" of the semi-circle.

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[1] A current of one amp flows through a one S/m sample with a cross section of one square meter, a length of one meter, and an applied potential of one volt.
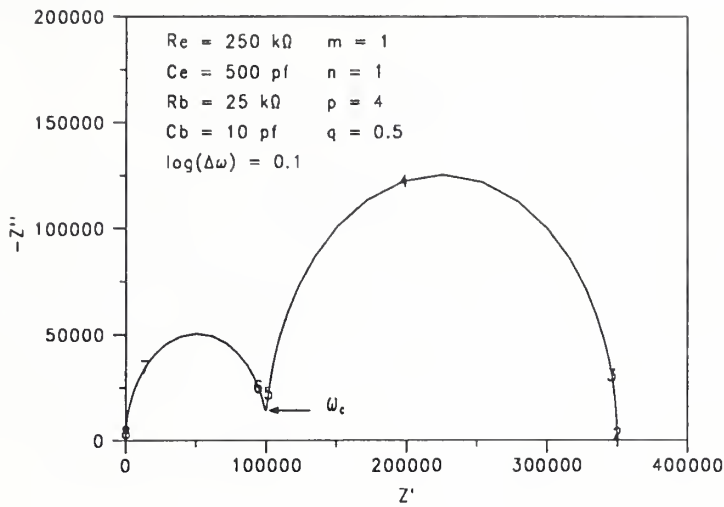
Figure 1: Demonstration of cut-off frequency, ω_c.

The two arcs shown in Fig. 1 are the electrode arc at low frequencies and the bulk arc at high frequencies. In the absence of the bulk arc, the electrode arc would intersect the origin. However, there exists an intermediate frequency which is high enough so that the electrode is effectively 'shorted' by its capacitor and is low enough so that the bulk capacitor has no effect, making the bulk purely resistive. This intermediate frequency, the cut-off frequency, ω_c, has a real impedance, Z', intercept at the bulk resistance. For the model system response shown in Fig. 1, the bulk resistance is approximately $10^5 \, \Omega$.

The cut-off frequency depends upon the resistive and capacitive components of the bulk and the electrode. The resistive and capacitive components, in turn, depend upon specimen shape and microstructure, electrolyte type, and the electrode contact mechanism. Therefore, since the cut-off frequency varies among samples, a fixed-frequency test would be inadequate to determine bulk resistance.

3   MEASUREMENT MODELLING

The electrical behavior of the sample-electrode system can be approximated by a resistor-capacitor (R-C) circuit, as shown in Fig. 2. The middle R-C pair represent the bulk response, and the R-C pairs on the ends represent the electrode response. The objective of the experimental setup is to separate, as much as possible, the characteristic frequencies of the electrodes and the bulk. This is typically achieved by reducing the resistance of the bulk in order to increase its characteristic frequency [7].

The value of the bulk and electrode resistor and capacitor depend upon specimen geometry. As the specimen length increases, the bulk resistance increases and the bulk capacitance decreases. Similarly, increasing the cross-sectional area increases capacitance and decreases resistance. Therefore, changes in specimen geometry affect the response of the specimen and the electrode.
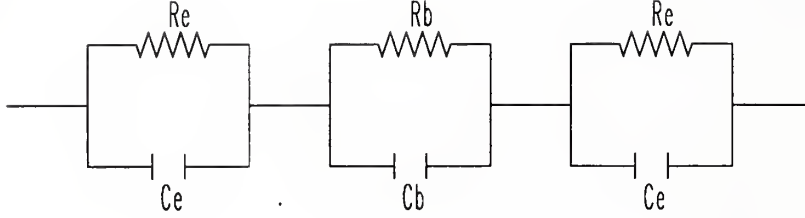
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Figure 2: R-C approximation of sample and electrode properties.

3.1 Unit Cell

To study the effects of geometry upon the impedance response, the material may be reduced to a fundamental unit cell of a resistor and capacitor in parallel. From this unit cell, a sample may be reconstructed into any arbitrary geometry. If the final geometry is simple (*e.g.*, cubic or cylindrical symmetry), the resistive and capacitive properties of the final geometry can be determined analytically from the properties of the unit cell.

Consider a specimen shaped in a cubic prism. Let the sample be m unit cells wide and p unit cells long. The admittance, Y_o, of a single unit cell having resistance R and capacitance C is [7]

$$Y_o = \frac{1}{R} + iwC \tag{3}$$

The admittance of m unit cells placed in parallel is mY_o. The impedance of p of these strips placed in series is

$$
\begin{aligned}
Z &= p\,[mY_o]^{-1} \\
&= \frac{p}{m}\left[\frac{R - i\omega R^2 C}{1 + \omega^2 R^2 C^2}\right]
\end{aligned}
\tag{4}
$$

The same approach can be used for the electrodes at the ends of sample; the resistor and capacitor values are simply changed accordingly.

This approach can be extended to three dimensions. For a sample n unit cells thick, the admittance of a $m \times n$ array of unit cells is mnY_o. Likewise, the impedance of sample p units long is

$$Z = \frac{p}{mn}\left[\frac{R - i\omega R^2 C)}{1 + (\omega RC)^2}\right] \tag{5}$$

3.2 Sample Geometry

Consider a system composed of bulk and electrode components, denoted with the subscripts "b" and "e", respectively. The system is m wide, and n thick, for a cross sectional area of

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mn. The bulk is p long and the total electrode length is q (equals twice the length of a single electrode-electrolyte interface). Note that m, n, p, and q are not required to be integers. The impedance of the entire system is

$$Z = \frac{p}{mn} \left[\frac{R_b - i\omega R_b^2 C_b}{1 + \omega^2 R_b^2 C_b^2} \right] + \frac{q}{mn} \left[\frac{R_e - i\omega R_e^2 C_e}{1 + \omega^2 R_e^2 C_e^2} \right] \tag{6}$$

An impedance response of a model bulk-electrode system is given in Fig. 1 with the values for p, $q/2$, m, and n noted.

The cut-off frequency (the frequency at which the bulk resistance is determined) can be approximated by differentiating the negative imaginary part of the impedance, and determining the minimum between the two characteristic frequencies. Assuming that the characteristic frequencies of the bulk and electrode are separated by a few orders of magnitude, the cut-off frequency, ω_c, can be approximated by

$$\omega_c \approx \frac{1}{R_b C_b} \sqrt{\frac{q}{p \frac{C_e}{C_b} - 1}} \tag{7}$$

Since the thickness of the electrode, q, remains relatively constant, increasing the specimen thickness, p, decreases the cut-off frequency, which is desirable from a practical sense. Since C_e is typically much greater than C_b, ω_c should decrease as the square root of the length increases.

4 EXPERIMENTAL METHOD

The objective of the experimental method is to obtain the most accurate measure of resistance possible. To obtain this, the specimen must be thoroughly saturated and there must be a coupling medium between the electrode and the bulk which has a very low resistance and capacitance.

Once the specimen is prepared its ends are covered with silver paste, placed between two 303 stainless steel (austenitic) disks, and connected to an impedance spectrometer. Using the capabilities of a microprocessor-based impedance analyzer, the bulk resistance is determined and recorded. For one-dimensional current flow, the conductivity can be simply calculated from the specimen's resistance, R, length, L, and cross-sectional area, A:

$$\sigma = \frac{1}{R} \frac{L}{A} \tag{8}$$

Once σ is established, and σ_o is known, the diffusivity is determined from the "free" diffusivity. As an example, consider the following case consisting of typical values: the conductivity of the specimen, σ, is 0.034 S/m and the conductivity of the pore solution, σ_o, is 17 S/m. The specific conductivity of the specimen, $\frac{\sigma}{\sigma_o}$, is 0.0020. The diffusivity of the specimen to any ion can be determined from the "free" diffusivity of that ion. For Cl^- ions originally bound to Na^+, the "free" diffusivity of the Cl^- ion is approximately $1.5 \times 10^{-9} m^2 s^{-1}$ [4]. Therefore, the diffusivity of the specimen to Cl^- ions originally bound to Na^+ ions can be calculated from

$$D = D_o \frac{\sigma}{\sigma_o} = 3.0 \times 10^{-12} m^2/s \tag{9}$$

Table 1: Data for various values of w/c.

w/c	Length (mm)	Resistance Ω	σ (S/m)	σ/σ_o	D_{Cl^-} ($10^{-12}m^2s^{-1}$)
.30	25	416	0.077	0.0047 (1/213)	7.1
.45	22	345	0.082	0.0050 (1/200)	7.5
.60	19	117	0.208	0.0126 (1/79)	18.9

5 SPECIMEN PREPARATION

After cutting and sanding, the specimens were vacuum saturated in a solution consisting of 0.27M $NaOH$, 0.87M KOH, and saturated $Ca(OH)_2$. The ratio of sodium hydroxide to potassium hydroxide was established from typical data collected at Northwestern University. Since the asymptotic pore solution conductivity of paste typically ranges between 15 and 20 S/m, the solution contains sufficient concentrations to create a solution of approximately 17 S/m.

Because of the moisture requirements of cement paste, a conductive, conformable interface was needed between the pore structure of the specimen and the stainless steel electrodes. Two interfacing mediums were tried: water and silver paste. Although the water made an effective electrical bond between the specimen and the electrodes, the extreme thickness of the water layer, and the presence of free water, made the results indefinite and suspect.

The silver paste proved to be the most effective interface. The silver paste is applied to the saturated, surface dry sample. Since acetone is used as the solvent, the paste dries in seconds, minimizing specimen moisture loss. Immediately following the silver paste drying, the sample is placed between the two stainless steel disks and tested.

Since the silver paste applied to the specimen is only micrometers thick, the specimen must be reasonably flat to achieve a good contact between the paste and stainless steel plates. To insure reasonable flatness, the specimens were sanded on a piece of glass covered with #80, #240, #400, and #600 grit sandpaper.

6 MEASUREMENTS

6.1 Effect of Water:Cement Ratio

A study of the effect of the water:cement ratio (w/c) upon the diffusivity of cement paste was performed upon specimens that had hydrated in a sealed container for approximately one year. Three Type I cylindrical cement paste specimens with w/c values of 0.30, 0.45, and 0.60 were used.

The results from the experiment are given in Table 1; all of the specimens were 31.5 mm in diameter. The numbers between parentheses, which are approximations of the preceding decimal number, are the inverse of the formation resistivity factor which typically has a power law relationship to porosity [8]. The chloride diffusivity shown is based upon a "free" diffusivity of 1.5×10^{-9} m^2/s for chloride initially bound to sodium.

Since divided cell diffusivity tests were not performed with similar specimens, corrobo-
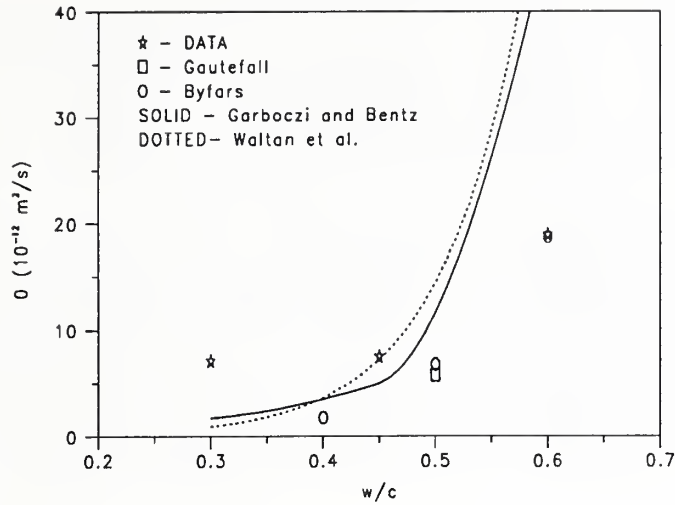
Figure 3: Experimental diffusivity calculations based upon impedance spectroscopy (IS) measurements compared to published data and analytical relations.

rating values of diffusivity had to be approximated using data and analytical relationships published in current technical journals. An analytical relationship between w/c and diffusivity established by Garboczi and Bentz [9] is

$$\frac{D}{D_o} = 0.001 + 0.07\phi^2 + 1.8H(\phi - 0.18)(\phi - 0.18)^2 \tag{10}$$

which requires the porosity, ϕ:

$$\phi = 1 - \frac{1 + 1.31\alpha}{1 + 3.2\frac{w}{c}} \tag{11}$$

where α is the degree of hydration attained by the sample. The function $H(x)$ is the Heaviside function which returns a zero when its argument is less than or equal to zero, and returns a one when its argument is positive. Degree of hydration was calculated from loss-on-ignition data performed on the conductivity specimens in Table 1. Using the relation from Eq. 10, specific conductivities were approximated for the specimens and plotted in Fig. 3.

An empirical relationship between diffusivity and w/c was established by Walton et al. [10] using data from Atkinson et al. [11]:

$$D_i(10^{-12}m^2/s) = 10^{(6.0\frac{w}{c} - 13.84)} \tag{12}$$

This relationship estimates the diffusion of Cl^- bound with Na^+ and is also plotted in Fig. 3.

Finally, experimental measurements of chloride diffusivity were obtained from the published reports of Gautefall [12] and Byfors [13]. These data, which were from specimens one year old, are included in Fig. 3 and are labeled accordingly.

A comparison of the conductivity measurement data, analytical predictions, and published data is given in Fig. 3. Both the analytical approximations and the published data agree with the calculations based upon conductivity measurements at 0.45 w/c. Although

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Table 2: Data for 0 and 10% sand, by volume.

Sand	Length (mm)	Resistance Ω	σ (S/m)	σ/σ_o	D_{Cl^-} $(10^{-12}m^2s^{-1})$
.00	7.60	220	0.0443	0.0148 (1/68)	22.2
.10	6.29	280	0.0286	0.00955 (1/104)	14.3

the results of the conductivity measurements do not agree with the analytical results at 0.60 w/c, the conductivity measurements do agree with the published result of Byfors. However, the conductivity of the 0.30 w/c specimen does not agree with the analytically predicted values. This disagreement is possibly due to plastic shrinkage cracking occurring during the first 24 hours of hydration. Small surface cracks were observed during specimen preparation. However, the specimens with the w/c values of 0.30 and 0.45 were not inspected for the presence of cracks. These results demonstrate the sensitivity of diffusivity to the curing of the specimens.

6.2   Effect of sand content

The experiment was repeated for two specimens of white cement pastes containing 0 and 10% sand, by volume. The w/c was 0.40 and the age was eight months. The results are shown in Table 2. The diameters of the 0 and 10% sand specimens were 31.5 and 31.6 mm, respectively.

Unpublished experimental results from Northwestern University indicate that the pore solution conductivity of these white cement paste specimens is typically 3.0 S/m for a w/c value of 0.40 at an age of eight months.

For the case of 0% sand, approximate values for the specific conductivity can be calculated in the same manner as the previous experiment. Combining the degree of hydration versus w/c data of Zhang et al. [14] with the result from Garboczi et al. [9] gives a specific conductivity of 0.0021. Similarly, using the equation established by Walton et al. [10], assuming a "free" diffusivity of $1.5 \times 10^{-9} m^2/s$, gives a specific conductivity of 0.0024. Unfortunately, these predicted values disagree with the experimental results in Table 2.

As expected, the specific conductivity of the specimen decreases with increasing sand content. The specific conductivity should follow an exponential relationship to porosity, ϕ [15]. For spherical particles, the specific conductivity should be proportional to $\phi^{1.5}$. Therefore, the expected value of specific conductivity for the 10% sand sample is 0.0126. The lower value of 0.0096 recorded could be due to the presence of the sand, effectively increasing the w/c near the sand-paste interfacial zones, decreasing the w/c for the bulk paste [16]. Therefore, low concentrations of sand can have a compound effect, lowering the bulk diffusivity below the value expected from the mere presence of noninteracting, nonconducting spheres.

7 FUTURE RESEARCH

As the IS conductivity test exists, it can be used to calculate the diffusivity of cement paste and mortar specimens. A likely candidate for future modifications will be a procedure to replace the pore solution of the specimen with a solution of known conductivity. This effort will require a very careful design of an apparatus to force the replacement fluid through the specimen and monitor the effluent. However, for very low w/c concretes, the permeability may be too low to make this approach feasible.

Further modifications for concrete specimens may require a more careful study of vacuum saturation of large specimens and the effect of specimen size upon measured conductivity. The vacuum saturation process may become prohibitively slow, requiring apparatus to force a replacement solution through the specimen. Also, there exists a limit on the minimum thickness of specimens. If the specimen is too thin, on the order of the largest aggregate diameter, the current will not be affected by the geometry of the aggregates, thereby giving erroneous conductivity results.

8 SUMMARY

This report has presented a new test method to calculate the diffusivity of cement paste and mortar specimens. This test is conducted independently of the specific ion diffusivity desired. The diffusivity for any ion can be calculated from the specific conductivity reported and the "free" diffusivity of the ion, which is reported in standard chemical reference handbooks.

Preliminary results of the test indicate that it is both expeditious and accurate, with the accuracy being determined from predictions using published data and empirical relations for diffusivity. Further improvements to the test may include accessory apparatus to replace the pore solution with a solution of known conductivity. However, this could greatly complicate the procedure for the test.

9 ACKNOWLEDGEMENT

References

[1] Clifton, J.R. and Knab, L.I., "Service Life of Concrete," NIST Internal Report, NISTIR **89-4086**, 1989.

[2] Clifton, J.R., Knab, L.I., Garboczi, E.J., and Xiong, L.X., "Chloride Ion Diffusivity in Low Water-to-Solid Cement Paste," *NUREG/CR-5727* and *NISTIR 4549*, June 1991.

[3] Bockris, J.O'M. and Reddy, A.K.N., Modern Electrochemistry, Vol. 1, Plenum Press, New York, 1970.

[4] CRC Handbook of Chemistry and Physics, Ed. R.C. Weast, CRC Press, Boca Raton.

[5] Powers, T.C., Copeland, L.E., Hayes, J.C. and Mann, H.M., "Permeability of Portland Cement Paste," *J. ACI*, **51**, 285–298, November 1954.

[6] Christensen, B.J., Mason, T.O., and Jennings, H.M., "Influence of Silica Fume on the Early Hydration of Portland Cements using Impedance Spectroscopy (IS)," *Journal of the American Ceramics Society*, **74** (4), 939–945, April 1992.

[7] Macdonald, J.R., Impedance Spectroscopy, John Wiley & Sons, New York, 1987.

[8] Archie, G.E., "The Electrical Resistivity Log as an Aid in Determining Some Reservoir Characteristics," *AIME Trans.*, **146**, 54–62, 1942.

[9] Garboczi, E.J. and Bentz, D.P., "Computer Simulation of the Diffusivity of Cement-Based Materials," *Journal of Materials Science*, **27**, 2083–2092, 1992.

[10] Walton, J.C., Plansky, L.E., and Smith, R.W., "Models for Estimation of Service Life of Concrete Barriers in Low-Level Radioactive Waste Disposal," NUREG/CR-5542 EGG-2597, 1990.

[11] Atkinson, A., Nickerson, A.K., and Valentine, T.M., "The Mechanism of Leaching from some Cement-Based Nuclear Wasteforms," *Radioactive Waste Management and the Nuclear Fuel Cycle*, **4** (4), 357–378, 1984.

[12] Gautefall, O., ACI SP-91-48, ACI, Detroit, 1986.

[13] Byfors, K., "Influence of Silica Fume and Flyash on Chloride Diffusion and pH Values in Cement Paste," *Cement and Concrete Research*, **17**, 115–130, 1987.

[14] Zhang, M.H. and Gjørv, O.E., *Cement and Concrete Research*, **21**, 800–808, 1991.

[15] Christensen, B.J., Mason, T.O., Jennings, H.M., Bentz, D.P., and Garboczi, E.J., "Experimental and Computer Simulation Results for the Electrical Conductivity of Portland Cement Paste," in **Advanced Cementitious Systems: Mechanisms and Properties**, Materials Research Society Proceedings, Vol. 245, 259–264, 1992.

[16] Snyder, K.A., Winslow, D.N., Bentz, D.P., and Garboczi, E.J., "Effects of Interfacial Zone Percolation in Cement-Based Composite Transport Properties," in **Advanced Cementitious Systems: Mechanisms and Properties**, Materials Research Society Proceedings, Vol. 245, 265–270, 1992.