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# ON THE RELATIONSHIP BETWEEN THE FORMATION FACTOR AND PROPAN-2-OL DIFFUSIVITY IN MORTARS

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## ABSTRACT

The applicability of resistivity-diffusivity relationships for mortars is addressed. The following equation

$$F = \frac{\rho_{\text{mortar}}}{\rho_{\text{porewater}}} = \frac{D_{\text{porewater}}}{D_{\text{mortar}}}$$

relating the formation factor (F) to the resistivity (ρ) and diffusivity (D) was investigated for Portland cement mortars and for mortars incorporating silica fume, fly ash and blast furnace slag.

## Introduction

When a particle is subjected to both chemical potential ($\nabla\mu$) and electric field ($\nabla\phi$) gradients, the flux is equal to the product of the particle concentration (C), the particle mobility (M) and the forces acting on the particle. When the gradients are unidirectional, the flux is,

$$J = -M \cdot C \cdot \left( \frac{\partial \mu}{\partial x} + q \cdot \frac{\partial \phi}{\partial x} \right) \tag{1}$$

where, q is the particle charge. From Fick's first law, the flux is,

$$J = -D \cdot \left( \frac{\partial C}{\partial x} \right) \tag{2}$$

In the absence of an electric field, and for ideal solutions[1], then Eq.[1] and Eq.[2] can be combined to yield the Nernst-Einstein equation.

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[1] $\frac{\partial \mu}{\partial x} = \left( \frac{R \cdot T}{C} \right) \cdot \frac{\partial C}{\partial x}$, where R is the universal gas constant, and T is the temperature in kelvin.

$$D = M \cdot R \cdot T \tag{3}$$

Incorporating Eq.[3] into Eq.[1] and for $\nabla\mu = 0$, the flux is,

$$J = \left(\frac{D}{R \cdot T}\right) \cdot C \cdot q \cdot \left(-\frac{\partial\phi}{\partial x}\right) \tag{4}$$

The current per unit area (I) is,

$$I = J \cdot q = \frac{1}{\rho} \cdot \left(-\frac{\partial\phi}{\partial x}\right) \tag{5}$$

where, the second equality represents Ohm's law, and $\rho$ is resistivity. Combining Eq.[4] and Eq.[5] gives the inverse relationship between D and $\rho$.

$$\frac{1}{\rho} = D \cdot \left(\frac{C \cdot q^2}{R \cdot T}\right) \tag{6}$$

For porous rocks saturated with saltwater and with solid phases of high resistivity, early work extended Eq.[6] to show that the ratio of the saltwater saturated rock resistivity to the resistivity of the saltwater was inversely related to the respective diffusivities (or permeabilities) (1-3). Atkinson and Nickerson (4), Buenfeld and Newman (5) and later Garboczi (6) realized the application to cement based systems particularly for the rapid determination of diffusivities. For mortar systems, the formation factor (F) was defined as,

$$F = \frac{\rho_m}{\rho_{pw}} = \frac{D_{pw}}{D_m} \tag{7}$$

where, $\rho_m$ is the mortar resistivity, $\rho_{pw}$ is the porewater resistivity, $D_m$ is the diffusivity in the mortar, and $D_{pw}$ is the diffusivity in the porewater. Atkinson and Nickerson (4) and Batchelor and co-workers (7, 8) replaced $D_{pw}$ by $D_o$, the molecular diffusivity in pure water, and calculated $D_m$.

$$D_m = D_o \cdot \frac{\rho_{pw}}{\rho_m} \tag{8}$$

The approximation of $D_{pw}$ by $D_o$ for all systems including those systems which have incorporated pozzolans represents an uncertain extrapolation because there will be a significant difference in the composition of ions present and the chemical potential of the porewater ions are not compositionally independent. Recently, Streicher and Alexander (9) saturated samples with a 5 M NaCl solution forcing the specimens to have the same $\rho_{pw}$. However, results from diffusion tests were not available to confirm F which was calculated from resistivity measurements. Therefore, the purpose of this investigation is to confirm the validity of Eq.[8] for ordinary Portland cement mortars and for mortars which incorporate silica fume, fly ash or blast furnace slag.

## Experimental

The mortar mix designs are given in Table 1. Mortars were cast into either cubes (2.54 cm x 2.54 cm x 2.54 cm) with stainless steel electrodes on two opposite faces for the resistivity measurements or cylinders (3 cm (o.d.) x 15 cm) for the diffusivity measurements. Mortars were hydrated at 100% rh for 7 or 28 days.

Mortar resistivities were determined using the procedure and apparatus described previously (10). Impedance data was collected using a 1260 impedance gain-phase analyzer from Schlumberger Technologies. Measurements were made logarithmically down in frequency range from 20 MHz to 1 Hz with 10 readings per decade. Subsequent to the mortar resistivity measurements, the mortar cubes were crushed and the porewater extruded. The porewater resistivity was measured with a calibrated resistivity probe (Microelectrodes Inc., MI-900 resistivity probe). The probe was calibrated against a 0.01 N KCl standard solution.

Slices of mortar cut from the 3 cm (o.d.) cylinders were used to measure the propan-2-ol diffusivity with the counter diffusion technique described in detail elsewhere (11, 12). The mortar disc slices were generally 1.14 mm thick. The discs were wiped free of excess water just before weighing. Subsequently, they were immersed in anhydrous propan-2-ol. The volume of the propan-2-ol in the containment vessel was large (1.5 l) compared to the size of the specimen (25 g). Specimen weight was recorded every few minutes and the propan-2-ol was renewed after 1, 2, 4, 8 and 24 h, and then every 24 h and less frequently after 7 days. The water-saturated mortar discs loses weight when immersed in propan-2-ol because the denser water is replaced by the propan-2-ol. Values of the propan-2-ol diffusivity can be calculated from Fick's law in the form,

$$\frac{W_t}{W_\infty} = 1.127\sqrt{\frac{D_m \cdot t}{L^2}} \tag{9}$$

where, $D_m$ is the propan-2-ol diffusivity into the mortar, t is the time, L is the half thickness of the specimen, $W_t$ is the quantity of propan-2-ol diffusing through the pores into the specimen, and $W_\infty$ is the quantity of propan-2-ol at equilibrium (240 h).

TABLE 1
Mortar Mix Designs (kg m$^{-3}$)

| | S1 | | S2 | | S3 | | S4 | | S5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| w/c* | 0.42 | 0.60 | 0.42 | 0.60 | 0.42 | 0.60 | 0.42 | 0.60 | 0.42 | 0.60 |
| Cement** | 370 | 280 | 338 | 275 | 118 | 85.4 | 241 | 175 | 81.4 | 58.7 |
| Silica Fume | | | 37.8 | 30.6 | 11.2 | 8.1 | 18.5 | 13.5 | 11.2 | 8.1 |
| Fly Ash | | | | | | | 111 | 81.0 | | |
| Slag | | | | | 240 | 174 | | | 277 | 200 |
| Sand*** | 745 | 840 | 752 | 915 | 740 | 801 | 740 | 810 | 740 | 801 |
| Water | 155 | 168 | 158 | 185 | 155 | 160 | 155 | 162 | 155 | 160 |

*w/c = water/( cement + silica fume + fly ash + slag).
**S1 = CSA Type 10, S2, S3, S4, S5 = CSA Type 50.
***ASTM C109.

TABLE 2
Experimental Results

| System | w/c | Cure (Days) | $\rho_{pw}$ ($\Omega$·m) | $\rho_m$ ($\Omega$·m) | $\frac{\rho_{pw}}{\rho_m}$ | $D_m$ x10$^{10}$ (m$^2$ s$^{-1}$) | $D_o \cdot \frac{\rho_{pw}}{\rho_m}$ x10$^{12}$ (m$^2$ s$^{-1}$) | $D_A \cdot \frac{\rho_{pw}}{\rho_m}$ x10$^{10}$ (m$^2$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| S1 | 0.42 | 7 | 28.98 | 0.18 | 0.0063 | 4.2 | 7.1 | 3.3 |
| | 0.42 | 28 | 43.89 | 0.14 | 0.0033 | 1.8 | 3.6 | 1.7 |
| | 0.60 | 7 | 19.11 | 0.23 | 0.0120 | 5.8 | 13 | 6.3 |
| | 0.60 | 28 | 35.30 | 0.19 | 0.0052 | 2.7 | 5.7 | 2.7 |
| S2 | 0.42 | 7 | 69.90 | 0.26 | 0.0037 | 2.1 | 4.0 | 3.6 |
| | 0.42 | 28 | 351.1 | 0.28 | 0.0008 | 1.1 | 0.9 | 0.8 |
| | 0.60 | 7 | 63.54 | 0.27 | 0.0042 | 5.2 | 4.7 | 4.3 |
| | 0.60 | 28 | 359.6 | 0.35 | 0.0010 | 3.3 | 1.0 | 1.0 |
| S3 | 0.42 | 7 | 48.65 | 0.31 | 0.0063 | 2.5 | 7.0 | 2.4 |
| | 0.42 | 28 | 184.9 | 0.51 | 0.0028 | 0.6 | 3.1 | 1.1 |
| | 0.60 | 7 | 28.55 | 0.36 | 0.0127 | 4.9 | 14 | 4.9 |
| | 0.60 | 28 | 155.7 | 0.47 | 0.0030 | 1.6 | 3.4 | 1.2 |
| S4 | 0.42 | 7 | 22.30 | 0.17 | 0.0077 | 1.5 | 8.4 | 0.7 |
| | 0.42 | 28 | 128.2 | 0.23 | 0.0018 | 0.5 | 2.0 | 0.2 |
| | 0.60 | 7 | 11.28 | 0.21 | 0.0183 | 1.1 | 20 | 1.6 |
| | 0.60 | 28 | 77.07 | 0.27 | 0.0035 | 0.6 | 3.8 | 0.3 |
| S5 | 0.42 | 7 | 56.33 | 0.33 | 0.0058 | 2.0 | 6.4 | 2.6 |
| | 0.42 | 28 | 219.1 | 0.42 | 0.0019 | 0.5 | 2.1 | 0.9 |
| | 0.60 | 7 | 45.59 | 0.53 | 0.0116 | 5.3 | 13 | 5.2 |
| | 0.60 | 28 | 288.0 | 0.50 | 0.0018 | 2.8 | 0.3 | 0.8 |

$D_A$ values from Table 3. $D_o$ value of 0.11x10$^{-8}$ m$^2$ s$^{-1}$ from Ref. (13).

## Results and Discussion

Values for $\rho_{pw}$, $\rho_m$, $\rho_{pw}/\rho_m$, and $D_m$ have been summarized in Table 2. The data confirms the marked influence of lower w/c ratios, longer curing times, and the incorporation of supplementary cementitious materials in reducing diffusivities. Table 2 also summarizes the diffusivities calculated using Eq. [8] with $D_o$ set at 0.11x10$^{-8}$ (m$^2$ s$^{-1}$) (13). In all cases, the diffusivities calculated using $D_o$ substantially underestimate $D_m$. Therefore, the approximation of $D_{pw}$ by $D_o$ is not valid. Furthermore, it appears that $D_{pw}$ is system specific; therefore, $D_{pw}$ depends on the cement/pozzolan composition. To this end, $D_m$ was plotted against $\rho_{pw}/\rho_m$ as indicated in Eq. [8]. The slopes of these plots represent the molecular diffusivity of propan-2-ol into the respective porewaters. Figure 1 is an example plot for S1. The data can be represented by the indicated solid least squares line. All other systems exhibited similar behavior. The slopes have been summarized as $D_A$ in Table 3. Clearly, $D_A$ is not equal to an ubiquitous $D_o$. Included in Table 2 are the diffusivities calculated using Eq. [8] with $D_o$ replaced by $D_A$ from Table 3. There is good agreement with the experimental $D_m$.

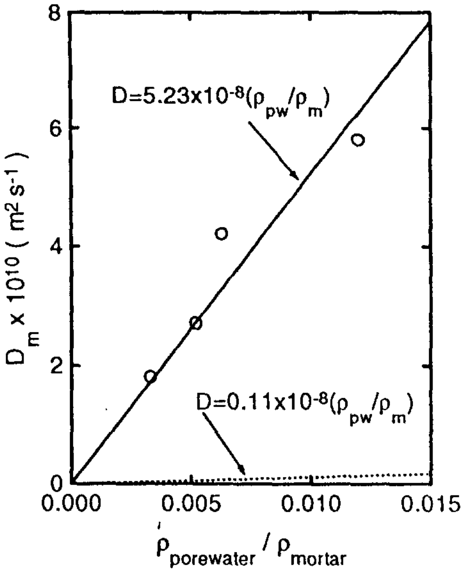

FIG. 1.
Experimental results for S1. The experimental data is well represented by the indicated solid least squares line The broken line is Eq.[8] with $D_o$.

## Conclusions

- The application of Eq.[1] appears to be valid, at least to a first approximation, for the calculation of diffusivities provided there is a suitable selection of $D_{pw}$.
- $D_{pw}$ depends mainly on the presence of supplementary cementitious materials and less on w/c and the length of hydration.

TABLE 3
Linear Fit for the Data

| System | $D_m = D_A \cdot \frac{\rho_{pw}}{\rho_m}$ |
|---|---|
| | $D_A$ ($10^8$ $m^2$ $s^{-1}$) |
| S1 | 5.23 |
| S2 | 10.2 |
| S3 | 3.84 |
| S4 | 0.87 |
| S5 | 4.52 |

## References

1. G.E. Archie, The Electrical Resistivity Log as an Aid in Determining Some Reservoir Characteristics, Transactions of AIME Journal **146**, 54-62 (1941).
2. B. MacMullin and G.A. Muccini, Characteristics of Porous Beds and Structures, AIChE Journal **2**, 393-403 (1956).
3. W.F. Brace, Permeability from Resistivity and Pore Shape, Journal of Geophysical Research **82**, 3343-3349 (1977).
4. A.Atkinson and A.K. Nickerson, The Diffusion of Ions Through Water-Saturated Cement, Journal of Materials Science **19**, 3068-3078 (1984).
5. N.R. Buenfeld and J.B. Newman, Examination of Three Methods for Studying Ion Diffusion in Cement Pastes, Mortars and Concrete, Materials and Structures **20**, 3-10 (1987).
6. E.J. Garboczi, Permeability, Diffusivity and Microstructural Parameters: A Critical Review, Cement and Concrete Research **20**, 591-601 (1990).
7. A.A. Kyi and B. Batchelor, An Electrical Conductivity Method for Measuring the Effects of Additives on Effective Diffusivities in Portland Cement Pastes, Cement and Concrete Research **24**, 752-764 (1994).
8. G.G. Taffinder and B. Batchelor, Measurement of Effective Diffusivities in Solidified Wastes, Journal of Environmental Engineering **119**, 17-33 (1993).
9. P.E. Streicher and M.G. Alexander, A Chloride Conduction Test for Concrete, Cement and Concrete Research **25**, 1284-1294 (1995).
10. P. Gu, P. Xie, J.J. Beaudoin and R. Brousseau, A.C. Impedance Spectroscopy I: A New Equivalent Circuit Model for Hydrated Portland Cement Paste, Cement and Concrete Research **22**, 833-840 (1992).
11. R.F. Feldman, Diffusion Measurements in Cement Paste by Water Replacement using Propan-2-ol, Cement and Concrete Research **17**, 602-612 (1987).
12. R.F. Feldman, Effect of Prdrying on Rate of Water Replacement from Cement Paste by Propan-2-ol, Il Cemento **85**, 193-202 (1988).
13. The Handbook of Chemistry and Physics 71st Edition, David R. Lide, Editor, CRC Press, Boca Raton, p. 6-152 (1990).