Relating Transport Properties to Performance in Concrete Pavements

Introduction

This MAP brief summarizes ongoing research that has been performed to assess fluid and vapor transport in concrete. In general terms the word "transport" is used to describe how vapor and liquids move through concrete, although there are several more specific terms that can be used to describe specific types of transport in concrete. The more specific terms described in this article include the following:

- Fluid absorption – Fluid absorption describes the uptake of a fluid in a partially saturated concrete primarily due to capillary suction although it can also include the effects of gravity (applicable primarily to large pores and cracks). While there are many papers on absorption a good general reference would be Hall and Hoff [1].

- Ionic diffusion – Ionic diffusion describes how an ionic species (e.g., chloride ions from deicing salts) move in a concrete (generally assumed to be a saturated concrete) due to a concentration gradient. While there are many papers on chloride ingress a good reference would be Tang et al. [2].

- Gas Permeability – Permeability describes how a gas or fluid will move through a concrete under a pressure gradient. While fluid permeation may be the critical mechanism for dams or tunnels, substantial pressure gradients are not typically present for pavements or bridge decks. As a result, while the coefficient of permeability (hydraulic conductivity) can be measured and may be useful, it is not discussed in great detail in this document. Gas permeability is typically measured in a partially saturated sample where one side of the sample is exposed to a gas that is under pressure. Gas permeability may be related to problems of carbonation or may provide a more rapid index of a materials permeability. A recent summary of test methods for gas permeability can be found in Kropp et al. [3].

While the transport processes are interesting on their own, the concrete community is generally interested in measuring transport properties for their use in describing a materials resistance to a potential type of deterioration. For example, in concrete exposed to deicing chemicals or sea water the diffusion of chloride ions from the surface of the concrete to the reinforcing steel describes the potential for reinforcing steel to corrode.

A diffusion coefficient can be used with information on the sample geometry and boundary conditions to provide an indication of how long it may take the corrosion to initiate. Similarly, the absorption of water can be related to freeze-thaw damage to initiate. The diffusion of a vapor phase like carbon dioxide can also play an important role in determining the time for carbonation corrosion or to quantify the availability of oxygen to initiate corrosion.

As a result, the pooled fund study "Evaluation of Test Methods for Permeability (Transport) and Development of Performance Guidelines for Durability" (TPF-5(179)) has taken a deliberate approach to link test methods to determine transport properties and a level of performance as shown in Figure 1. Step

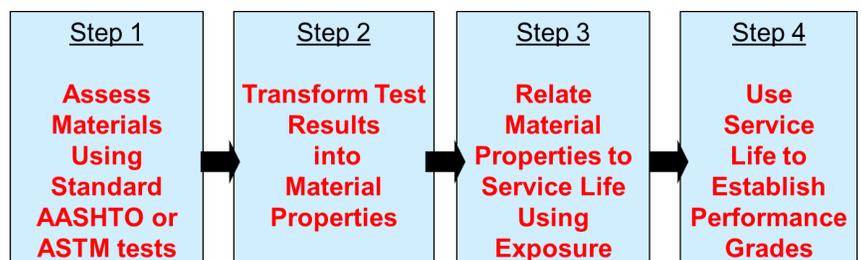| Step 1	Step 2	Step 3	Step 4
Assess Materials Using Standard AASHTO or ASTM tests	**Transform Test Results into Material Properties**	**Relate Material Properties to Service Life Using Exposure**	**Use Service Life to Establish Performance Grades**

Figure 1. A General Approach to Linking Transport Tests and Performance Grades or Specifications

1 indicates that the test method needs to be standardized to describe how to properly condition a sample and to perform a test. Step 2 describes how the measured response obtained from Step 1 can be analyzed to obtain a material property (e.g., a secondary rate of sorption).

For Step 3 an equation or equations are developed to relate the transport properties to a deterioration mechanism. The measured material property can be used in conjunction with sample geometry and boundary conditions (i.e., a description of the environment the concrete is placed in) to model a service limit state (e.g., the onset of corrosion) or ultimate limit state (i.e., spalling of concrete). Step 4 describes a procedure where the information from Step 3 can be related to anticipated level of performance (i.e., for concrete that was continually exposed to seawater with 50 mm of cover that needs to last 50 years a diffusion coefficient of value X or lower is needed).

Importance of Conditioning and Pore Structure

Before discussing the transport tests, it should be noted that sample conditioning must be carefully considered for tests that evaluate transport properties. While more traditional tests such as strength show relatively minor impacts of sample temperature and moisture at the time of testing, transport tests are very sensitive to the state of moisture and temperature during testing [11].

The reason for the strong dependence on moisture is due to the fact that transport occurs in the pores and samples conditioned to different relative humidity values will have proportions of fluid or vapor in the pores. For example, ionic diffusion describes the movement of ions in a liquid and as a result changes in the volume of the fluid can impact diffusion rates. Similarly water absorption is related to the filling of these vapor filled pores and as such knowing the volume of open pores is important.

The role of sample conditioning can be described using a desorption diagram (Figure 2) where the degree of saturation of the sample (ratio of the volume of fluid absorbed to the total volume of fluid absorbed if the pores are completely full) is related to the relative humidity at which the sample is stored. The size of the pores that are emptied at each relative humidity can be estimated using the Kelvin equation assuming the fluid in the pores is water and absorbed water on surfaces is not considered (these effects can however be considered in a more detailed analysis). At relative humidities greater than 80% the large pores (with radius larger than about 5 nm) are progressively emptied. The large

pores were named capillary pores by Powers [5], and are the remnants of the space that began as space between cement (or SCM) particles.

The capillary pore volume is related to water-to-cement ratio (decreases when decreasing the water-to-cement ratio) and decreases as the system hydrates. As the relative humidity is decreased below 80% a series of smaller pores referred to as gel pores are emptied. These pores have a radius smaller than about 5 nm. The gel pores may have a small amount of remnant pores however they are most commonly associated with pores that form in the 'paste portion' of a cementitious system as a part of the hydration products. These gel pores are largely independent of the water to cement ratio and actually increase in volume as hydration progresses. Transport occurs much more readily in the capillary pores and as a result the capillary pores are the dominant feature.

While the degree of saturation can have a dramatic influence on transport, the temperature can also dramatically influence transport as it changes the speed at which ionic species move, changes the properties of the fluids being absorbed (i.e., the surface tension and the viscosity) and can alter the degree of saturation. The degree of saturation can also be impacted by hysteretic effects due to the filling and emptying of pores being influenced by an entry pore diameter (i.e., the ink-bottle effect).

It should be remembered that it can take a relatively long time (months to a year for samples 50 mm thick) for typical test samples to be conditioned to obtain a uniform moisture content throughout the sample (i.e., to dry to a particular level of saturation and to minimize moisture gradients across the sample) [6]. To accelerate the drying process the research team has been exploring the use of a vacuum oven and has had very promising results to this point.

Diffusion

The diffusion of chlorides into concrete is typically measured using two types of tests. The first test consists of placing a
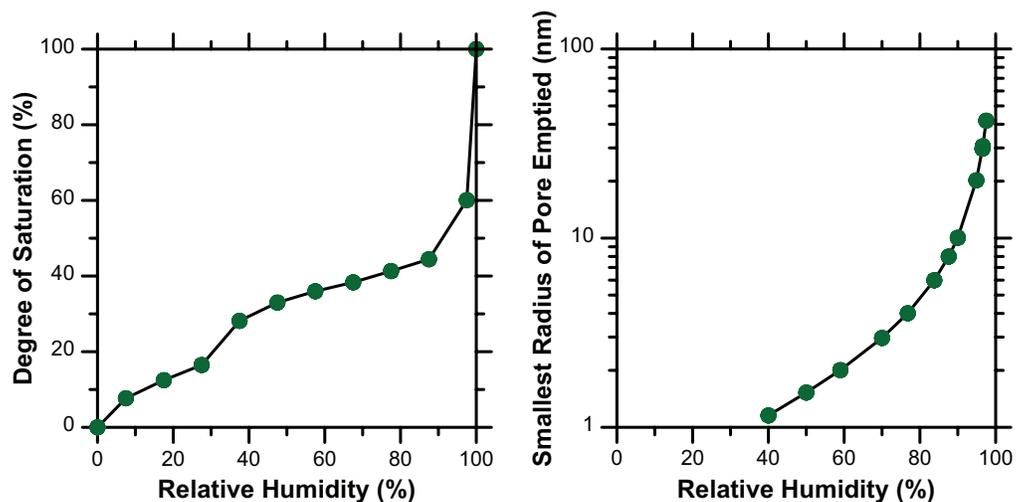
Figure 2. Desorption Spectra for a Mixture with a w/c of 0.42 at 65% DOH (left) and an Approximate Size of the Smallest Pore Emptied at Different values of Relative Humidity (right)

concentrated solution on one surface of the sample previously saturated in lime water and monitoring how the concentration changes in the sample over time (ASTM C1543, C1556).

At some predetermined amount of time, layers of the concrete are ground off and titrated to determine the chloride concentration as a function of depth. This information is then used to back calculate a diffusion coefficient (D_A) and surface concentration (C_S) using a closed form approximation of Fick's second law commonly referred to as the error function solution (erf) (Equation 1).

$$\frac{C_x - C_o}{C_s - C_o} = 1 - erf\left(\frac{x}{2\sqrt{D_A t}}\right) \tag{1}$$

where C_O is the initial background chloride content of the sample, x is the position from the surface and t is time. There are two important features to recognize in using this approach. First, the diffusion coefficient that is obtained is an apparent diffusion coefficient which implies that it is influenced by the binding of chloride with the matrix. Second, as this is an empirical test, the results depend on the specific ionic species used in the test. As a result, the apparent diffusion coefficient (D_A) is dependent on the concentration of the ionic solution and on the ionic species tested (i.e., the type of salt and any associated ions).

The second type of test can be performed to measure the steady state diffusion coefficient [7]. In this approach an electrical field is applied to a saturated concrete sample to accelerate the movement of the ionic species. During the first few days of the test ionic binding occurs; however, at later ages the speed of an ionic species through the concrete can be determined since the binding process has completed. The influence of ionic binding is generally considered in a separate test. The advantage of the second approach (the steady state diffusion coefficient) is that a single diffusion coefficient can be obtained that can be used for different ionic species and concentrations.

Both approaches have great applicability in the design and qualification of a mixture; however, the time required to perform these tests may make them more difficult to use for quality control practices in many DOTs. To overcome this limitation many groups have moved to the measurement of electrical properties as a surrogate test. While the measurement of electrical properties of concrete has been performed for 80 years [8], the development of portable hand held testing devices that enables electrical testing to be more easily implemented in the field is a recent advancement [9,10,11].

While electrical testing is fast and easy to perform, it is important to note that many factors can influence the measurement of electrical properties including geometry, temperature, moisture state, and leaching as described by Spragg et al. [12].

The resistivity can be related to the diffusion coefficient (D) using Equation 2 (Nernst-Einstein Equation).

$$D = \frac{D_i \rho_o}{\rho} \tag{2}$$

where D_i is the self-diffusion coefficient of a particular ion, (i.e., its speed on an open system of low concentration where $D_i = 2.032 \times 10^{-9}$ m^2/s for Cl$^-$), ρ_O is the resistivity of the pore solution, and ρ is the resistivity of the bulk concrete. This can also be written in terms of a value called the formation factor (F) which on one hand can be thought of as a microstructural property (the inverse of the product of porosity and connectivity) and on the other hand can simply be thought of as the ratio of the bulk resistivity and pore solution resistivity for a saturated sample.

$$D = \frac{D_i \rho_o}{\rho} = \frac{D_i}{F} \tag{3}$$

This implies that if one knows the self-diffusion coefficient and the initial pore solution resistivity, a simple measurement of the resistivity can provide a rapid measure of the diffusion coefficient. This is important since the most common variation that one may expect in practice (the addition of water) can easily be detected by measuring the resistivity [13], since the diffusion coefficient (i.e., resistivity) is very sensitive to changes in porosity and connectivity both of which are influenced stringing by the water-to-cement ratio (water to binder ratio). Determining the pore solution resistivity is a bit more difficult. The resistivity of the pore solution can be determined in three ways: pore solution expression [14], a pore solution sensor [15], or estimated using calculations such as those available at [16].

The resistivity can be related to the rapid chloride permeability test (ASTM C1202 [17]) using equation 4 (neglecting heating or polarization that occurs in the RCPT sample).

$$\rho = \frac{VA}{QL}t = \frac{60\,volts}{Q\,coloumbs}\frac{8103\,mm^2}{50.8\,mm}21600\,sec \tag{4}$$

where V is the applied voltage, A is the cross sectional area of the sample, Q is the charge passed, L is the sample length and t is the testing duration. This can provide end users with a level of comfort as they are in many cases already familiar with the values from the RCPT (charge passed or Q) for their mixtures. An example of the relationship between charge passed and resistivity is shown in Table 1.

Table 1. RCPT vs equivalent resistivity using equation 4

ASTM C1202 Classification[1]	Charge Passed (Coulombs)[1]	Resistivity (kOhm•cm)[2]
High	>4,000	< 5.2
Moderate	2,000 - 4,000	5.2 - 10.4
Low	1,000 - 2,000	10.4 - 20.7
Very Low	100 - 1,000	20.7 - 207
Negligible	< 100	> 207

[1]from ASTM C1202-12
[2]calculated using first principles

While many would like to develop a specification using resistivity, it may be prudent to begin to think about formulating the specification using the formation factor, as the formation factor is independent of the properties of the pore solution and as such is more directly related to the diffusion coefficient and to the predicted performance than resistivity or RCPT which is the charge passed at 6 hours [14, 18].

Gas Permeability

Gas transport tests have been proposed as potential methods for use in service life prediction. Gas transport tests are specifically attractive due to their ability to be performed rapidly and their ability to be repeated on the same sample. The South African permeability cell (Figure 3) [19] has been used frequently throughout the world to measure gas permeability and was one of the methods evaluated in the recent pooled fund study. The test consists of placing oxygen at a given pressure on one side of the partially saturated sample and allowing the other side of the sample to be open to atmospheric pressure. The test consists of monitoring the decay in pressure over time and using that information to determine the permeability. Villani et al. [20] have suggested that the formulation for determining the gas permeability as measured using a falling head gas permeameter may be modified to develop a solution that is independent of the pressure used in the test. This new formulation is shown in equation 5.

$$\frac{\tanh^{-1}\left(\frac{P_0}{P}\right) - \tanh^{-1}\left(\frac{P_0}{P_i}\right)}{\left(1 + \frac{b}{P}\right)\frac{AP_0}{2\,\mu\,L\,V}t} = k_{in} \tag{5}$$

where P is the recorded pressure at time t, P_o is the atmospheric pressure, b is the Klinkerberg parameter (related to the slope of the permeability decay with pressure), A is the cross sectional area of the sample, µ is the gas viscosity, L is the sample thickness, P_i is the initial pressure applied to the sample and V is the volume of the oxygen vessel.

Figure 3. A Schematic Illustration of the South African Permeability Cell
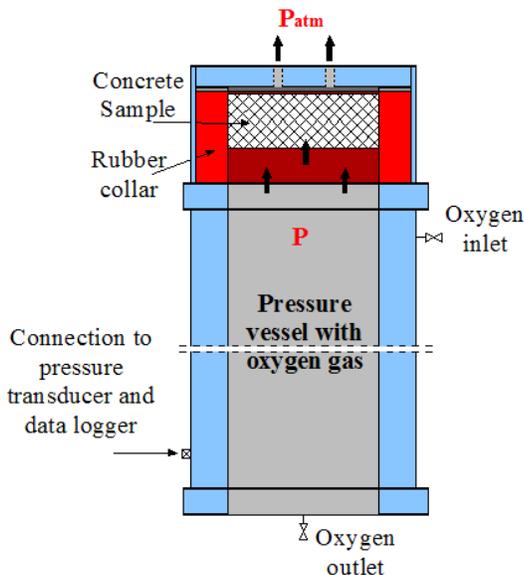
Absorption

When concrete is partially saturated it can absorb water. This concept is illustrated in Figure 4. Currently, water absorption tests are typically performed using a test procedure like ASTM C1585 where a relatively thin concrete sample (2 inches thick) is conditioned to a known relative humidity (degree of saturation [21]). This sample is then placed in a contact with a fluid (water is frequently used) and fluid is absorbed. The test procedure requires to plot the mass of water absorbed normalized by the surface area of the sample as a function of the square root of time. The data typically illustrates two distinct slopes. An initial water absorption shown by the blue line in Figure 4 and the secondary absorption is shown in red. For the standard test the transition between initial and secondary absorption occurs between 10 and 18 hours; however, in reality this depends on the height of the sample and on the properties of the fluid being absorbed. This will be delayed for taller samples as well as samples where the fluid is more viscous.

Figure 4 illustrates the concept of what is happening in the sample as water is being absorbed. During the initial phases of the test water is being absorbed (from the left hand side of the sample) and is filling the gel and capillary pores. The transition between initial and secondary rates of absorption appears from neutron radiography measurements to be due to the water front reaching the top of the sample [22]. The increase in sample mass from points 5 to 8 appears to be the filling of larger voids that may include entrained or entrapped air which occurs slowly over time (on the order of months or years).

While the mass of the fluid absorbed is directly measured, recent research has suggested that it may be very useful in converting this to the the degree of saturation (S), which is defined as the ratio of the absolute volume of absorbed water
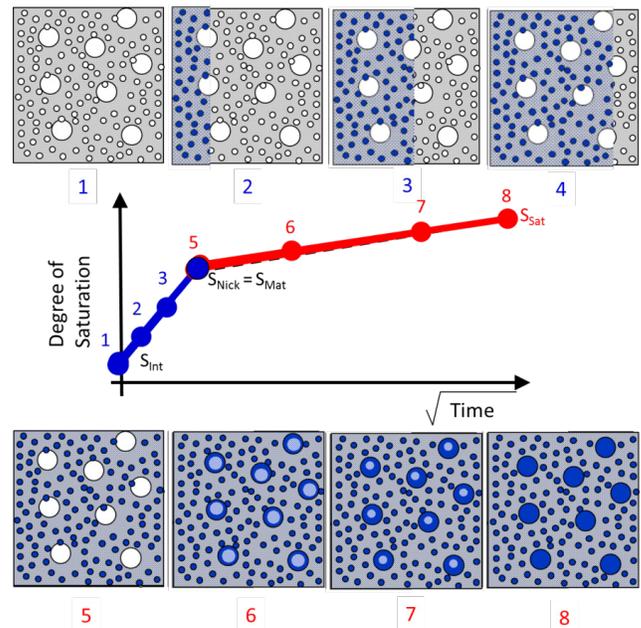

Figure 4. Water Sorption Illustrating the Filling of the Gel and Capillary Pores (1-4) During Initial Absorption and Filling of the Entrained and Entrapped Air Voids During the Secondary Absorption

to the total volume of pores (i.e., the total volume of water that can be absorbed by concrete).

One reason for performing this correction is to use this method to help predict freeze-thaw damage. It has been suggested by Fagerlund [23] that there is a critical degree of saturation (S_{CR}) beyond which freeze and thaw damage can begin to initiate. Li et al. [24] demonstrated the applicability of this approach for paving mixtures with and without air where S_{CR} was approximately 0.85. As such, the water absorption test can be used to suggest how long it may take a sample to reach a critical degree of saturation and consequently show F/T deterioration.

Recommendations

Concrete has historically been specified and accepted based on strength, air content, and water-to-cement ratio. This article summarizes how transport properties can be measured for concrete and how judicious selection of the transport properties can be used to specify the concrete with a level of performance given certain exposure conditions.

First, it should be noted that unlike many other tests for concrete, transport properties are sensitive to sample conditioning and temperature. As such, if these tests are implemented, the users of the tests must develop a keen awareness of how critical these parameters are while being vigilant to make sure that testing protocols are properly developed and followed.

Diffusion testing is performed using two general types of tests. The first test method consists of applying a concentrated solution on one face of the previously saturated sample, allowing this solution to diffuse into the sample for a specified length of time, and measuring a diffusion coefficient by grinding layers of the concrete and titrating the samples to determine a chloride ingress profile. This data is empirically fitted to Fick's second law of diffusion to determine an apparent diffusion coefficient. This type of testing generally results in an apparent diffusion coefficient to be determined since it measures diffusion as well as chloride binding with the cement paste at the same time and is dependent on the concentration/type of the salt solution (it should be noted that the Nord test is conceptually similar to this test however an electrical field is used to accelerate chloride ingress).

The second approach to describing diffusion uses the Nernst-Plank equation with a separate function to account for binding. While this approach requires a certain amount of time to reach a steady state, it determines a unique diffusion coefficient that is independent of boundary conditions.

Electrical resistivity testing provides a test method that is easy to perform, low cost, and descriptive of transport properties. Electrical resistivity has a great potential to be used widely to specify the performance of concrete and to measure the properties during production. Electrical tests are sensitive to sample geometry, test temperature, the degree of saturation of the sample and how the sample is stored (due to changes in moisture content or alkali leaching). While many would like

to simply specify a resistivity, this work suggests that specifying the formation factor (a property that describes the product of pore volume and connectivity) may be the most appropriate way to specify the pore structure as this directly relates to diffusivity and corrosion initiation time. If the formation factor is specified it would require the use of a correction (i.e., the pore solution composition) to relate this to resistivity once the binder composition is known. This can easily be approximated using the NIST approach [16].

Water absorption (sorptivity) measurements are performed by measuring the mass change of a partially saturated sample. The measurements are influenced by how the sample is conditioned (i.e., if the sample is brought to a relative humidity from a dry state or from a wet state) due to hysteresis and by the amount of moisture present in the sample (i.e., S). The results are also influenced by the surface tension and viscosity of the fluid. This can be the fluid used in the test or the fluid that is already in the pores. As such, care needs to be exercised when certain admixtures are used or when field samples are used that may have been exposed to deicing salts. This work also recommends that if absorption is measured, it is helpful to determine the degree of saturation of the sample.

Gas permeability and diffusion were also measured as a part of the pooled fund study. The South African permeability cell was used in this investigation, where oxygen at a given pressure is placed on one side of the sample and the decay in pressure over time is used to determine the permeability. This is a promising test method to use in cases where gas permeability is needed. Villani et al. [25] have proposed a new formulation to assess the experimental results that enables a single unique permeability value to be determined irrespective of the initial pressure used to perform the test.

For More Information

For more information about transport properties or concrete service life modeling, please contact Jason Weiss, Purdue University, 765-412-8358.

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5

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