Estimating the electrical conductivity of cement paste pore solutions from OH⁻, K⁺ and Na⁺ concentrations

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Abstract

A proposed method for estimating the electrical conductivity of cement paste pore solution at 25 °C is based on the concentrations of OH⁻, K⁺ and Na⁺. The approach uses an equation that is a function of the solution ionic strength, and requires a single coefficient for each ionic species. To test the method, the conductivity of solutions containing mixtures of potassium hydroxide and sodium hydroxide with molar ratios of 4:1, 2:1 and 1:1, and having ionic strengths varying from 0.15 to 2.00 mol/l were measured in the laboratory and compared to predicted values. The proposed equation predicts the conductivity of the solutions to within 8% over the concentration range investigated. By comparison, the dilute electrolyte assumption that conductivity is linearly proportional to concentration is in error by 36% at 1 mol/l and in error by 55% at 2 mol/l. The significance and utility of the proposed equation is discussed in the context of predicting ionic transport in cement-based systems.
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1. Introduction

Recent studies of multicomponent diffusive transport in porous materials indicate that the formation factor and porosity are the only material parameters required to fully characterize diffusive ionic transport in a nonreactive porous solid, regardless of the number of ionic species present [1–4]. The formation factor Υ is defined as the ratio of the pore solution electrical conductivity σ_p to the bulk (solid and pore solution) conductivity σ_b [5]:

$$\Upsilon = \frac{\sigma_p}{\sigma_b} \tag{1}$$

While it has been shown that the bulk conductivity can be measured using readily available laboratory equipment [6], determining the pore solution conductivity is more difficult.

The direct method for determining the electrical conductivity of the pore solution uses pore solution expression [7] to obtain a sample of the pore solution. The sample can then be analyzed using a conductivity meter. Unfortunately, the

sample obtained from moderate and low water to cementitious ratio specimens older than 56 days may be exceedingly small, making it difficult to construct a conductivity cell for such a sample. Alternatively, quantitative methods such as ion chromatography can be used to determine the concentration of the ionic species present. Since the conductivity of concentrated electrolytes is not linearly proportional to concentration [8], the conductivity of the cement paste pore solution would have to be estimated from an equation that accounted for the nonlinearity.

In some cases, pore expression is either impractical (virtually no expressed fluid) or impossible (limited concrete accessibility). Under these circumstances, the pore solution conductivity can be estimated from the ion concentration predicted from a model. For example, the model of Taylor [9] predicts the concentration of various ionic species in the pore solution from the cement composition and the degree of hydration, and has been shown to be reasonably accurate [10]. From the estimated concentrations, one could, as in the direct method, estimate the pore solution conductivity using the proposed equation.

Presented herein is an equation for estimating the electrical conductivity of a well-hydrated cement paste pore

solution. The equation is a function of the ionic strength and requires an empirical coefficient for each ionic species. The model is intentionally simplified to include only a single parameter for each ionic species; interaction terms in the model are excluded. To test the model, laboratory measurements of the electrical conductivity of potassium hydroxide and sodium hydroxide mixtures are compared to the predicted values.

2. Conductivity

Calculated electrolyte conductivity σ_{calc} can be expressed as a weighted sum of the equivalent conductivity λ_i of each ionic species [11]:

$$\sigma_{calc} = \sum_i z_i c_i \lambda_i \qquad (2)$$

The quantities z_i and c_i are the species valence and molar concentration, respectively. At low concentrations ($c \ll 0.01$ mol/l), the equivalent conductivity is practically constant and the solution conductivity is proportional to concentration. At higher concentrations, the equivalent conductivity decreases noticeably with increasing concentration. The OH^- concentration in pore solution is typically in the range 0.1–1.0 mol/l [12]. Therefore, accurately estimating pore solution conductivity requires accurately estimating the equivalent conductance concentration dependence.

While a number of highly accurate equations containing numerous coefficients exist for estimating the equivalent conductivity [8], a new single-parameter model is proposed for its simplicity, with the objective that the equation should be accurate to within 10% for typical pore solutions. Previous work [6] indicates that the uncertainty in estimating the bulk conductivity σ_b can be less than a few percent. From Eq. (1), an uncertainty of 10% in pore solution conductivity σ_p would translate into a similar uncertainty in the calculated formation factor Υ. Such a level of uncertainty would be difficult to improve upon using existing diffusion cell experiments.

The concentration dependence of the individual equivalent conductivities at 25 °C is approximated using the following single-parameter model that characterizes low concentration data well, and remains reasonably accurate at concentrations near 1 mol/l:

$$\lambda_i = \frac{\lambda_i^\circ}{1 + G_i I_M^{1/2}} \qquad (3)$$

The quantity λ° is the equivalent conductivity of an ionic species at infinite dilution, and is only a function of temperature; the values of λ° for Na^+, K^+, OH^-, Ca^{2+}, Cl^- and SO_4^{2-} at 25 °C can be found in the literature [8], and are shown in Table 1. The quantity I_M is the ionic strength (molar basis) and has the following definition [11]:

$$I_M = \frac{1}{2} \sum_i z_i^2 c_i \qquad (4)$$

Table 1
Equivalent conductivity at infinite dilution λ° and conductivity coefficients G at 25 °C

Species	$z\lambda^\circ$ (cm² S/mol)	G (mol/l)$^{-1/2}$
OH^-	198.0	0.353
K^+	73.5	0.548
Na^+	50.1	0.733
Cl^-	76.4	0.548
Ca^{2+}	59.0	0.771
SO_4^{2-}	79.0	0.877

Reference data typically report the product $z\lambda^\circ$ (z: species valence).

The empirical coefficients G_i are chosen to best agree with published data for the electrical conductivity of solutions. In principle, the coefficient G_i will also depend upon temperature.

The algebraic form of Eq. (3) is based on previous work on the conductivity of electrolytes. It is known that the leading term in the correction should be proportional to $c^{1/2}$ [13]. At higher concentrations, however, this is an overcorrection. Onsager and Fuoss (OF) [14] gave additional terms that are proportional to $c \log c$ and c. Although rigorous, using the OF equation would require multiple coefficients for each species, which violates the objective of simplicity desired here. As a compromise, Eq. (3) is a modification of a relationship (for binary salts) by Walden [15] that is a function of the salt concentration and requires an empirical coefficient for each salt. The extension to electrolytes containing many ionic species was achieved by changing the salt concentration to the molar ionic strength I_M. This change is motivated by similar relationships for estimating the activity of ionic species in concentrated electrolytes [8].

Based on Eq. (2), the most significant contributor to the pore solution conductivity of a cementitious system is the OH^- ion; its equivalent conductivity is a factor of two greater than that for sodium or potassium (see Table 1) and it is present at the highest concentration. Because the equivalent conductivity of the remaining ionic species in the pore solution of a well hydrated specimen are all of the same magnitude, the Na^+ and the K^+ should be secondary contributors due to their relatively high concentrations after 1 day [12].

Two other species to consider are calcium and sulfate. Due to high alkalinity, the equilibrium calcium concentration in pore solution is typically on the order of 0.001 mol/l [10]. The corresponding calcium contribution to the overall conductivity (assuming $I_M = 1.0$ mol/l and $\sigma_p = 20$ S/m) is on the order of 0.003 S/m and so can be neglected. Using the pore solution speciation model by Taylor [9], the concentration of sulfate can be roughly approximated by the potassium and sodium concentrations:

$$c_{SO_4^{2-}} \approx \alpha (c_{K^+} + c_{Na^+})^2 \qquad (5)$$

$\alpha = 0.06$ l/mol. Using this approximation, sulfate will make the greatest relative contribution when the sum of the potassium concentration and the sodium concentration

approaches 1 mol/l (it is unlikely they will be significantly greater). The corresponding sulfate contribution to the pore solution conductivity is approximately 0.25 S/m or <2% of the anticipated total conductivity.

Therefore, the electrical conductivity of most pore solutions of well-hydrated cement-based materials could be accurately estimated from the contribution of the Na^+, K^+ and OH^- ions alone. In those cases where other species are present at significant concentrations, additional coefficients are provided in Table 1, but are not part of the validation experiment.

3. Empirical coefficients

Comparisons among various solutions can be simplified using the solution equivalent conductivity Λ. The solution equivalent conductivity Λ of a 1:1 binary solute solution can be related to the solution conductivity σ:

$$\Lambda = \frac{\sigma}{c} \quad (6)$$

where c is solute concentration. The solution equivalent conductivity can also be related to the equivalent conductivity of each ionic species in the solute [11]:

$$\Lambda = \sum_i \lambda_i \quad (7)$$

Since the value of λ° varies by only a factor of two for most ionic species, the equivalent conductivity Λ of many common binary salt solutions can fit conveniently on a single graph.

The empirical coefficients G_i in Eq. (3) have been determined previously for use in a multicomponent diffusive transport equation [16], and the values for Na^+, K^+ and OH^- are shown in Table 1. The coefficients were determined using data for binary salts given in Harned and Owen [13]; the Harned and Owen data were chosen over those in the *CRC Handbook of Chemistry and Physics* [17] because the Harned and Owen data appeared to have less variability. Unfortunately, the Harned and Owen data ranged from 0.001 to 0.1 mol/l. Therefore, estimates at higher concentrations must rely on Eq. (3) to capture the concentration dependence of λ at high concentrations.

The coefficients G_i were chosen in a self-consistent manner for a number of ionic species simultaneously, e.g., if the coefficient for Na^+ was determined from NaCl and the coefficient for I^- was determined from KI, the coefficients were adjusted, if needed, for the model to also be reasonably accurate for NaI. As such, the values were chosen to achieve a sufficient level of accuracy among all the possible binary salts (seven cations and eight anions in the complete database) for which there were published data.

Fig. 1 shows the resulting calculations from Eq. (3) (solid curves), along with the data from Harned and Owen (filled symbols); data for NaCl and KCl are shown in Fig. 1(a) and data for a strong acid and two bases are shown in Fig. 1(b).
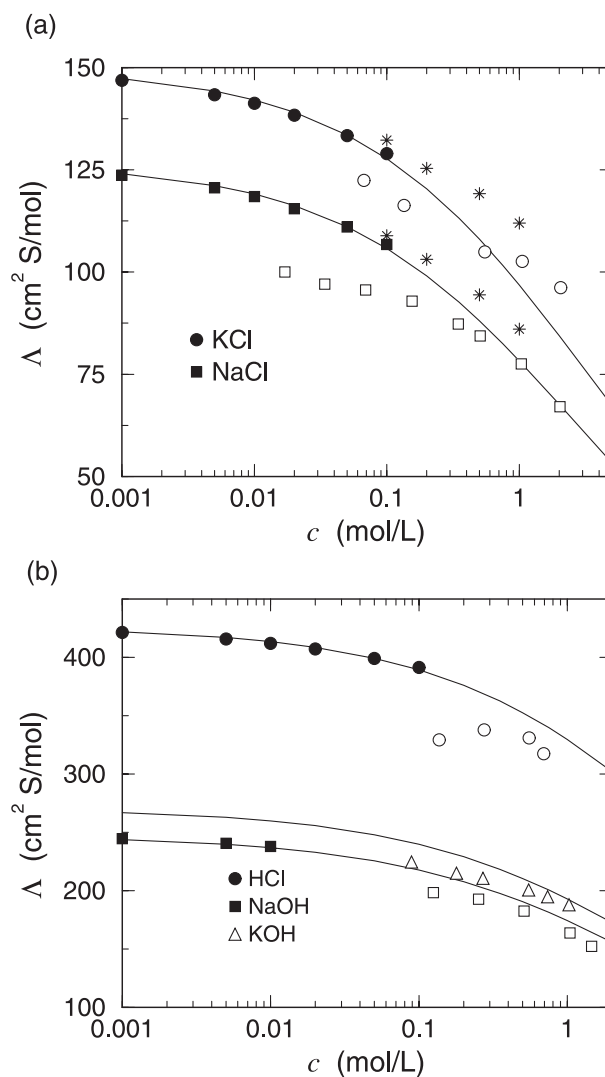

Fig. 1. Estimated equivalent conductivity Λ of various binary solutes as a function of molar ionic strength I_M: (a) NaCl and KCl; (b) strong acids and bases. The filled symbols are data used to determine the individual G coefficients. The open symbols are from the CRC Handbook [17]. The stars are data measured in the laboratory. Solid curves are from Eq. (3).

Also appearing in the figure are data from the *CRC Handbook* (open symbols). Note that for a number of the salts, the data from the *CRC Handbook* do not agree with the Harned and Owen data at 0.1 mol/l. To resolve this discrepancy, measurements of solution conductivity (using the experimental methods discussed subsequently) were also performed and shown as 'stars' in the figure. These laboratory measurements confirm the reliability of the Harned and Owen data, and the ability of Eq. (3) to capture the equivalent conductivity concentration dependence in concentrated electrolytes.

4. Experiment

For this experimental program, the solutions chosen to represent pore solution are composed solely of potassium

hydroxide and sodium hydroxide. The molar ratios of potassium to sodium studied were 4:1, 2:1 and 1:1, as these appear to represent the vast majority of possible pore solution compositions beyond 28 days [18–21]. The potassium hydroxide concentration was varied up to 1 mol/l and the sodium hydroxide concentration was adjusted according to the predetermined molar ratio.

The solution conductivities were determined using a glass conductivity cell containing platinum electrodes. The conductivity cell was cylindrical, with an inside diameter of approximately 25 mm, and had an electrode separation of approximately 320 mm. The cell constant (the effective ratio between the apparatus length to area) was 5.0578 ± 0.0030 cm^{-1} and was determined from 0.01 and 0.10 mol/l standard potassium chloride solutions [22]. The uncertainty reported in the cell constant is the difference between the two calculated cell constants for the two standard solutions; the individual precisions were each less than this reported uncertainty.

All measurements were performed in a walk-in environmental chamber that was maintained at 25.0 ± 0.4 °C; the reported uncertainty is the standard deviation of the temperature control hysteresis. The pore solution was allowed to thermally equilibrate overnight in a volumetric flask. The conductivity was determined using a commercial impedance spectrometer. Measurements were repeated until the calculated conductivity changed by <0.2% over 1 h; because of safety concerns due to the caustic nature of the solutions, the cell was filled outside the chamber, resulting in a small thermal measurement drift after returning the cell to the environmental chamber. Given the uncertainty in the cell constant, a 0.2% uncertainty would characterize the uncertainty in the reported conductivity measurements.

5. Results

The measured solution conductivities σ_{exp} are shown in Table 2, along with the estimated conductivities σ_{calc} calcu-
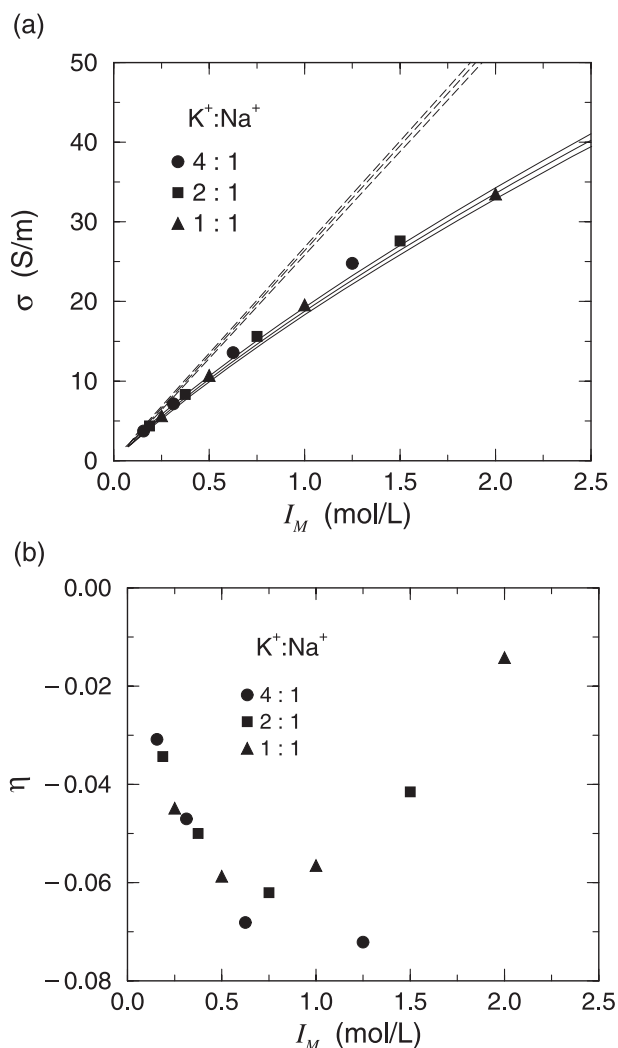
Fig. 2. Measured and predicted solution conductivity σ as a function of molar ionic strength I_M: (a) comparison among measured conductivity (filled symbols), estimated conductivity (solid curve) from Eq. (3) and estimated conductivity (dashed curve) from Eq. (9); and (b) coefficient of variation η between estimated conductivity and measured conductivity.

lated from Eq. (2). Within the table, the results are divided among the three molar ratios. Also shown in Table 2 are the coefficients of variation η:

$$\eta = \frac{\sigma_{calc} - \sigma_{exp}}{\sigma_{exp}} \tag{8}$$

Because the coefficients G_i were not optimized for these three ionic species, all the estimated values lie below the measured values. Optimizing the G coefficients for only these three ionic species may not be warranted because the empirical relation in Eq. (3) is a coarse approximation. Moreover, the present error is already <8% over the entire concentration range.

The performance of Eq. (2) is relatively uniform over the range of ionic strengths investigated. The data from Table 2 are plotted in Fig. 2(a) (filled symbols) as a function of the solution ionic strength I_M. The predictions from Eq. (2) are

Table 2
Measured solution conductivities σ_{exp}, calculated solution conductivities σ_{calc} and the coefficient of variation η

[K$^+$] (mol/l)	[Na$^+$] (mol/l)	σ_{exp} (S/m)	σ_{calc} (S/m)	η
0.125	0.03125	3.707	3.591	−0.031
0.250	0.06250	7.133	6.796	−0.047
0.500	0.12500	13.56	12.64	−0.068
1.000	0.25000	24.78	22.99	−0.072
0.125	0.0625	4.346	4.201	−0.033
0.250	0.1250	8.330	7.913	−0.050
0.500	0.2500	15.60	14.63	−0.062
1.000	0.5000	27.61	26.45	−0.042
0.125	0.125	5.642	5.387	−0.045
0.250	0.250	10.70	10.07	−0.059
0.500	0.500	19.57	18.45	−0.057
1.000	1.000	33.50	33.02	−0.014

The uncertainty in σ_{exp} is approximately 0.2% (see text).

shown as solid curves, one for each of the potassium to sodium ratios. The three curves are nearly collinear, as are the measured values.

For comparison purposes, also shown in Fig. 2(a) are estimates that neglect the concentration dependence of the equivalent conductivity:

$$\lambda_i = \overset{\circ}{\lambda}_i \tag{9}$$

This idealized approximation is mathematically equivalent to setting all the G_i coefficients to zero in Eq. (3). These approximations are shown as dashed curves in Fig. 2(a), one curve for each of the three potassium to sodium ratios. At an ionic strength of 1.0 mol/l, the idealized approximation differs by 36% from the experimental data and differs by 55% at 2.0 mol/l.

The graph of the coefficient of variation η plotted in Fig. 2(b) shows that the relative error is fairly constant over the entire range of ionic strengths. This suggests that small extrapolations of either the ratios or concentrations beyond the parameter space investigated here should not introduce extensive uncertainty.

6. Discussion

Estimating the pore solution conductivity is significant to transport models that distinguish between the chemical and the physical behavior. Ionic transport through a porous media is hindered by both the solid microstructure (physical effects) and ion–ion interactions (chemical effects). The physical effects can be uniquely characterized by the formation factor (or tortuosity) and the porosity [3], which are experimentally determined material coefficients. Because macroscopic bulk concrete conductivity measurements can be performed using readily available equipment [6], estimating the pore solution conductivity is vital to estimating the formation factor.

In addition to the material parameters, a transport equation for concentrated electrolytes must also estimate the ionic mobility because an internal diffusion potential will arise due to the differences in self-diffusion coefficients [23]. The internal diffusion potential creates the electrical field necessary to ensure zero total electrical current. The coefficient of proportionality between an electric field and the drift velocity is the mobility, and is proportional to the species equivalent conductivity. Therefore, the magnitude of the mobility determines the resulting diffusion potential and is directly related to the pore solution conductivity.

Furthermore, migration (or driven diffusion) tests that use an external electric field to transport ionic species through a porous material are actually determining the bulk ionic mobility. If the objective is to predict future behavior of concrete exposed to the same external electric field and chemical environment, the observed experimental behavior is indicative of future behavior. By contrast, if the migration

test is used to predict future behavior in the absence of an external electric field, the objective of the experiment must be considered carefully.

The response of the migration test is a measure of both the physical microstructure and the concentration dependence of the mobility. Therefore, future predicted behavior based on a transport model that considers chemical and physical effects separately will require a method for extracting the true formation factor from the migration test by accounting for the chemical effects in the test. In the migration experiment, the bulk drift velocity (experimental observation) $\vec{v}$ will be proportional to the external electric field $\vec{E}$:

$$\vec{v}_i = \frac{u_i}{\Upsilon}\vec{E} \tag{10}$$

The quantity u_i is the mobility of the ion within the pore solution (it incorporates the chemical effects) and the formation factor Υ represents the physical microstructural barrier. The concentration dependence of the mobility ($Fu_i = \lambda_i$, F = Faraday constant) from Eq. (3) can be incorporated in the formation factor estimation:

$$\Upsilon = \left(\frac{\overset{\circ}{\lambda}_i}{F}\frac{\vec{E}}{\vec{v}}\right)\frac{1}{1 + G_i I_M^{1/2}} \tag{11}$$

If the chemical effects of the migration test had been neglected, only the quantity within parentheses would have been attributed to the formation factor, as is typically done when estimating the diffusion coefficient from a migration test. Therefore, the true formation factor is a factor of $(1 + G_i I_M^{1/2})^{-1}$ smaller than what would otherwise be expected; a material with a smaller formation factor would present less of a physical barrier to transport. For the case of a chloride migration test in a pore solution having an ionic strength $I_M = 0.75$ (as is typical [10]), the quantity $(1 + G_{Cl^-} I_M^{1/2})^{-1} = 0.68$. Therefore, neglecting the chemical effects results in a microstructural transport coefficient that is in error by 30%.

7. Conclusion

A simple model for estimating the pore solution conductivity can be constructed using only single parameters for each ionic species. The equation proposed here is accurate to within 8% for K^+:Na^+ ratios ranging from 4:1 to 1:1 and for ionic strengths as high as 2 mol/l. The coefficient of variation in the predicted conductivities is relatively constant over the entire range, suggesting that minor extrapolations should not lead to excessive errors. In addition, the chemical and physical effects during a migration test can be separated using the equation, allowing one to extract a true microstructural transport coefficient.

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