NISTIR 5592

Survey of Concrete Transport Properties and their Measurement

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February 1995

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ABSTRACT

In this report we present a survey of the current knowledge of the transport properties of concrete. The basic theory and measurement methods are discussed. Emphasis is placed on transport properties (or mechanisms), such as diffusion, permeability, and capillary flow, that may play an important role in degradation processes in high performance concrete. It is concluded that standard test methods used to predict the service life of concrete via measurement of transport properties, especially in high performance concrete, are, in general, inadequate or need to be developed.

Keywords: Building materials, building technology, capillary flow, cement, chloride ions, concentration profiles, concrete, computer modelling, diffusion, electric migration, impedance spectroscopy, Katz-Thompson relation, mercury intrusion porosimetry, mortars, nuclear magnetic resonance, permeability, rapid chloride test, sorptivity, X-ray tomography.

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1. INTRODUCTION

1.1 IMPORTANCE OF TRANSPORT PROPERTIES TO THE SERVICE LIFE AND UTILITY OF CONCRETE

Concrete is one of the most widely used building materials in the construction of the nation's infrastructure [1,2] including highways, bridges, water supply and sewage systems, harbors, locks, dams, tunnels and buildings. Over 500 million tons of concrete are produced in the United States each year of which a significant fraction is used for repair and rehabilitation rather than new construction. The service life and utility of concrete strongly depends on its transport properties (i.e. permeability, sorptivity and chloride permeability). For example, concrete is a building material with potential use for long term storage of hazardous substances such as nuclear and toxic wastes. In such applications it is essential that concrete have a very low permeability. On the other hand, it has been suggested that very low permeability high-performance-concrete (HPC) may have serious deficiencies as a building material due to possible spalling [3,4] when subject to high temperatures resulting from fires. Although concrete is commonly thought of as a static or unchanging material, it is, over the typical service life of a structure, a dynamical changing composite material which may undergo considerable degradation. The ingress of potentially deleterious materials such as chlorides, sulfates and water by diffusion and capillary transport can lead to the corrosion of steel reinforcement or a reduction of strength due to cracking by frost or sulfate attack. Clearly, a variety of transport mechanisms play an important role in the degradation of concrete and must be better understood to mitigate such processes.

1.2 NEED FOR STANDARD TEST MEASUREMENTS

Depending on its mix design, preparation and environmental exposure, concrete's material properties can be highly variable. Thus it is of great importance to the construction industry to have standards regarding the processing and the quality assessment of concrete. In order to make assessments of the quality and condition of materials, standard experimental test methods are needed to measure key transport properties such as permeability to fluids, sorptivity and the diffusion of ions. Without standard measurement methods it is difficult to develop objective criteria needed for the prediction and assessment of the service life of concrete as a construction material and barrier. Presently, there are no American Society for Testing and Materials (ASTM) standards concerning the measurement of water permeability and

capillary- driven moisture transfer for cement-based materials. In addition, recent studies [5] have brought to question the validity of the new American Association of State Highway Transportation Officials (AASHTO) standard test for the measurement of chloride diffusivity by the so called "rapid chloride permeability test." A better understanding of fluid and ion transport in concrete is crucial to the development of standard test methods and criteria for predicting its service life.

1.3 THE RESEARCH CHALLENGE OF CONCRETE

1.3.1 MICROSTRUCTURE OF CONCRETE

A close examination of concrete [2] reveals a very rich and complex microstructure. It is comprised of a variety of phases with diverse material properties. For simplicity we may think of concrete as composed of cement paste, sand and aggregate (fig. 1). Each phase can be characterized by a different length scales which corresponds to a typical pore diameter, the size of which spans over many decades ranging from nanometers to millimeters in concrete. Let us first consider the cement paste. At the smallest scale, cement paste is largely composed of a calcium silicate hydrate (C-S-H) gel which is comprised of nanometer size C-S-H particles and pores. At the micrometer scale, the cement paste appears as a composite of hydrated products, unhydrated particles and capillary porosity. At the millimeter scale and larger, the cement paste and aggregate (sand and stones) form a composite material which, in addition, may contain air voids (at the millimeter scale). Another feature that may be present in concrete is the so-called interfacial zone. The interfacial zone is a region of order 10-40 micrometers near the cement paste/aggregate boundary where there is an increase of porosity. The increase of porosity is probably a result of an inability of cement particles to densely pack near the paste/aggregate boundary. The interfacial zone can dramatically enhance the transport properties of concrete. For instance, when there is a large volume fraction of aggregate, it is easy for the interfacial zone to percolate through the system forming a highly permeable path.

The complexity of concrete's microstructure makes the theoretical and experimental investigation of its transport properties a great challenge. Transport of fluids and materials depend on a large number of factors [6] such as porosity, pore size distribution, connectivity, and tortuosity. Such factors, in turn, depend on the volume fraction of materials used, details of cement hydration, and the processing of concrete. In addition, new high-performance concretes (HPCs) are being developed which are composed of a wide variety of materials such as silica fume, blast furnace slag, fly ash, and plastisizers, to name but a few, which can greatly alter concrete's transport properties by modifying its pore structure. In this report, we present a review of current knowledge, mathematical models and test methods pertinent to the main transport properties of concrete. Such properties and transport mechanisms

include permeability, diffusion, electrical conductivity, and capillary transport. The purpose of this document is to form a basis for the development of a modeling and experimental laboratory, in order to carry out the fundamental research of transport processes in concrete and to develop needed test methods.

2.0 FLUID PERMEABILITY

A random porous medium is a network of pores of varying size. When this network forms a connected path through the medium, it is capable of transporting fluid. The permeability, k, of a characterizes the ability of a fluid-saturated porous medium to transport fluids when subject to an applied pressure gradient and is defined by Darcy's law [6,7]:

$$\vec{V} = -\frac{k}{\mu}\vec{\nabla}P \qquad (1)$$

where **V** is the average fluid velocity, k is the fluid permeability, μ is the fluid viscosity, and P is the pressure. Note that the units of permeability are length squared. For simplicity we will assume that the porous medium is isotropic, otherwise permeability must be expressed as a second rank tensor. For many materials permeability is expressed in units of the Darcy, with one Darcy approximately 1 micron^2. Values of permeability [2] for low water to cement ratio (w/c) cement paste are of order 10^{-22} m^2 while for typical concrete $k \approx 10^{-18}$ m^2. These values of permeability are orders of magnitude lower than common porous media such as soil and sandstone rock and are hence much more difficult to measure.

In many engineering fields, such as soil hydrology where the main transport fluid is water, Darcy's law is written as [6,7]:

$$V_f = K_h A h / L \qquad (2)$$

where V_f is the volumetric flow rate in units of m^3/s, K_h is the hydraulic permeability in units of m/s, A is the cross-sectional area of the porous medium, h is the head of water in meters, and L is the length of the sample. Explicitly, $K_h = K\rho g/\mu$, where ρ is the density of water, g the gravitational constant, and μ the water viscosity. To convert K_h to K (from units of m/s to m^2) $K = K_h \times 10^{-7}$ for water.

Several methods are used to measure permeability. In one method, borrowed from soil hydrology [8], a head of water is placed above the concrete specimen and then the

height of the head is monitored over time to determine the volumetric flow through the concrete. Correcting for evaporation, the permeability is determined by Darcy's law. Due to the low permeability of concrete, this method's main drawback is that it may take weeks or longer to obtain sufficient flow to determine permeability, especially in the case of HPC with low w/c ratio. Also, in newly formed concrete, hydration may be taking place at a significant rate so that the permeability is changing as the measurement is made.

To shorten the time of measurement, an additional pressure may be applied by a piston-driven device which pushes the fluid through the concrete. To reduce leakage of fluid along the sides of the concrete an effective seal must be established. For lower permeability concrete such as HPC, high pressures may be necessary to obtain sufficient flow. In this case, the so-called triaxial configuration has shown promise. Concrete is placed in a pressurized sleeve to prevent leakage from the sides. A high pressure difference across the sample may then be maintained to obtain adequate flow for measurement of permeability [9]. It is claimed this apparatus has the capability to measure a permeability of the order of $10^{-22}m^2$ which is found in low w/c cement pastes. It is not known to what degree the high applied pressure may modify the pore structure of HPC thereby giving misleading results. Regardless of this complication, this method or a modification of it, has potential to determine the permeability of, or at worst case a reasonable upperbound to, the permeability of HPC. A second approach [10] used to make tight seals is to compress room-temperature-vulcanized silicone rubber about the sides of a concrete specimen placed in a confining cylinder. It is estimated that permeabilities as low as $10^{-23}m^2$ can be obtained with such a method. Clearly, these methods merit further research, especially for the case of HPC. It should also be pointed out that, recently, the former method has been described in the Corp of Engineering Handbook (CRD-C 163-92).

2.1 CROSS-PROPERTY RELATIONS FOR ESTIMATING PERMEABILITY

2.1.1 KATZ-THOMPSON RELATION

In addition to the direct measurement of permeability there are several methods for estimating permeability based on cross-property relations. Here estimates of permeability are determined from, presumably, easier to measure transport processes such as electrical conductivity and diffusion. Probably the most well known cross-property relation for permeability is the Katz-Thompson (KT) relationship [11,12,13]:

$$k = c_{kt} \frac{d_c^2}{F} \tag{3}$$

where $F = \sigma_0/\sigma_B$ is the so called formation factor (with σ_0 being the conductivity of the fluid used to fill the pore space, and σ_B the conductivity of the entire system) and the critical diameter, d_c, is a length scale estimated by mercury intrusion porosimetry (MIP). Roughly, d_c, is the smallest pore of the set of largest pores that percolate through the porous medium. The constant, c_{kt}, was originally suggested to equal 1/226 by KT. Although it is not well known, it was later shown that there was an inconsistency in KT's derivation and that c_{kt} is closer to 1/100 depending on the pore structure (it ranges from about 1/60 to 1/110 for many pore structures). Regardless, the KT relation has proven useful in providing good estimates of permeability of sandstones commonly investigated in the oil recovery industry. Recently, there has been an effort to use the KT relation to estimate permeability of concrete. However, there has generally been questionable agreement between theory and experiment. Experimentally obtained values [14,15] of c_{kt} typically range from approximately 1/180 to 1/2000 for mortars, with values closer to the KT constant in the higher w/c range. As a result, estimates of permeability may be off by an order of magnitude or more if one strictly uses a single KT constant. Since there is no obvious theoretical reason why such a small value of c_{kt} is obtained experimentally for cements, it is not clear if, in general, the KT relation can give a reliable estimate of the concrete's permeability. Unless there is an explanation for the anomalously small KT constant in terms of the pore structure, which would be of fundamental interest in itself, there is a likelihood that estimates of d_c are simply too large due to the experimental procedure. The drying of samples, in order to perform MIP, may modify the pore structure forming cracks so that permeability estimates may not be representative of the original saturated sample. Furthermore, due to the high pressures needed for MIP in cements and concrete, there is the possibility of damage to the pore structure. Presumably, such effects are likely to be more dramatic for HPC which typically has very small pores. Further research is needed to determine to what degree such factors affect permeability estimation. It would also be useful to compare pore size distribution from other methods including nuclear magnetic resonance, sorption isotherms and thermoporsimetry [16] with that obtained from MIP.

2.1.2 DIFFUSION-BASED PREDICTIONS OF PERMEABILITY

Another promising approach towards permeability estimation has been to consider diffusion bounds [13,17]. Ideally, such methods would be useful for determining the permeability of concretes with an extremely low connected porosity and thus very low permeability.

To understand how diffusion might be related to permeability, consider a set of uniformly distributed particles that are allowed to diffuse in a porous medium. The

average time it takes the particles to reach a wall is called the mean lifetime , $<\tau>$, of the particles. It is easy to see that $<\tau>$ increases with pore size. The root mean squared distance the particles traveled until hitting a surface can be thought of as an effective pore radius [17] and can be showed to scale as the square root of $<\tau>$. It has been rigorously shown that [17]:

$$K \leq \phi D <\tau> \tag{4}$$

where ϕ is the porosity and D is the diffusion constant. Note, for a simple tube, the above relation is an equality. For highly porous materials, this diffusion bound produces reasonably tight bounds; however, as porosity is decreased, the upper bound quickly becomes orders of magnitude too large in part because the above expression does not take into account the connectedness of the pore space as well as the tortuosity.

The diffusion of particles can be simulated on computer with so-called "blind ant" or random walker algorithms. While the random walk simulation is an abstract construct there have been attempts to map it to Nuclear Magnetic Resonance (NMR) experiments [13]. In this case the diffusing particles (or blind ants) are analogous to diffusing magnetic spins and $<\tau>$ corresponds to the mean lifetime of the total magnetization. The total magnetization decreases with time as magnetic spins, which have been initially aligned by an external magnetic field, later become unaligned as they diffuse through the pore space and eventually interact with the pore/solid interface. While, tests of eqn. 4 have been carried out by computer simulation, it remains to be seen how well estimates of permeability can be made from NMR data. For instance, a better understanding of the details concerning boundary conditions associated with magnetic spins at pore-solid interface may be needed. Clearly, further research is needed to determine the utility of such methods.

Other hybrid relations combining relaxation times from NMR experiments with diffusivity and conductivity measurements may provide better estimates at lower porosities. We only mention the following recently suggested hybrid relation [13] which has demonstrated success in permeability estimation:

$$k \approx \phi D <\tau> / F \tag{5}$$

where, ϕ is the porosity. Again, the product $D<\tau>$ acts as an effective radius squared

that represents a typical pore size while the formation factor, F, provides an estimate of the tortuosity and pore space connectedness. When the pore space becomes disconnected F approaches infinity and hence, K, goes to zero. Results from numerical simulation have shown good agreement between the above estimate and the direct calculation of permeability by the solution of the Stoke's equations in microstructural models of porous media. Again, without further modification to take into account the interaction of magnetic spins with the pore walls in NMR experiments, it is most likely that the above relationship would typically obtain an upper bound to the actual permeability.

2.1.3 CORRELATIONS BETWEEN TRANSPORT PROPERTIES

Another possible approach to permeability estimation, or at a minimum, an estimation of the quality of a material, may be to utilize correlations between transport properties. For instance, it is reasonable to expect that if the effective diffusion coefficient of chloride ions or the bulk conductivity of a material increases over time, say due to some degradation process, the permeability will also increase. However to utilize such correlations from sample to sample there must be an understanding of the physical length that sets the scale for permeability in each sample. An understanding of how characteristic length scales vary from sample to sample (or over time) is crucial if data based on correlations is to be meaningful or to have any predictive capability. While the usage of correlations between transport coefficients may be useful for certain classes of porous materials, it is doubtful that such behavior is universal and would most likely be limited to common mixtures since they may have a similar characteristic length scale.

2.2 THE ONSAGER RELATION

Recently, a novel approach to measuring permeability has been developed by Po-zen Wong [18] which utilizes Onsager's Relation:

$$J_e = -\sigma_r \nabla \Phi_e - L_{12} \nabla P \tag{6}$$

$$J_f = -L_{21} \nabla \Phi_e - \frac{k}{\mu} \nabla P \tag{7}$$

where, for a saturated porous medium subject to both a potential drop and a pressure drop, J_e and J_f are the electric and fluid currents respectively, σ_r is the conductivity,

Φ_e is the electrical potential and L_{12} is a constant with $L_{12} = L_{21}$. By properly adjusting the electrical potential and pressure such that J_e and J_f are equal to zero we, obtain

$$G_1 = \frac{\nabla \Phi_e}{\nabla P} = \frac{L_{12}}{\sigma_r} \tag{8}$$

and

$$G_2 = \frac{\nabla P}{\nabla \Phi_e} = \frac{\mu L_{21}}{k} \tag{9}$$

so that $G_1/G_2 = k/(\mu\sigma_r)$. If G_1 , G_2 and σ_r, are determined by experiment, then we can obtain the permeability. In practice G_1 and G_2 are difficult to obtain from dc measurements due to signal to noise problems, however, measurements may be made at finite frequency using digital lock-in techniques to overcome this problem. While presently being tested on mortars, this method may be useful for measuring permeability of concrete, at least, for higher w/c concretes. However, at low w/c, the permeability may be too small for this approach to work. Also, there may be limits to the system size that can be addressed by this method. Given these potential deficiencies, it remains to be seen how useful this method will be for the measurement of transport properties in HPC.

2.3 PERMEABILITY ESTIMATION BY ANALYSIS OF MICROSTRUCTURE

2.3.1 KOZENY-CARMEN RELATION

One of the first theoretical estimates of permeability based on the analysis of the porous medium's microstructure was the Kozeny-Carmen [6,7] relation:

$$k = \frac{\phi^3}{2s^2} \tag{10}$$

where s is the specific surface (pore surface area divided by the total volume of the porous medium). The role of the specific surface is to properly scale permeability data obtained from porous media characterized by different intrinsic length scales. For instance the rescaling (or magnification) of a porous medium by a factor of n will preserve its porosity but change the permeability by a factor of n^2 (s decreases by a factor of n). For some relatively homogeneous materials, such as glass bead packs, the Kozeny-Carmen relation works well. However, for more complex materials, Kozeny-Carmen breaks down, especially in high and low porosity regimes. Over the years, empirical modifications to the Kozeny-Carmen relation have been made to

include such factors as tortuosity and pore space connectedness in order to fit experimental data, but only with limited success.

Recent studies have shown that, for a wide class of materials, reasonably good estimates of permeability may be directly obtained from a porous material's microstructural parameters. For instance, one need only determine the specific surface and porosity of a porous material and then refer to a universal permeability curve [19] to determine permeability for a large class of porous media. Such estimates have been used successfully to predict the permeability of various sphere packings and sandstone. Further improvements to the estimation of permeability can be made by carefully determining the specific surface associated with the dynamically connected pore space. It has also been shown that incorporating the value of critical porosity where the pore space becomes disconnected into the universal scaling scheme described above significantly improves permeability estimation.

2.3.2 ESTIMATES OF SURFACE AREA TO PORE VOLUME RATIO IN POROUS MEDIA

The surface area (s) to pore volume (v) ratio of a porous medium plays an important role in determining permeability and affects absorption in diffusion-based processes [6]. Several methods are used to determine s/v. They include nitrogen gas adsorption-desorption, mercury intrusion porosimetry (MIP), and NMR. Reasonably good agreement is seen in estimates of the specific surface from MIP and nitrogen adsorption for a wide range of porous materials. However, agreement between MIP and nitrogen sorption is poor for hardened cement pastes. Possible reasons for discrepancies between the two methods are the ink bottle effect, where large pores are not reached unless the mercury moves through smaller pores, and structural changes in the pores due to drying techniques. Experimental determinations of the surface area to volume ratios have demonstrated that the surface area appears to decrease as a result of sample drying. In effect there is a coarsening of the pore space and as a result, higher permeabilities are measured in samples that have been dried out. Recently, NMR [20,21] has shown great promise in determining s/v of hardened cement pastes. An important advantage of NMR is that it can be applied to fresh cement paste and, indeed, be used to follow the evolution of the microstructure as the cement hydrates. Furthermore, NMR has the capability to determine pore size distributions and relative diffusivity coefficients.

2.4 MODELING PERMEABILITY

Due to the existence of the many length scales [22,23,24] that characterize the various components of concrete, it is not possible to simulate flow through concrete such that all pore size scales are explicitly represented. Pore sizes may range from nanometers in the cement paste, to microns in the interfacial zone and capillary pores, to the millimeter scale in air voids. Furthermore, cracks due to shrinkage or frost attack can greatly influence transport. Due to the similarity between Ohm's law and

Darcy's law, it may be possible to estimate the bulk permeability of a random microstructure where the local permeability, which corresponds to transport through different phases, is a function of position. The problem of estimating the bulk permeability may then be mapped to that of a random resistor network [25] where the electrical conductances are now replaced by hydraulic conductances. There has also been some success in estimating the permeability of mortars dominated by transport through the interfacial zone by modeling the interfacial zone as an interconnected network of shells about sand [25] grains. Further research is needed to understand how to combine information from different length scales to determine the macroscopic properties of concrete.

2.4.1 RENORMALIZATION GROUP METHODS

A recent development in permeability estimation, is the use of renormalization group (RG) methods [26,27]. RG methods have been successful in the calculation of permeability of porous media that have a broad pore size distribution such as that found in large geological regions studied by the oil recovery industry. Since concrete may be composed of pores with diameters that vary over many decades in magnitude (from nanometers to millimeters), RG methods may be suitable for the calculation of the permeability of concrete. As an brief overview of the RG procedure, suppose that a material has a permeability that is a function of position. If one samples different regions in the material, the measured local permeabilities will form a distribution. Now, assume that a set of nearby permeabilities can be replaced by a single effective permeability which is representative of that region. The new set of permeabilities for the entire porous medium, formed in this way, will now have a narrower distribution. Assuming that this coarse graining process can take place ad infinitum, the distribution of permeabilities will become infinitely narrow. At this so called *fixed point* a reasonably good estimate of the bulk permeability should be obtained.

2.5 AIR PERMEABILITY

The study of air permeability is important for understanding the ability of HPC to encapsulate hazardous materials or act as a barrier to gasses such as radon. Air permeability studies may also aid understanding the ingress of carbon dioxide which results in the carbonation of concrete. The following equation gives the air permeability [28,29] of a porous material:

$$\vec{V}=\frac{K}{\mu}\frac{(P_i-P_o)}{L}\frac{(P_i+P_o)}{2P_i} \tag{11}$$

where K is the air permeability (generally not equal to the water permeability), μ is the air viscosity, P_i and P_o are the inlet and outlet pressures, respectively, and L is the distance over which the pressure difference is applied. The sum of the two pressures is needed to account for the compressibility of air. Air permeability is in principle an easier measurement to make than water permeability. However, it may not be easy to relate measurements of air permeability to water permeability except in an empirical fashion. Air permeability in concrete is typically greater than liquid permeability. This difference can become substantial as porosity is decreased. As a result, air permeability is not likely to be reliable predictor of water permeability for the case of HPC. In addition, air permeability measurements entail the drying out of the sample, which may lead to shrinkage and cracking, hence producing higher values of permeability. On the other hand it may be useful to study the air permeability of partially saturated concretes since, in general, concrete is neither fully saturated or unsaturated.

2.6 ON-SITE CHARACTERIZATION OF CONCRETE PERMEABILITY

Over the course of a concrete structure's lifetime various degradation processes may take place which will affect the material properties such as strength and permeability. To estimate the degree of degradation for proper maintenance it would be useful to have an in-situ capability of measuring transport properties. Several methods have been developed [31,32,33] to measure the air and water permeability of in-service concrete. It is important that such measurements be easily carried out, not take much time, and be non-destructive.

Recently, a novel method called surface air flow (SAF) [32] has shown moderate success in permeability estimation. Here, instead of forcing air into the concrete, a vacuum is created at the surface forcing air to flow out of the concrete along the pressure gradient. While there is no claim that such a method would accurately determine permeability, it is believed that flow rates measured by SAF would give a relative estimate of the permeability of materials (i.e. low flow rates would correspond to low permeability concretes and high flow rates would indicate high permeability concretes). A weakness of this method is that surface roughness controls the accuracy of measurement. Better seals at the instrument/surface interface may be needed to improve the accuracy (or consistency) of measurements. Also, SAF is limited to dry concrete. High variability in flow rates has been found in studies of partially saturated concretes. Tests of a field device have shown results which differ by a factor of more than two from measurements made in the laboratory. Although the method shows some potential for estimating the penetrability of materials in situ, more research is needed to establish needed correlations between measurement and the quality of concrete.

In another approach [33] to measuring permeability, a hole first is drilled into the

concrete. A test probe which injects pressurized water into the concrete is then inserted into the hole. The hole is sealed about the probe so that no water escapes directly to the surface. Water is injected and allowed to permeate the surrounding concrete radially. The permeability is then determined from solutions of Darcy's equation using a radial geometry. In situ measurements of permeability have been approximately 70% higher than measurements on similar samples carried out in the laboratory. It is not clear if the authors inserted the probe far enough so that spherically symmetric flow holds. At long enough times the water should reach the surface creating larger than anticipated pressure gradients and breaking the spherical symmetry. While, presently, the anomalously large flow is unexplained, this method does provide a reasonable estimate of water permeability in a short time and merits further investigation.

In the so called Figg test [34], catalyzed liquid silicone rubber is used to seal a small drilled hole in the concrete. A hypodermic needle is inserted through the rubber, and under a fixed head, the time it takes for a specified amount of water to flow is determined and related to permeability. Results from this measurement strongly depended on the water saturation state of concrete and the internal relative humidity. Also it is not clear if the author had taken capillary effects into account. At low water saturation, it is likely capillary forces will dominate the flow. Indeed, this may be the case since it was shown that flow rates decreased with increasing water content. Furthermore, it is not clear what role spatial inhomogeneities play in such measurements since the hypodermic needle used has a very small cross section. It is possible that placing the needle at different points of the concrete specimen could produce dramatically different values of permeability as a result of structural inhomogeneities in the concrete.

3.0 UNSATURATED FLOW

In general, the pore space of concrete is not fully saturated [35,36,37]. The degree of saturation of the pore space can depend on several factors such as the previous exposure of concrete to moisture and the relative humidity. Any attempt to fully understand transport mechanisms in concrete depends on knowledge of the partially saturated pore space. In addition, capillary transport and the injection of fluids such as steam or grease (which is practiced in the construction of structures including penetration barriers for hazardous wastes) can only be correctly understood in terms of unsaturated flow models. Values of unsaturated permeability may be considerably smaller (several of orders of magnitude smaller) than saturated values so it is important to have realistic values of the permeability for more accurate estimates of service life in different environmental conditions.

The general equation describing unsaturated flow is given by [6,7]:

$$\frac{\partial(\phi\rho_\alpha S_\alpha)}{\partial t}+\nabla\cdot(\rho_\alpha\vec{q}_\alpha)=F_\alpha \tag{12}$$

where ϕ is the porosity, S is the degree of saturation, ρ is the density, F is a source or sink term, q is the volumetric flux, and α is a label corresponding to the fluid (liquid or gas).

The volumetric flux is given by a general Darcy equation:

$$\vec{q}_\alpha=-\frac{Kk_{r\alpha}}{\mu_\alpha}(\nabla p_\alpha-\rho_\alpha\vec{g}) \tag{13}$$

Here, K is the saturated permeability, $k_{r\alpha}$ is the relative permeability, p is the pressure and g is the gravitational force. The measurement of relative permeability is not a trivial exercise and is the subject of considerable research [6,36]. Relative permeability is history dependent, depends on whether fluids are being injected or removed, and strongly depends on the wetting properties of the fluids. While it remains a challenge to measure relative permeability in concrete, it is reasonable to expect that experimental methods developed in the soil sciences to determine relative permeability should be applicable [6].

3.1 CAPILLARY TRANSPORT

An important mechanism of fluid invasion in concrete is capillary transport. The presence of small pores in concrete (and especially HPC) produces a large capillary force which controls the ingress of fluids (and constituents like chlorides). To model suction due to capillary forces a capillary potential Ψ is introduced in equation (13). Defining the water content $\theta=\phi S$, $K_\theta=Kk_r/\mu g$, and $\Phi=h+P/\rho g+\Psi(\theta)$, where h is the height at which the flow is being evaluated, the following relation may be obtained from equations 12 and 13 [35,36,37,38]:

$$\frac{\partial\theta}{\partial t}=\nabla K_\theta\nabla\Phi \tag{14}$$

Note, the capillary potential as well as the relative permeability is dependent on the water content. Equation (14) is often written in the form of a diffusion equation:

$$\frac{\partial\theta}{\partial t} = \nabla D \nabla\theta \tag{15}$$

where the capillary diffusivity $D = K(d\Psi/d\theta)$. The capillary diffusivity, potential and relative permeability are typically obtained from analysis of saturation curves [35,36]. In many building materials such as brick, mortar and concrete it has been empirically found [35] that $D(\theta) \approx \exp(\varepsilon\theta_r)$ where ε is a fitting parameter and $\theta_r = (\theta-\theta_o)/(\theta_1-\theta_o)$ is the normalized water content. Here, θ_1 is the water content at the absorbing boundary and θ_o is the initial water content in the porous medium. To our knowledge no such studies have been applied to HPC.

3.2 SORPTIVITY MEASUREMENT

The exposure of concrete to fluids and the occurrence of wetting/drying cycles can greatly enhance the ingress of foreign materials into concrete. The penetration of liquids in concrete is a result of capillary forces which allow the wetting fluid to be drawn along the solid-pore surface. The smaller the pores, the greater the suction. (In contrast, a non-wetting fluid such as mercury must be forced to enter pores). The simplest yet most direct measure of the concrete's ability to absorb fluids is its sorptivity [36,37] S, which is defined by the following equation:

$$M(t) = S\sqrt{t} \tag{16}$$

Where **M** is the total fluid absorbed normalized to the exposed surface area (Mass of fluid/(density x area)), and **S** is the sorptivity of the fluid in units of length/time$^{1/2}$

.

To derive the square root of time scaling factor, we will present the following simple argument. Assume that a porous medium is saturated from the inlet to some internal distance x. For simplicity, we will assume that the macroscopic front is flat and that the region invaded is fully saturated. The capillary pressure across the air water interface in a pore is given by the Laplace formula:

$$\Delta P = 2\cos\theta_c / r \tag{17}$$

where θ_c is the static contact angle and r is the pore radius (assuming a tube geometry). Assuming that a typical pore in concrete is approximately one micrometer diameter, the static contact angle is zero, and the surface tension for the air/water interface is about 7×10^{-2} N/m then eq. (17) gives $\Delta P = 140\times10^{3}$ Pascals for the

pressure drop across the interface, which is much larger than hydrostatic pressures present in sorptivity experiments. Then from Darcy's law we have:

$$V = KA\Delta P/(x\mu) \tag{18}$$

where A is the cross-sectional area of the porous medium. If the fluid ingressed a distance x, the total mass absorbed $M = \rho Ax/\phi$ and then:

$$\frac{dM}{dt} = \frac{\rho A}{\phi}\frac{dx}{dt} \tag{19}$$

Now since

$$\frac{dx}{dt} = \frac{V}{A\phi} = \frac{KP_c}{x\phi\mu} \tag{20}$$

the evaluation of x as a function of time gives:

$$x(t) = \left(\frac{2KP_c t}{\phi\mu}\right)^{\frac{1}{2}} \tag{21}$$

And hence,

$$M(t) = St^{\frac{1}{2}} + M_0 \tag{22}$$

where M_0 is a constant associated with the initial water content. For typical porous media (or high w/c concrete) the total amount of water absorbed scales as $t^{1/2}$. However for HPC or low w/c mortar and concrete there is evidence that this scaling does not hold. For instance it has been found [39] that a much smaller exponent (ranging from about 1/5 to 1/3) works well in describing water absorption in low w/c

mortars over longer periods. Several reasons may explain this anomalous scaling. First, the ingress of water may cause expansion or initiate the further hydration of the cement paste hence, altering (reducing) the available pore space. It has also been claimed that the anomalous scaling may simply be due to leaching which results from the use of distilled water in sorptivity tests. Due to the very low permeability of HPC, the gas phase may not exit sufficiently and thus produce a build-up of pressure which would reduce the pressure gradient driving the fluid through the pore space. Further research is needed to clarify this anomaly. Another issue is the morphology of the invading fluid. Sorptivity does not provide information on the shape or pattern formed by the invading fluid. Some experiments have shown that the depth a fluid penetrates exhibits a square root with time scaling in concrete samples. However, the penetration depth can depend greatly on the pore structure and the fluid's wetting properties. Clearly, further research is needed to understand the sorptivity of HPC. For instance it would be useful to carry out a systematic study of sorptivity as a function of w/c, sand size distribution, fluid type and so forth. It is also important to develop models of the ingress of fluids that take into account surface tension effects and other effects such as expansion as water enters the material and the compression of air entering non-percolating pores.

As a final note, it should be pointed out that a power law scaling of moisture sorption can only be true over relatively short periods since the total moisture absorbed will diverge with such scaling. A more general approach is needed [39] to account for sorption over longer times where the material either saturates or the rate of sorption has been reduced due to, for instance, modification of the microstructure.

3.3 MODELING CAPILLARY FLOW

The numerical simulation of capillary transport is a challenging problem in computational fluid dynamics since it entails the detailed description of an interface separating two fluids (liquid/liquid or liquid/air) moving through a random porous medium. At the pore scale, the flow of fluids is described by the Navier-Stokes equation [7]:

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho \, (\vec{v} \cdot \vec{\nabla}) \, \vec{v} = \nabla^2 \vec{v} - \frac{1}{\nu} \vec{\nabla} p \tag{23}$$

where ρ is the fluid density and ν is the fluid viscosity. For an incompressible fluid in the low Reynolds number regime, or in the limit of very slow, flow we may ignore the non-linear terms and solve the following Stoke's equations:

$$\rho \frac{\partial \vec{v}}{\partial t} = \nabla^2 \vec{v} - \frac{1}{\nu} \vec{\nabla} p \tag{24}$$

$$\vec{\nabla}\cdot\vec{v}=0 \tag{25}$$

where in the case of steady state flow the left hand side of eq. (24) is equal to zero.

The boundary condition along a pore/solid interface for a viscous fluid moving through the pore is that the fluid velocity is zero (the so called no slip boundary condition). In the case of immiscible displacement of fluids, such as capillary flow, there are the following boundary conditions. There is a pressure drop across the liquid/liquid (or liquid/air) interface given by the Laplace formula [6,7]:

$$\Delta P=\gamma\,(\kappa_1+\kappa_2) \tag{26}$$

where γ is the surface tension and κ_1 and κ_2 are the principle radii of curvature (see figure 2). The interaction of the fluid with the solid leads to wetting (or non-wetting) effects. Hence, contact line motion, or motion of the boundary line formed where the fluid/fluid interface meets the solid, becomes an important factor. Although this subject has been the subject of intense research it still is not completely understood. In the case of a stationary contact line, the fluid/fluid and fluid/solid interface satisfies the Young's equation:

$$\gamma_a-\gamma_b=\gamma\cos\theta_c \tag{27}$$

where γ_a and γ_b are the Fluid A/solid and Fluid B/solid surface tensions and θ_c is the static contact angle between the fluid/fluid interface and a fluid/solid interface. Typically, when the contact angle is small the fluid is considered to be wetting (although in many cases the term wetting is reserved for fluid having zero contact angle).

When a fluid is invading a porous medium the measured contact angle will not necessarily equal the static contact angle. The case of the moving contact line is the subject of ongoing research . It is found that in many experiments the contact line moves with the velocity, V_{cl} , described by Tanner's law [40]:

$$V_{cl}\sim\theta_d^{1/3} \tag{28}$$

where θ_d is the dynamic contact angle.
The numerical solution of the Navier-Stokes equation with the above boundary

conditions is very difficult using standard computational methods such as finite difference and finite element, especially in complex microgeometries. However, recent developments in alternative computational fluid dynamics methods called "lattice gas" and lattice Boltzmann [41,42,43,44] have shown promise in the modeling of multi-component and multi-phase flow in random porous media. These methods have the advantage over direct simulation of the Navier-Stokes equation in that they can handle complex fluid/fluid and fluid/solid boundaries. In the future, such simulations should help improve our understanding of moisture transport at the pore scale. With detailed knowledge of the moving capillary front, the next step would be to scale up results to describe wetting and non-wetting flow at macroscopic scales. It should then become possible to predict the sorptivity of materials as a function of the microgeometry and wetting properties of fluids.

4. DIFFUSION

To predict the durability and make quality assessments of HPC it is crucial that the diffusive transport of ions in HPC is well understood. In this section we will review basic concepts concerning diffusive transport and discuss a variety of methods used to measure the diffusivity of ions or molecules in concrete.

4.1 FICK'S FIRST AND SECOND LAW

The diffusion of ions or molecules is the result of their random motion in a medium. As a ion or molecular species diffuses there is a tendency for it to move from regions of higher concentration to regions of lower concentration. This phenomena is described by Fick's first law [6,7]:

$$J_D = D\nabla C \tag{29}$$

where J_D is the diffusive flux density, D is the diffusion constant in units of m^2/t, and C is the concentration in units of gm/l. The time evolution of the concentration is obtained from the divergence of the flux density:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{30}$$

Equation 30 is also known as the diffusion equation or Fick's second law. Clearly, D depends on the microstructure in which the material is diffusing in. In a simple test scenario to determine D, one places a mortar or concrete specimen in contact with a constant chloride concentration solution. The concentration of chloride as a function of depth in the specimen is then measured. An apparent diffusion coefficient D_{eff} is

then determined by a fit to solution of eq. (30) with appropriate boundary conditions. If, for example, the concentration at the solution/specimen boundary, C_b, is taken to be a constant and $C=0$ at $t=0$ elsewhere (the specimen is assumed to be infinite in length), the solution of the above equation with the given boundary conditions is

$$C(t)=C_b(1-erf(\frac{x}{2(D_{eff}t)^{\frac{1}{2}}})) \tag{31}$$

where erf is the well-known erf function available from standard mathematical tables or computer programs.

For cement pastes and mortar, typical values of D_{eff} for chloride ions range from about 0.1 to $20\times10^{-12}m^2/sec$. Lower values of diffusion coefficients are reported for concretes made with silica fume or as w/c ratio decreases from 0.6 to 0.4 . An empirical formula, $\log_{10}(D_{eff})=6(w/c)-13.84$, gives a reasonable estimate of D_{eff}. in units of m^2/sec [53]. In general, diffusion coefficients for other dissolved ions are close to that for chloride ions, although there are some exceptions. For more complex mixtures and at lower w/c ratios the above empirical formula may not be sufficiently accurate. For instance, it does not take into account the effect of the interfacial zone which can increase the diffusivity for a given w/c.

4.2 DIFFUSION CELL MEASUREMENT

The diffusion cell [54] monitors concentrations of ions on opposite sides of a thin slice of material sandwiched between two solutions with ion different concentration (see figure 3). The diffusion coefficient may be obtained by monitoring the concentrations in a cell with use of the following equation:

$$D=\frac{V_oL\log_e(1+\frac{C_B}{C_A-C_B})}{A(t-t_o)} \tag{32}$$

where C_A and C_B are the concentrations of the diffusing material at the inlet and outlet of the porous medium. The cross-sectional area is given by A, V_o is the volume of the outlet region and t_o is the initial time. For HPC, the time period needed to make an accurate determination of D may be of order several weeks or more.

4.3 DRIVEN DIFFUSION

4.3.1 ADVECTION DIFFUSION EQUATION

In the case where there is advection in addition to diffusion, the spread of a solute (dispersion) is described by the advection diffusion equation [7]:

$$\frac{\partial C}{\partial t}+\vec{V}\cdot\nabla C=D\nabla^2 C \tag{33}$$

A dimensionless number characterizing the competition between diffusion and advection is the Peclet number $Pe = \langle V \rangle L/D$ where L is a length scale which depends on the pore structure [6,55]. When Pe is $>> 1$, advection dominates, and when Pe $<< 1$, diffusion dominates the spread of the solute. In general, Pe is small for concrete. However, in media with a broad range of pore sizes such, as in a fractal porous medium Pe may be large [55]. Another example would be dispersion through a crack where the size of the crack becomes the characteristic length scale and flow velocities may be higher [55,56,57]. Presently, very little is know about the role advection plays in hydrodynamic dispersion through concrete.

4.3.2 ELECTRICALLY-DRIVEN DIFFUSION

Another interesting approach to estimating the diffusivity of chloride ions in HPC is to measure the dispersion of a dilute solution of ions when driven by an applied electric field [58,59,60]. Diffusion coefficients obtained by this method are reported to be in good agreement with those obtained by typical diffusion cell measurements. Such methods may hold promise for determination of the diffusion coefficient of chloride ions in HPC where lower porosities (hence much lower diffusion coefficients) imply much longer measurement times. Electrically-driven diffusion is described by

$$\frac{\partial C}{\partial t}+\vec{V}_i\cdot\nabla C=D\nabla^2 C \tag{34}$$

The ion velocity, V_i, driven by an electric field, is given by $V_i = \nu zFE$, where ν is the ion mobility, z is the ion charge number, F is Faraday's constant and E is the electric field. The solution of the above equation assuming constant concentration C_0 at the

inlet and a sample of infinite length is [58]:

$$C=\frac{C_o}{2}\left[e^{ax}erfc\left[\frac{x+aDt}{2\sqrt{Dt}}\right]+erfc\left[\frac{x-aDt}{2\sqrt{Dt}}\right]\right] \tag{35}$$

where a = zFE/RT. Note that, in the limit of E = 0, the above equation is the same as eq. (31). An improvement to the above analysis would be to explicitly include the loss of a diffusing material due to absorption or chemical interaction with the constituents of concrete. Also, to properly use such methods it is important to understand the chemistry of electro-osmosis and ionic migration in cement paste and concrete.

4.4 DIFFUSIVITY PREDICTED BY ELECTRICAL CONDUCTIVITY

The conductivity of a material is given by Ohm's law [6,7]:

$$\vec{j}=\sigma\vec{E} \tag{36}$$

where j is the current density, σ is the bulk conductivity, and **E** is the electric field due to an applied potential difference. The application of a potential difference across a concrete sample has been used to protect steel reinforcing bars in concrete by driving out chloride ions. Knowledge of the conductivity of materials is also important because it can be used to determine the relative diffusivity of an invading material by the Nernst-Einstein relation [61]:

$$\frac{D_{eff}}{D_o}=\frac{\sigma_{eff}}{\phi\sigma_o}$$

Where D_o is the diffusivity of a material in solution and D_{eff} is the diffusivity of the same material in the pore space. Similarly σ_o is the conductivity of the salt solution of interest, e.g., sodium chloride and σ_{eff} is the conductivity of the porous medium when saturated with the same species. The ratio σ_o/σ_{eff} is also know as the formation factor. The porosity, ϕ, is included to account for the diffusion in the pore space only. The ratio of the conductivities is also know as the reciprocal of the formation factor. In general, conductivity measurements should be easier to perform and less time-consuming than the direct measurement of the diffusion of a materials in concrete.

In making direct measurements of conductivity care must be taken in accounting for the impedance of the electrodes. A sufficiently large voltage drop may be needed to reduce this effect. Another approach to reducing the effects of polarization would be to use a multi-probe set-up (three or four probes) when measuring conductivity.

4.5 IMPEDANCE SPECTROSCOPY

Impedance spectroscopy (IS) [62,63,64] may be a useful method for determining the conductivity of fluid saturated concrete. It has some advantages over presumably simpler and direct current measurements. For instance, in the case of two-probe measurements, IS can separate voltage drops associated with the bulk sample and the electrodes. Ideally, if concrete behaves as a simple parallel RC circuit in series with the electrodes having it's own impedance, then the total impedance is

$$Z_T = \frac{R_b}{1 + i\omega R_b C_b} + \frac{R_e}{1 + i\omega R_e C_e}$$

where R_b and C_b are the bulk resistance and capacitance, and R_e and C_e are the electrode resistance and capacitance. Figure 4 shows a plot of the real and imaginary impedance for the above circuit. The dip corresponds to the resistance of the bulk which is taken to be much less than that of the electrodes. Such an approach can reduce the effect of the electrodes to more accurately determine the conductivity of concrete. Again, with knowledge of the solute diffusivity and conductivity, the diffusivity of ions in cement-based materials may be determined using the Nernst-Einstein relation.

4.6 TIME-DEPENDENT DIFFUSIVITY

Recent studies [46] have indicated a possible dependance on time of the effective diffusion coefficient where D_{eff} scales as $D_i t^{-m}$ where D_i is an initial diffusion coefficient and m is an empirical coefficient which is strongly dependent on w/c and initial curing. Analysis of data indicate that, over a period of a few months, D_{eff} can decrease by a factor of two. However, a problem with such analysis is that at long enough time it predicts that D_{eff} asymptotically goes to zero which is unphysical and therefore is probably a transient effect albeit over time scales of perhaps a few years. Another problem with the above suggested scaling is that the dimensions are not properly accounted for. Perhaps a more suitable scaling form would be $D_{eff} = D_i(t/T_o)^{-m} + D_\infty$ where T_o is an intrinsic time scale and D_∞ is the asymptotic value of the diffusion

constant as t approaches infinity. It should also be pointed out that time dependence of permeability of other transport properties has been reported. Further research is needed to find a suitable scaling approach.

Also, the ingress of chlorides into portland cement-based materials is known to involve reaction as well as diffusion. For instance, chloride and sulfate may react with aluminate hydrates to form compounds such as chloroaluminate and sulforaluminate. Such reactions would lower the measured diffusivity and in fact have been interpreted as implying a time-dependent diffusion coefficient.

Another important issue is how does the saturation of concrete affect the diffusivity of chlorides and sulfates [65,66]. The above analysis, in general, depends on the pore space being fully saturated. In many cases this may not be true especially close to the concrete surface. Furthermore, over long time scales, the saturation may vary depending on a number of environmental factors. Again, as in the case of relative permeability, more research is needed to understand conductivity and diffusion in partially saturated conditions to better estimate the role these transport properties may have in degradation processes and in the prediction of service life.

4.7 MODELING OF DIFFUSION-BASED PROCESS

Greater computer memory and speed make possible large-scale three-dimensional simulations of diffusion in complex pore spaces. While finite difference (or finite element) methods have been utilized to study the diffusion of materials in a variety of model porous media, diffusion in large complex pore structures may be more suitably studied using random walker techniques [13]. The advantage of random walker techniques is that they require relatively small computer memory allowing for simulations of very large systems. A time-dependent diffusion coefficient, D(t), is defined, by keeping track of the mean squared displacements of the walkers (in three dimensions):

$$D(t) = \frac{\langle |r(t) - r(0)|^2 \rangle}{6t}$$

where r is the position vector of each walker. At long times, D(t), approaches the diffusivity of the porous medium. The relative diffusivity may also be obtained from the numerical determination of conductivity and application of the Nernst-Einstein relation. Of course, one may also obtain the conductivity of a porous medium by determining the diffusivity first and then using the Nernst-Einstein relation. More detailed simulations of different processes such as reaction and absorption of chemical species under a variety of conditions are now possible. Such simulations will aid interpretation of experimental data. By coupling diffusion simulations with

computational studies of fracture it should be possible to improve predictions of service life and yield information about the strength of materials as a function of environmental exposure to damaging elements.

5. STANDARD TEST METHODS : PENETRABILITY OF CHLORIDE IN CONCRETE

The ingress of chlorides, acids, and sulfates by diffusion through an aqueous phase frequently leads to the degradation of concrete [45,46,47,48]. Several standard tests used to evaluate the durability of concrete, such as the rapid chloride permeability test and the ponding test [49,50,51,52], give estimates of the penetrability of chloride ions through concrete.

5.1 AASHTO PONDING TEST

A commonly used standard test to determine the ingress of chlorides into concrete in a somewhat realistic situation is the so called ponding test (AASHTO DESIGNATION T 259-80 (1990)) [49]. Basically, a specified solution of chloride is placed on top of a diked section of a concrete slab. The penetration of chloride over time is then monitored by taking cores of various depths and measuring the amount of acid soluble chloride as a function of depth. Since the overall chloride ingress is slow such tests are designed to take 90 days. It is not clear how the ponding test separates capillary effects from pure diffusion. Diffusion alone will only take place in the fully saturated case. Partially saturated materials should produce smaller diffusion coefficients since there is less saturated pore space to move in. However, samples are typically dried for two weeks before the ponding test so that capillary effects will significantly increase the ingress of chlorides. It is important, when preforming such measurements, that it is understood what transport mechanism the experimenter is truly characterizing. In fact, instead of attempting to correlate the ponding test with the rapid chloride permeability test, as is commonly done, it may make more sense to correlate the ponding test with sorptivity measurements.

5.2 RAPID CHLORIDE PERMEABILITY TEST

The rapid chloride permeability test [5] is widely used to determine the resistance of concrete to the penetration of chloride ions. In this test a concrete specimen is immersed in a saturated sodium chloride solution. A 60 Volt potential drop is applied across the specimen and the total charge passed over a period of 6 hours is monitored and related to the chloride permeability. While this test is has been approved as a standard by AASTO and ASTM, it has recently been subject to much criticism. For instance, in the rapid chloride test, the total current measured is due to several current carriers, hence the transference number for chloride must be known to better interpret experimental results. Also, any reactions of chloride with the cement paste, e.g.,

aluminate hydrates, need to be taken into account. Rapid chloride permeability testing can induce changes in the pore structure (polarization causes temperature to increase and hence accelerate hydration) modify the resistivity of concrete specimens. Ohmic heating may also disturb the local flow of current.

Other criticisms are that the rapid chloride permeability test does not really measure permeability (hence a misnomer) and that it has been misused when attempting to correlate the total charge passed to chloride penetrability as defined by the ponding test. One the other hand, recent studies have indicated that the rapid chloride permeability test may be used to obtain the bulk conductivity of concrete if one uses the total charge passed over short a duration in order to avoid polarization and heating effects [59]. Clearly, further research is needed to better determine the utility of the rapid chloride test for estimating the service life of concrete.

6. MICROSTRUCTURAL MODELS/ X-RAY TOMOGRAPHY

Major progress has been made in the development of computational models for the simulation of transport in mortars and concrete [13,67]. Their utility is that one may gain an understanding, at a fundamental level, of the key microstructural factors which control transport in concrete. Although concrete is composed of pores and aggregates, having many length scales, which cannot be accurately represented in toto, it is possible to describe transport in concrete by use of scale-up methods. For instance, realistic digital image-based models of cement paste have been developed with which calculations of its transport properties can be carried out. Results from these simulations can then serve as input to model transport at the coarser level of the mortar. Results from the mortar level calculations can then be used as input to model concrete where aggregates are now included as part of the microstructure.

Recently, X-ray micro-tomography [68,69] techniques have been utilized to create three-dimensional images of mortars (see figure 5). Using these state-of-the-art methods, length scales down to approximately one micrometer can be probed revealing a wealth of detailed microstructure. The key problem in X-ray tomography imaging is identifying the separate phases such as sand grains, air voids, cement paste and other features such as formation of cracks and perhaps ettringite resulting from sulfate attack. For instance, certain phases such as cement and sand produce signals that do not strongly differ. Improvements in image processing techniques should overcome these difficulties. With three dimensional X-ray micro-tomography images available it should be possible to carry out transport calculations such as diffusion and sorption on realistic microstructures. Further, by properly tagging an entering material it should be possible to experimentally verify simulation methods for use in modeling the degradation of cement-based materials.

7. RECOMMENDATIONS FOR FUTURE RESEARCH

A careful analysis of diffusive and capillary transport in conventional and high performance concrete is needed since they are the primary transport mechanisms in concrete. Both experimental and theoretical studies are needed to provide a database and improve our understanding of these transport mechanisms. Also, diffusion in a partially saturated porous media needs to be better understood in order to make more reliable estimates of the service life concrete. Experimental methods need to be evaluated to determine the appropriate procedure for measuring transport properties. This research should lead to the development of new standard test methods to evaluate the transport properties of concrete. In order to better predict the service life of concrete it is also important to directly relate transport to degradation processes by comparing the ingress of materials over time with, for example, the strength of the concrete.

8. CONCLUDING REMARKS

In summary, we have presented a review of the current knowledge of transport in concrete. Due to its microstructural complexity, the understanding of transport in concrete is of fundamental interest and remains a great challenge. Results from the research of concrete's transport properties should increase its utility and lead to better estimates of its service life. The development of standard test methods to measure transport in concrete will help lead to more objective criteria for its quality assessment. Ultimately, progress in concrete research will lead to the reduction of costs in the building and rehabilitation of concrete structures and increase their service life.

9. ACKNOWLEDGMENTS

The author would like to thank, Dale Bentz, Jack Douglas, Chiara Ferraris, Geoffrey Frohnsdorff, Edward Garboczi, Ken Snyder, Paul Stutzman, Rachel Detwiler, and Pozen Wong for useful conversations. The author would especially like to thank James Clifton for many careful readings of the text and for making numerous useful suggestions.

TABLE OF SYMBOLS

A	cross section area
C	capacitance
c	concentration
c_{kt}	Katz-Thompson constant
D	diffusion constant
d_c	critical diameter
$\mathbf{E}$	Electric field
F	formation factor
F_α	source or sink term associated with fluid labeled by α
$\mathbf{J}_e$	electric current density
$\mathbf{J}_D$	diffusive flux density
$\mathbf{J}_f$	fluid current
g	gravitation constant
K	permeability
K_h	hydraulic conductivity
K_θ	water content dependent permeability
$k_{r\alpha}$	relative permeability
L	sample length
L_{ab}	Onsager coupling
M	amount of absorbed fluid
P	pressure
q	volumetric flux of fluid
R	resistance
S	degree of saturation
S_f	sorptivity
s	specific surface
t	time
$\mathbf{V}$	fluid velocity
V_{cl}	contact line velocity
V_f	volumetric flow rate
Z	impedance

γ	surface tension
θ	water content
θ_c	static contact angle
θ_d	dynamic contact angle
κ	curvature
μ	viscosity

ρ	density
σ	conductivity
τ	life time of random walker
Φ_e	electric potential
ϕ	porosity
Ψ	capillary potential
ω	angular frequency

TABLE OF FIGURES

Figure 1. Microstructure model of concrete. The dark circular areas represent aggregate (sand and rock). The light thin region surrounding the aggregate represents the interfacial zone. The light grey section of a circle in the upper right corner represents a rebar. The remaining darker regions represent cement paste. This figure was provided courtesy of Dale P. Bentz of NIST.

Figure 2(a). A static contact angle, θ, defined where the fluid/fluid interface meets the solid surface, is obtained as the result of the balance of surface tension forces, γ. In figure 2(b) a pressure drop results from the curvature, $\kappa = \kappa_1 + \kappa_2$ (where the subscripts refer to the principal radii of curvature) in the interface.

Figure 3. Diffusion cell. The C corresponds to concentration, L is the thickness of the sample with cross section area A.

Figure 4. Complex impedance curve for the illustrated circuit with resistances R and capacitance C. Z' and Z" are the real and complex impedances, respectively.

Figure 5. Image of an ASTM C109 mortar, subject to sulfate attack, obtained using X-ray microtomography. The inner dark regions represent air voids, the dark grey regions are sand grains, the light grey regions between sand grains is cement paste and the small white regions are likely calcium hydroxide or possibly gypsum or ettringite.

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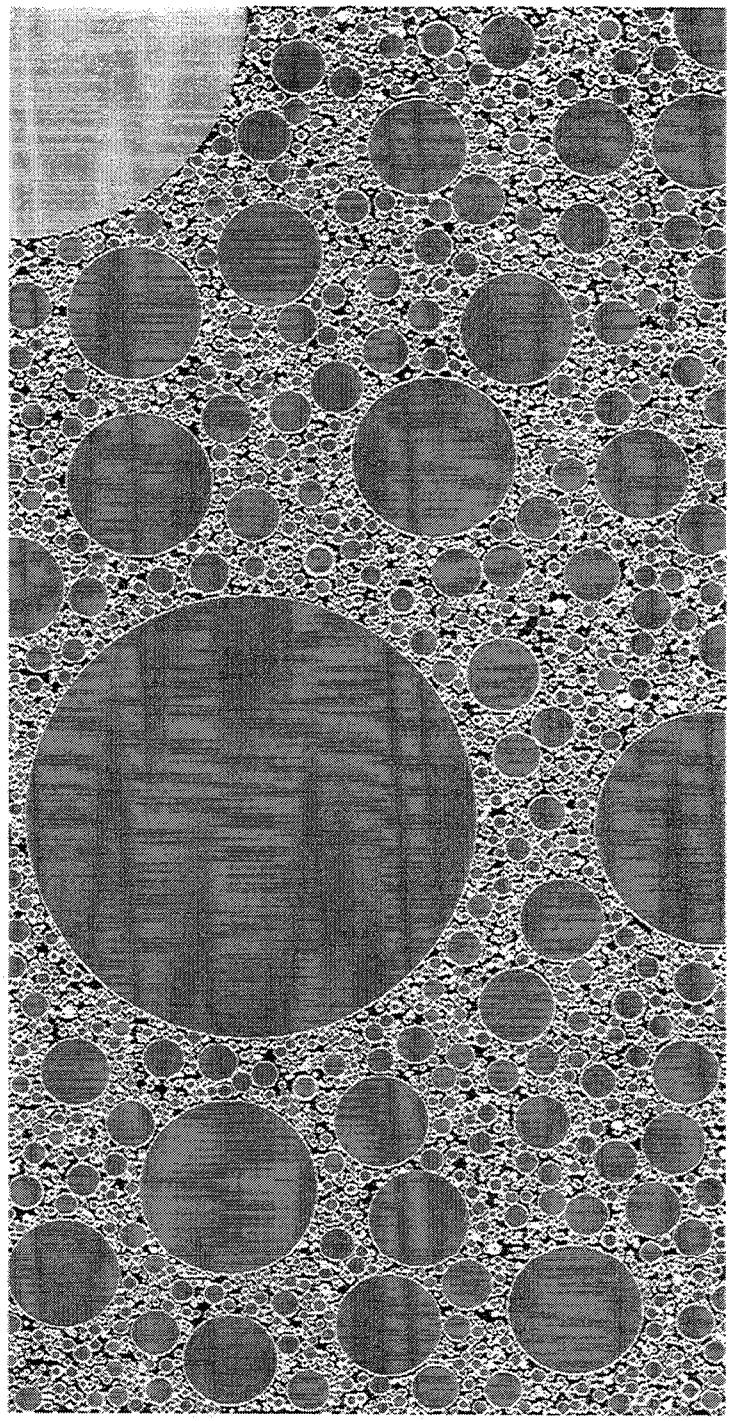
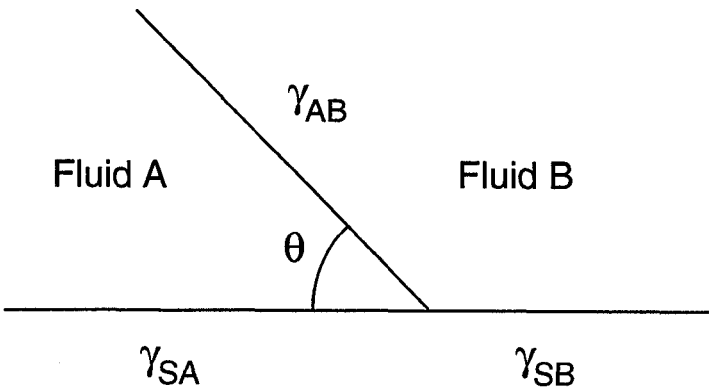
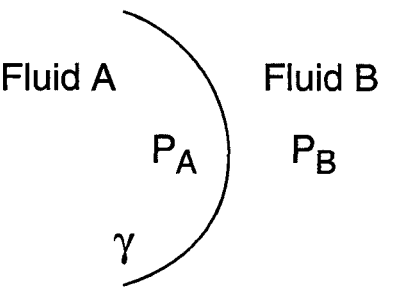


Figure 1. Model of concrete microsturcture.



Young's Equation: $\gamma_{AB} \cos \theta + \gamma_{SA} - \gamma_{SB} = 0$



Laplace's Formula: $P_A - P_B = \Delta P = \gamma (\kappa_1 + \kappa_2)$

Figure 2. Surface tension forces.

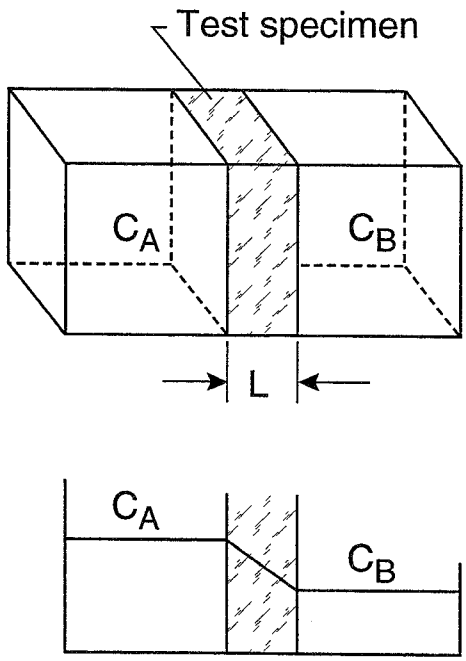


Figure 3. A diffusion cell configuration

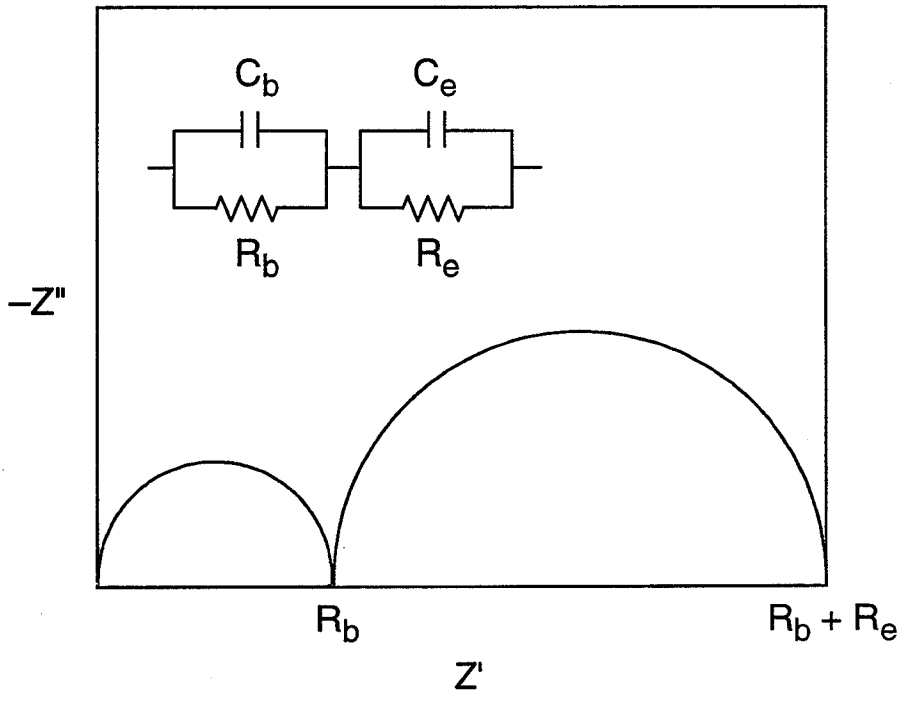


Figure 4. Impedance spectroscopy

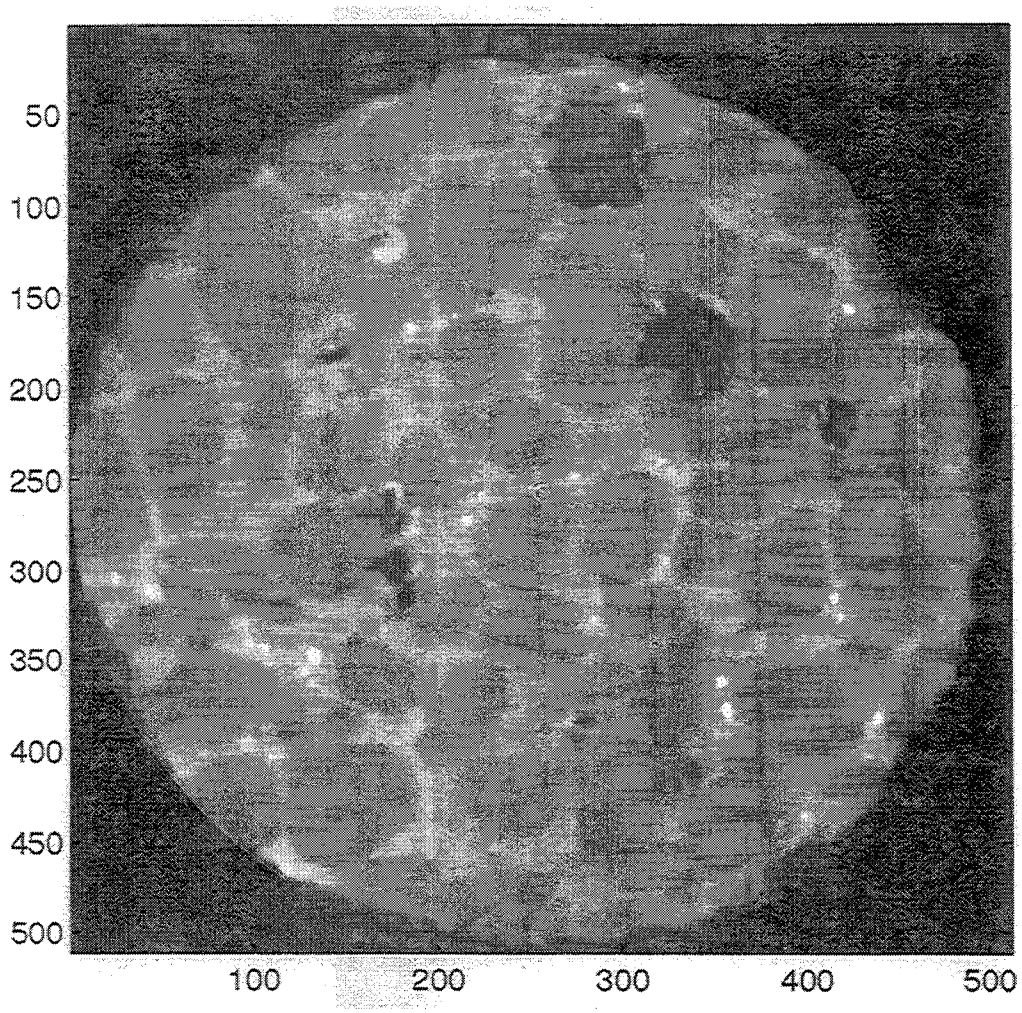


Figure 5. X-ray tomography image of an ASTM C109 mortar.