

# 48 RECENT DEVELOPMENTS IN THE MEASUREMENT OF TRANSPORT PROPERTIES IN CEMENT-BASED MATERIALS

J.D. SHANE, J-H. HWANG, D. SOHN, T.O. MASON,  
H.M. JENNINGS

Northwestern University, Evanston, IL, USA

E.J. GARBOCZI

National Institute of Standards and Technology, Gaithersburg,  
MD, USA

## Abstract

Fundamental to understanding and controlling the durability of cement-based systems is the relationship between microstructure and transport properties, particularly ionic diffusivity and hydraulic permeability. While our understanding of cement paste microstructure and interfacial zone contributions has improved considerably over the past few years, largely due to advances in nondestructive methods and modelling, there is a demonstrated need for improved laboratory and field techniques for determining diffusivity and permeability. This work provides an overview of existing and emerging techniques for measuring or predicting the transport properties of cement-based materials. Although a major focus will be impedance spectroscopy, alternative methods will also be considered, including solvent exchange kinetics, mercury intrusion porosimetry, nuclear magnetic resonance, microstructure-based modelling, and the more conventional permeameter and rapid chloride penetration techniques. The applicability of the Nernst-Einstein (diffusivity) and Katz-Thompson (permeability) equations to cement-based materials will be considered. Ramifications for rapid testing and field testing of concrete will also be discussed.

Keywords: Diffusivity, impedance spectroscopy, mercury intrusion porosimetry, modelling, nuclear magnetic resonance, permeability, solvent exchange, transport properties.

## 1 Introduction

Establishing the relationship between microstructure and transport properties is a critical step in predicting the durability of cement-based materials. Unfortunately, the conventional methods used to measure transport properties in cement-based materials, particularly ionic diffusivity and hydraulic permeability, are often time-consuming, labor-intensive, and inconsistent. Some typical measurements include ponding/profiling diffusivity, divided cell diffusivity, differential pressure permeability, and the rapid chloride penetrability test. Unfortunately, the usefulness of these methods is somewhat limited for reasons discussed subsequently.

Recently, several new techniques have emerged that measure or predict transport properties in cement-based materials. These novel techniques include impedance spectroscopy, solvent exchange kinetics, nuclear magnetic resonance, and microstructure-

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based modelling. In addition to providing fundamental microstructure/transport-property relationships, the information can be used to predict important durability-related parameters using the Nernst-Einstein (diffusivity) and the Katz-Thompson (permeability) equations.

## 2 Conventional Techniques

### 2.1 Diffusion Measurements

#### 2.1.1 Ponding/Profiling

A common way to measure the diffusion of a species into concrete is by direct exposure. For instance, the rate of ingress of chloride and sulfate ions can be determined from cores taken from structures exposed to aggressive environments. This exposure is simulated in the laboratory with ponding experiments. In these tests, specimens are immersed in a solution (e.g., 1 molar NaCl) for a specified length of time. They are then removed from the solution and the concentration of the diffusant is determined as a function of depth within the sample. The diffusion coefficient can be found by fitting the concentration profile with a modified version of Fick's second law.

When the total diffusant content is determined for profiles, the diffusion coefficient includes contributions from diffusion as well as reaction with the microstructure, which is known as binding. When binding is not accounted for, the coefficient calculated is known as the apparent diffusion coefficient ( $D_{app}$ ).

The major limitation of ponding/profiling testing is the time required to make measurements, which, for many concretes, is on the order of months. For example, the AASHTO T-259 standard ponding test requires a 90 day exposure [1]. This restricts the use of ponding/profiling tests to the measurement of mature pastes, concretes, and mortars.

#### 2.1.2 Divided Diffusion Cell

An alternative to the ponding test is known as the divided diffusion cell test. This method involves placing a disk-shaped specimen between two ionic solutions, one of which is a reservoir, the other a sink. This is shown schematically in Figure 1. Often chloride is chosen as the diffusing species because of its importance to the durability of steel-reinforced structures. Hydroxide solutions are normally used in both compartments to minimize leaching of  $\text{Ca}(\text{OH})_2$ . Chloride concentration is monitored with time in both compartments, and is maintained at a constant level in the reservoir, while the increase in concentration in the sink is recorded. When steady state flow is reached, the rate of change of concentration in the downstream side is used to calculate a diffusion coefficient using Eq. (1). Because Eq. (1) requires steady state diffusion, the effect of binding is not a factor and an effective diffusion coefficient ( $D_{eff}$  in  $\text{cm}^2/\text{s}$ ) is calculated.

$$D_{eff} = \frac{Jl}{(C_A - C_B)} \quad (1)$$

where  $J$  is the unidirectional flux of the species ( $\text{mol}/\text{cm}^2\text{s}$ ),  $C_A$  and  $C_B$  are the concentration of the diffusant in cells  $A$  and  $B$  ( $\text{mol}/\text{cm}^3$ ), respectively, and  $l$  is the sample thickness (cm).

The major drawback of the divided cell test is that can take weeks to achieve steady state flow. During the period of the test, the microstructure is continually changing from

hydration and leaching of  $\text{Ca}(\text{OH})_2$ . This makes it virtually impossible to test samples with a low degree of hydration.

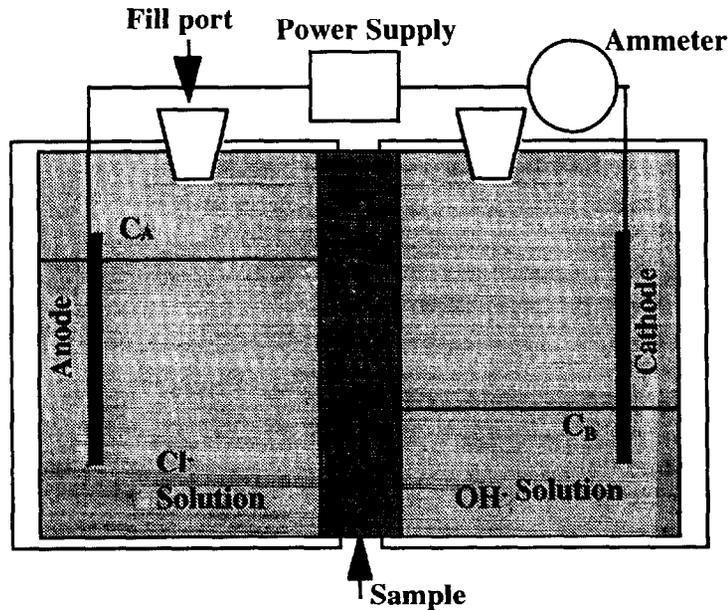


Fig. 1. Schematic of a diffusion cell used for the divided diffusion cell, the rapid chloride penetrability, and Norwegian tests. Note for the divided diffusion cell test, the electrodes, power supply, and ammeter are not present, and for the Norwegian test, the ammeter is not required.

### 2.1.3 Rapid Chloride Penetrability\* Test

Because the time involved in long term diffusion measurements is undesirable, a faster test was developed which makes use of a strong electric field which drives ions through the concrete. This rapid chloride penetrability test, as developed by Whiting [2], has been adopted by both the AASHTO [3] and ASTM [4] as a standard test method. The test itself consists of monitoring the amount of charge passed through a cylindrical sample during a 6 hour test period. A d.c. potential difference of 60 volts is maintained across the sample, one end of which is immersed in a NaCl solution (anode), while the other end is immersed in a NaOH solution (cathode). The apparatus is shown schematically in Figure 1. The total charge passed is then related to a penetrability, which gives a qualitative measure of the durability.

The current passing through the sample can result in a temperature increase from Joule heating. This heating is especially a concern in permeable samples that pass large amounts of current, because a rise in temperature can have a profound effect on the diffusion coefficient. Moreover, Feldman *et al.* concluded that the rapid chloride penetrability test induced changes in pore structure and resistivity of the concrete specimens [5]. We have recently demonstrated that high fields can affect the microstructure [6]. Therefore, because the microstructure of the specimen is being changed, it is impossible to know if a representative specimen is being tested.

The resistance of cement-based materials is strongly dependent on the type and concentration of the ions in the pore fluid. The rapid chloride penetrability test does not discriminate between the ions that carry charge. Therefore, when comparing the results

\* Commonly referred to as "permeability," however we prefer "penetrability" or "ion migration" and reserve permeability for fluid flow situations

from two concretes with different pore solution chemistries, the difference in charge passed cannot be assumed to be purely a result of microstructural differences.

Nonetheless, the test has become a standard adapted by both the AASHTO and ASTM and has quickly become a popular tool used by many researchers to characterize the relative durability of concrete.

#### 2.1.4 Modified Rapid Chloride Penetrability Test (Norwegian Test)

The Norwegian test, described by Detwiler *et al.*, was designed to correct some of the shortcomings of the rapid chloride penetrability test [7]. There are two major modifications. First, the applied potential is lowered from 60 to 12 Volts. The lower voltage decreases the rate of charge passed, thus reducing Joule heating. Unfortunately, this increases the time required to perform the test. Second, instead of current passed, the Norwegian test measures the concentration of chloride ions in solution directly. This eliminates the sensitivity of the test to changes in pore solution chemistry. Unlike the rapid chloride penetrability test, the Norwegian test allows a diffusion coefficient to be calculated.

From a practical point of view, there are several limitations to using the Norwegian test. For instance, the duration of the test is both longer and less predictable than the rapid chloride penetrability test. Experiments can take anywhere from days to weeks, depending on the quality of the concrete. Also, to determine that steady state flow has been reached, the apparatus requires constant monitoring. Measurement of the chloride concentration in solution presents its own set of problems, including the need for laborious titrations or expensive analytical equipment.

## 2.2 Permeability Measurements

Permeability of concrete plays an important role in durability because it controls the movement and the rate of entry of water, which may contain aggressive chemicals. Banthia *et al.* called permeability, "...by far the most important property of concrete for determining its durability." [8]

Fluid flow through cement-based materials is dictated by the porous nature of the microstructure. As cement hydrates, capillary porosity is being consumed while gel porosity increases, and the permeability drops by approximately 10-12 orders of magnitude [9]. Powers *et al.* showed that the permeability in neat pastes was influenced by the overall volume of capillary porosity [10, 11]. Later, Goto *et al.* showed that the volume, distribution, connectedness, and shape of the pores control the fluid flow through the microstructure [12].

The measurement of permeability relies on Darcy's law, which states that the coefficient of permeability is proportional to the flow rate per unit area and unit pressure gradient. When studying the permeability of cement-based materials, water is by far the most commonly used fluid. Unfortunately, water will react with any unhydrated cement grains, thus changing the pore structure during the test. Since it can take several weeks to reach equilibrium flow, data for younger samples is questionable.

The general design for a device to measure permeability is relatively straightforward. A fluid under pressure is applied to one surface of a specimen disk, while the other surface is maintained at a lower pressure. The fluid flow rate on the low pressure side is monitored and, knowing the sample geometry and pressure head, a coefficient of permeability can be calculated. A simple device to measure permeability was proposed by Ludirdja *et al.*, where the flow rate induced by a column of water was monitored using a burette [13]. This had the advantage of being a low-cost, easy-to-build apparatus. Unfortunately, the design was limited by low fluid pressures and the imprecise nature of the flow rate measurements. Mills and Hearn [14], and later Hooton [15], have designed and used more advanced devices to measure the permeability. Here, the applied pressure

from a weighted mechanical arm provides pressures much higher than a column of water. The flow rates are monitored using LVDT's (linear variable displacement transducers) interfaced to a personal computer. This has the advantage of a much higher sensitivity in flow rate detection, as well as continuous collection of data. The limitation of this design is the relatively high cost of construction. Regardless of design, fluid-tight sealing of the cement/concrete specimen to the apparatus can be problematic.

### 3 Recent Developments

#### 3.1 Impedance Spectroscopy

Cement paste relies on the pore solution to carry electrical charge, thus the pore structure plays an important role in governing the resistance to the flow of charge. The most important factors are the capillary porosity, concentration and types of ions in the pore fluid, and the continuity of the pore network. The effect of these factors can be easily probed with various electrical measurements, particularly impedance spectroscopy.

Impedance spectroscopy (IS) is an experimental technique which is becoming increasingly prevalent in the study of materials [16]. The technique involves applying an a.c. excitation signal to the specimen of interest and recording the time-varying response. This is repeated over a large range of frequencies, and the gain and phase angle differences are monitored. This information is often represented graphically by plotting on a complex plane the negative of the imaginary part of the impedance versus the real part of the impedance. This type of representation, known as a Nyquist plot, has the advantage of representing different responses as distinct semi-circular arcs, as is shown in Figure 2. Several parameters can be determined from an analysis of IS data. The most reliable parameter obtained is the specimen resistance which is determined from the intersection of the bulk cement paste arc with the Real Impedance axis (see Fig. 2).

There are several important advantages of IS over other methods used to examine cement-based materials. First, IS is an in-situ, nondestructive technique, which, unlike many methods, does not require a dried, and therefore altered, specimen. Moreover, geometry constraints are much less severe for samples tested with IS, compared to many commonly used methods, which might allow in-field testing of concrete structures. Another useful trait of IS is the ability to test a single sample continuously, monitoring the evolution of properties over time, without the need for multiple samples.

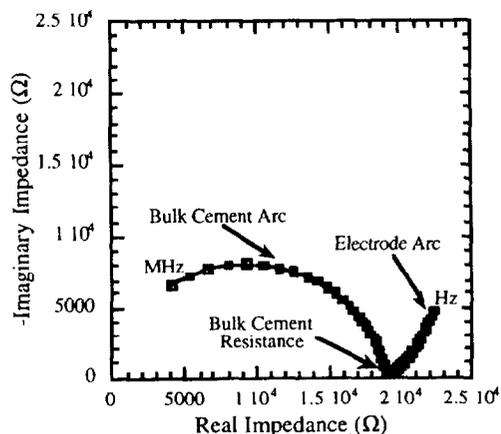


Fig. 2. Nyquist plot of water/cement = 0.4 Type I ordinary portland cement paste hydrated for approximately 24 hours. Note location of bulk cement arc, electrode arc, and the value of cement resistance, as well as the frequency values [17].

During hydration, the microstructure and pore fluid composition of cement based materials change. This change can be represented using the following relationship: [18]

$$\frac{\sigma}{\sigma_0} = \phi_{\text{cap}}\beta \quad (2)$$

Where  $\sigma$  is the overall bulk conductivity ( $\Omega\cdot\text{cm}$ )<sup>-1</sup>,  $\sigma_0$  is the pore solution conductivity ( $\Omega\cdot\text{cm}$ )<sup>-1</sup>,  $\phi_{\text{cap}}$  is the capillary porosity, and  $\beta$  is the connectivity (inverse tortuosity) of the capillary pore network.

The fraction,  $\sigma/\sigma_0$ , is often called the normalized conductivity, but is also known as the inverse formation factor, or the inverse MacMullin number. It is assumed that the current is carried by the pore fluid exclusively, and the contribution from the solids within the microstructure is negligible. The value of  $\sigma_0$  is obtained by measuring the conductivity of the pore fluid expressed from the hardened paste or estimating it based on chemical analysis of the cement powder [19].

### 3.2 Microstructure-Based Modelling

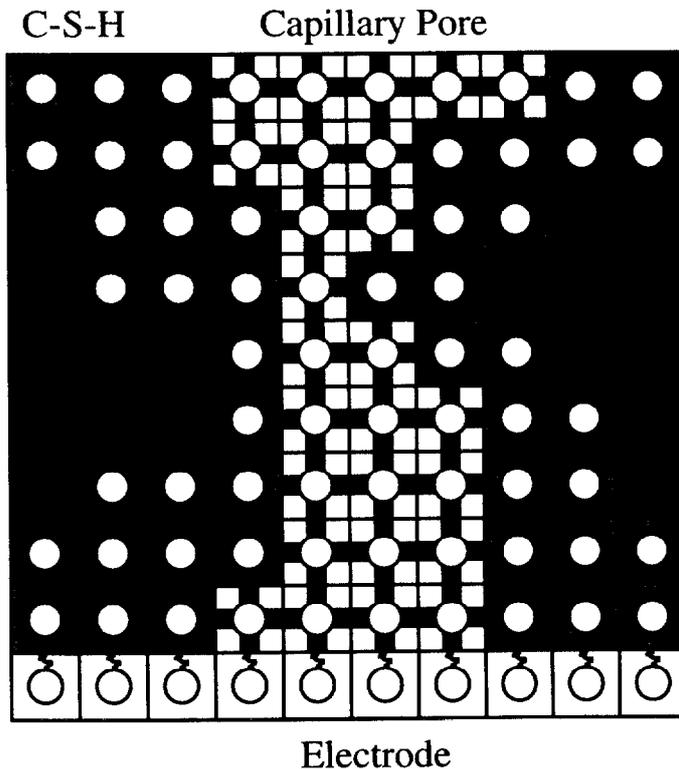
The pore structure dictates the transport properties of cement-based materials. Analysis of the influence of the pore structure, however, is often difficult as a result of the ongoing cement hydration process and the destructive nature of many testing techniques. Recently, microstructure-based modelling has been used to predict the transport properties in a number of cement-based systems.

Modelling the transport properties allows one to predict the characteristics of a particular microstructure. Output from the computer is compared to experimental data to validate the model and its underlying assumptions. The model can then contribute to the understanding of microstructure/transport property relationships by the use of computer simulations. Model parameters can be varied to assess their effects on microstructural development and, ultimately, transport properties.

An example of the use of microstructure-based models is the prediction of the diffusivity of cement paste. In this model, the 3D microstructure of the cement paste is simulated using a pixel based model. Each pixel will have an identity defining its location and composition. When water is "added", the surfaces of the cement particles are allowed to dissolve, and, following random walk algorithms, diffuse through the water. When the diffusing particles collide with another particle, there is a probability that they will react and form a reaction product, which is predominantly C-S-H gel or calcium hydroxide.

Once the microstructure is built up, specific conductivities are assigned to each pixel, forming a random conductor network, similar to Figure 3. The overall electrical conductivity is determined using a method outlined in reference [20]. When the conductivity has been determined, it can be related to diffusivity using the Nernst-Einstein relation, which equates electrical conductivity and ionic diffusivity. This will be discussed in more detail in Section 3.5.

The importance of this model, and computer simulations in general, is that once a model has been designed and verified, a large number of experimental variables can be examined. This is important, for instance, when predicting the diffusivity of cement pastes at early times. Experimentally it is difficult test young pastes owing to the rapid rate of hydration, coupled with the long time required to make the measurement. With microstructure-based modelling, however, any degree of hydration can be simulated, and properties such as diffusivity can be predicted. Agreement between model-based diffusivities/conductivities and those determined by IS is quite encouraging [19].



Unreacted  
cement  
and  $\text{Ca}(\text{OH})_2$

Fig. 3. Schematic diagram of the digital image for a random conductor network map used to compute electrical conductivity of the cement paste model. Conductances of different bonds are predetermined [20].

### 3.3 Nuclear Magnetic Resonance

Analysis of nuclear magnetic resonance (NMR) relaxation has been used with considerable success to study porous materials such as sol-gel glasses, sandstones, and borosilicate glasses. Only recently, however, has this technique been applied to cement-based materials [21]. The advantage of using NMR is that it allows the in-situ analysis of the evolving pore structure during hydration.

Although complete description of the theoretical background for this technique is beyond the scope of this text, a few basic aspects will be discussed. First, NMR analysis of cement-based materials relies on the spin-echo relaxation from protons in the free water contained in the capillary pore network. It is established that NMR relaxation rates are enhanced near a solid-liquid interface. By applying a magnetic field, and measuring the spin decay rates when the field is removed, one can determine the distribution of bulk and near-surface water. This information can then be used to calculate a pore size distribution of the cement-based material [22].

This technique also has the potential to measure effective diffusion coefficients (e.g., protons or chloride ions). In order to increase the magnitude of the magnetic field, which increases the sensitivity of the measurement, a pulsed NMR signal is used. With this method, direct information about the evolution of the mean square displacement of water molecules with time is obtained. In particular, it can be determined if classical diffusion occurs during the time frame of the NMR experiments. If this is the case, the mean-square displacements are linearly proportional with time, and the relationship  $\langle r(t)^2 \rangle = 6D_{\text{eff}} t$  holds. Here  $\langle r(t)^2 \rangle$  is the mean-square displacement,  $D_{\text{eff}}$  is the effective diffusion coefficient, and  $t$  is time. The mean-square displacements can be determined by fitting the decay of the spin echo from the specimen. The technique has been successfully employed to monitor diffusion in other porous media, but not, to date, in cement-based materials.

### 3.4 Katz-Thompson Equation

In 1986 A.J. Katz and A.H. Thompson proposed the relationship shown in Equation (3) to predict the hydraulic permeability of porous rocks using indirect measurements [23].

$$K = cd_c^2 \left( \frac{\sigma}{\sigma_o} \right) \quad (3)$$

where  $K$  is the permeability ( $m^2$ ),  $d_c$  is the critical pore diameter (m),  $\sigma$  is the electrical conductivity of the sample ( $\Omega \cdot cm$ )<sup>-1</sup>,  $\sigma_o$  is the conductivity of the pore fluid ( $\Omega \cdot cm$ )<sup>-1</sup>, and  $c$  is a constant.

To predict the permeability of a material using the Katz-Thompson equation, the critical pore diameter ( $d_c$ ) and the normalized conductivity ( $\sigma/\sigma_o$ ) must be measured. Katz and Thompson related the critical pore diameter to the inflection point in mercury intrusion curves. The physical interpretation of the critical diameter is that it is the smallest continuous pore size that percolates through the sample. The normalized conductivity is determined using electrical methods, particularly impedance spectroscopy, and is a measure of the heterogeneity of the pore network. For the electrical measurements, it is necessary that the pore structure be saturated with a conductive pore fluid (e.g., brine).

The main advantage of the Katz-Thompson relation is that the time required to make these measurements is much shorter and much less labor intensive than is required to make permeability measurements. Also, unlike permeameters, there is no limit of permeability that can be predicted, once set has occurred, and  $d_c$  can be measured. This allows specimens of any age, or composition, to be evaluated.

The Katz-Thompson relation has been shown to predict the permeability of porous rocks quite accurately. Christensen *et al.* tested this procedure on young cement pastes and found agreement with permeameter data to be quite encouraging [19].

### 3.5 Nernst-Einstein Equation

Ionic diffusion is a critical issue for the design of structures, such as those with steel reinforcement and those used for waste containment. There can be numerous difficulties in accurately measuring diffusion coefficients. However, using IS and the Nernst-Einstein equation, shown in Equation (4), an estimate of the diffusion coefficient can be easily determined,

$$\frac{\sigma}{\sigma_o} = \frac{D_{eff}}{D_o} \quad (4)$$

where  $\sigma$  and  $\sigma_o$  are as defined previously,  $D_{eff}$  is the effective diffusivity of a given ion in the porous medium, and  $D_o$  is the intrinsic diffusivity of that ion in 100% pore fluid. Intrinsic diffusivities are readily available in the literature, and show no more than a 15% change from pure water to concentrated (0.5 molar) solutions. Using Eq. (4), determining the diffusion coefficient of any ion in the bulk is simply a matter of measuring the normalized conductivity, and multiplying by  $D_o$ , the intrinsic diffusion coefficient.

Agreement between  $\sigma/\sigma_o$  and  $D_{eff}/D_o$  is quite good [19].

There are several advantages to using the Nernst-Einstein equation to predict diffusivities. First, it is possible to make estimates of the diffusivities for young pastes (approx. 1 day), something that is not possible with the Norwegian test,

ponding/profiling, or divided diffusion cell techniques. This allows the continuous monitoring of the diffusivity versus time for a particular sample. Also, because of the shorter time involved in making individual measurements, a larger number of samples can be tested in a given period.

### 3.6 Solvent exchange Kinetics

Cement-based materials have a water-filled, porous microstructure. When immersed in an organic solvent (e.g., isopropanol, methanol), the pore fluid is replaced by the solvent. The rate of this replacement can be investigated with methods such as weight loss or electrical conductivity changes, and provides insight concerning the pore network (e.g., amount and connectiveness). The use of impedance spectroscopy allows continuous, in-situ measurements of the conductivity during the exchange process. Specimens that have been hydrated to different times show different rates of exchange, as shown in Figure 4.

As originally suggested by Feldman *et al.* [24], solvent exchange kinetics could potentially be used to establish parameters such as diffusivity and permeability. We are currently investigating the solvent exchange rate as an alternative parameter to  $d_c^2$  in the Katz-Thompson equation (Eqn. (3)). The advantage of this method is the ease of the test, in terms of both time and labor. Also, although the pore fluid is being exchanged with an organic solvent, the microstructure is perturbed very little, especially when compared with mercury intrusion porosimetry and BET, which both require drying of the samples prior to measurement.

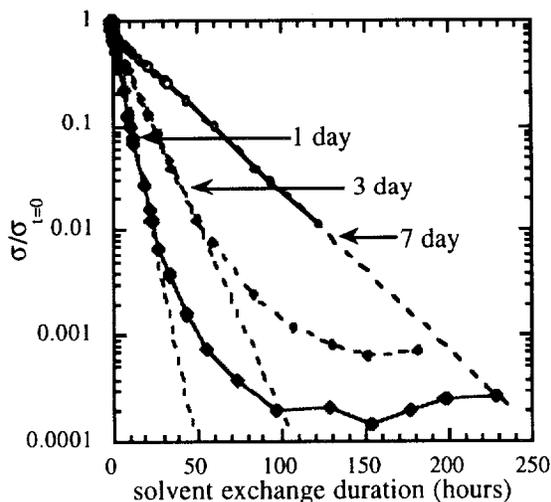


Fig. 4. Solvent exchange data for a Type I OPC, water:cement = 0.4 hydrated for 1, 3, or 7 days prior to solvent exchange in isopropanol. Conductivity, normalized by pre-immersion conductivity is plotted as a function of exchange duration [25].

## 4 Conclusion

In summary, the measurement of transport properties is important in predicting the durability of cement-based materials. Unfortunately, many established techniques are time-consuming, labor-intensive, and inconsistent. These techniques include ponding/profiling, divided diffusion cell, rapid chloride penetrability test, and the Norwegian test, as well as the differential pressure permeameter.

A number of techniques have recently emerged that have the potential to measure or predict transport properties in an accurate and efficient manner. Often, the tests are nondestructive, fast, and relatively easy to perform. Some examples of these techniques include impedance spectroscopy, microstructure-based modelling, nuclear magnetic

resonance, and solvent exchange kinetics. Additionally, the information gathered in these novel methods can be used to predict important durability-related parameters, such as diffusivity (by the Nernst-Einstein equation) and permeability (by the Katz-Thompson equation).

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