

PII S0008-8846(97)00052-5

CAPILLARY TRANSPORT IN MORTARS AND CONCRETE

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(Refereed)
(Received May 23, 1996; in final form February 25, 1997)

ABSTRACT

Results are presented of a study concerning capillary transport of water in concretes and mortars as a function of water/cement ratio, sand size distribution, and curing. Our studies indicate that the capillary sorption (1) of water in concrete exhibits a complex time dependence. At early times, of the order of one hour, the total water uptake increased with the $t^{1/2}$ behavior of typical capillary sorption theories. At longer times, of the order of tens of days, a slow crossover regime is seen as the rate of capillary suction decreases. At very long times, of order hundreds of days, a slower uptake which may be driven by the capillary forces in the smaller gel pores is found. Again the $t^{1/2}$ behavior is recovered but with a much smaller sorptivity coefficient. We describe an empirical fitting form for data which describes capillary suction at both short and long times. Aspects of the experimental design including sample drying and exposure to air are discussed. The utility of service life predictions from such measurements is discussed. ©1997 Elsevier Science Ltd

Introduction

Moisture transport in porous media plays an important role in a wide variety of processes of environmental and technological concern, such as the degradation of building materials (e.g. mortar and concrete), the spread of hazardous wastes in the ground, oil recovery, and the containment of nuclear wastes (2),(3),(4),(5). The presence of water in building materials can lead to cracks which result from freeze/thaw cycles or, in combination with very low permeabilities, to the spalling (6) of high performance concrete exposed to fires. In addition, the invasion of water in building materials provides a mechanism and path for the penetration of deleterious materials like chloride and sulfate ions. While the primary transport mechanisms by which chloride and sulfate ions ingress concrete are diffusion and capillary action, diffusion alone can be a very slow process, hence it may be that capillary transport, especially near an unsaturated concrete surface, is the dominant invasion mechanism. Clearly, an understanding of moisture transport in concrete and mortar is important to estimate their service life as a building material and to improve their quality.

Presently, the only standard test for the ingress of chlorides into concrete which, at least in part, depends on capillary transport, is the so called "Ponding Test" (7). In this test, a specified solution of a chloride salt is placed on top of a diked section of a concrete slab. The penetration of chloride ions is then monitored by taking cores and measuring the amount of acid-soluble chloride as a function of depth over a period of about 90 days. Since the concrete slabs are typically dried for two weeks prior to initiation of the ponding test, it is likely that capillary transport is the main driving mechanism for the chloride ion transport, at least at early times as the surface pores rewet. It is interesting that there have been attempts to correlate another standard test, the rapid chloride test (8), with the ponding test although the rapid chloride test is more a measure of the conductivity (or diffusivity) of chloride ions. Indeed, recent studies (9) have shown that such correlations can be weak. Clearly, an improved understanding of moisture transport is needed to separate the contributions of diffusion and capillary action to mass transport in order to better predict the penetration of chloride or other deleterious ions in concrete.

Tests which directly measure the rate of capillary sorption, such as the Covercrete Absorption Test (CAT) (10) and the Initial Surface Absorption Test (ISAT) (11) typically fit the total water uptake to the following equation

$$W/A = St^{1/2} + S_0 (1)$$

where W is the volume of water absorbed, A is the sample surface area exposed to water, S is the sorptivity coefficient, t is time and S_o is a correction term added to account for surface effects at the time the specimen is placed in contact with the water (see the appendix for a more detailed description of this equation). Such tests are made over a period of less than one hour. Clearly, measurements over such short periods of time will only probe surface effects and cannot provide sufficient information for the modelling of capillary transport over longer periods, which is needed for service life prediction.

Further, Equation 1 is based on parallel tube models of porous media (see appendix) and hence cannot accurately model capillary suction in a random porous material like concrete. The pore surface topology is far more complex so that, as the air/water interface moves through the porous medium, there are many orientations of the local interface which may be stable despite the smallness of the pore size. As an example, Figure 1 shows a meniscus, subject to a small applied pressure from below, which is unstable in a narrow pore yet is stable in a neighboring pore. In addition, the above theory of capillary suction applies to the case where the porous medium is initially dry. Clearly, the rate of capillary sorption will depend on the degree of saturation of the porous medium (5). Finally, analysis of the flow through concrete is further complicated by the fact that water can react with the solid matrix, possibly causing a change of the pore structure with time or changing the pore solution composition.

Previous experiments measuring the capillary suction of water in concrete have exhibited conflicting results concerning the time dependence of the total water uptake. Instead of the standard $t^{1/2}$ behavior of simple capillary sorption theories other t^{α} behavior (also called anomalous scaling) (12), (13) where $0.25 < \alpha < 0.5$ has been observed. It has been suggested that this anomalous scaling in concrete is the result of modification of the pore structure due to leaching (15) or further hydration as the water is absorbed. For instance, while hydration will reduce the typical pore size in the cement paste matrix, slowing the sorption of water, leaching opens up pores, making them larger and more connected such that capillary sorption could be enhanced. However, it has not been quantitatively demonstrated how such alterations of the

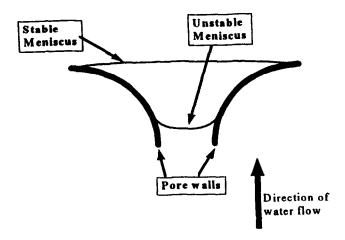


FIG. 1. Stable and unstable menisci in a pore.

pore structure affect a material's sorptivity. In addition, the dissolution of salts may reduce the rate of capillary sorption (14). Finally, as mentioned above, moisture transport in concrete must depend on factors such as the degree of saturation and environmental conditions.

In this paper we present results of a study concerning capillary transport, over periods of about one year, in mortars and concrete. The validity of Equation 1 is tested. Variables considered were the water-to-cement ratio (W/C), sand size distribution, and amount of curing. We discuss several issues concerning sample preparation and boundary conditions. The existence of two different regimes associated with capillary sorption in mortar and concrete was found. An empirical function which describes capillary sorption over much longer periods is introduced. We also discuss the utility of sorptivity measurements for service life prediction.

Experiment

The measurement of water capillary sorption is, in principle, a very simple experiment. After a standard preparation method described below, mortar and concrete cylindrical specimens were exposed to a liquid on one of the plane ends by placing them in a pan as shown in Figure 2. The fluid level in the pan was maintained at a constant height throughout the experiment. At regular intervals, the mass of the specimens were measured using a balance. The amount of fluid absorbed was then calculated and normalized by the cross-section area of the specimen exposed to the fluid.

Compositions of the Mortar and Concrete Mixtures. In our study, we examined a variety of mortar and concrete mixtures. In this paper we will present results for the following mixture compositions. We studied capillary sorption in two mortars: an ASTM C109 (17) mixture (w/c = 0.485, s/c = 2.75) and a second mixture (HPM) where w/c = 0.29 and s/c = 1.4. The maximum aggregate size for these mixtures was about 2mm. We also used two concrete mixtures to compare sorptivity in high and low porosity specimens. Mixture 1 had a w/c = 0.6, s/c = 2.75, and a gravel/cement mass ratio of 1.43. The air content of mixture 1 was 6%. Mixture 2 (HPC) had a lower air content of about 2%, with w/c = 0.36, s/c = 2.02, and a gravel/cement mass ratio of 1.12. The sand was a mixture of four sand grades. In addition, to improve workability,

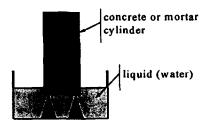


FIG. 2.

Experimental set-up. A mortar or concrete specimen is placed in a tray filled with water. The fluid level is kept constant. The mass of the specimen was monitored to determine the amount of liquid absorbed.

a high-range water reducer (0.09% by mass) was used in mix 2. The maximum aggregate size for the concrete mixtures was about 20mm. The concrete specimen were made about 7 times wider than the maximum aggregate size in order to limit finite size effects due to aggregate size.

Sample Curing and Drying. Before the capillary sorption measurements were made, the specimens were cured in limewater for periods of 1, 7 and 28 days at 20°C. Two methods for drying the samples were used. In the first, the samples were dried in an oven at 50°C until a constant mass was obtained, which took about 20 days. The second method was to air dry (also referred to as "bench dried") samples in a laboratory environment (at 20°C and 30% RH) for four days and then in a desiccator containing a desiccant for three days. Figure 3 compares the sorption of water for the air dried and oven-dried mortar (Mix 1). Clearly the degree of saturation of the material plays a strong role in controlling the uptake of water. Over a period of about 100 days the oven-dried sample absorbed nearly three times as much water as the air-dried samples. Also fits of data to Equation 1 showed that the sorptivity of the oven-dried sample was three times greater than that of the air-dried sample. It is also possible that the

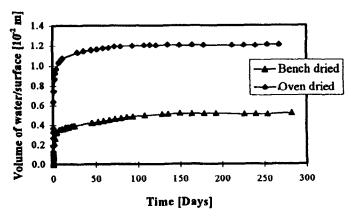


FIG. 3.

The influence of specimen treatment before exposure to water is shown by the rate of absorption versus time.

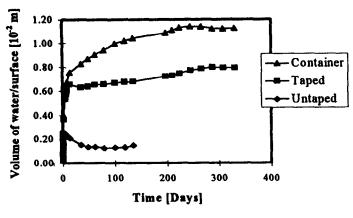


FIG. 4.

The influence of the method of exposure of the specimen to water is shown by the rate of absorption versus time. Container: specimen placed in a box; Taped: sides were covered with tape; Untaped: no protection on the sides and not in a container. All specimens were bench dried before exposure to the water.

oven drying process may have formed some cracks due to drying shrinkage resulting in greater sorption.

Boundary Conditions. We also examined how boundary conditions affect water absorption. In Figure 4, we show the sorption versus time of bench dried samples for the following boundary conditions. Samples were either exposed to air, taped on the sides (with a vinyl tape), or placed in a closed container without taping the sides. Note that the sample exposed to air actually decreased in weight after an initial rise. Since theses samples had been bench dried for a specified time and not to a constant weight they were partially saturated at the start of the capillary sorption measurements. As a result, an observed rapid decrease in the rate of capillary suction coupled with the evaporation of moisture from the samples sides led to a reduction of the samples moisture content after the initial increase. In the other extreme, samples exposed to air but placed in a closed container had the greatest amount of sorption since there was little or no evaporation and moisture could enter from the sides due to the high humidity in the container. We also examined the case of the specimens taped on the sides only versus the case of taping sides and top. We saw only a small difference in the sorption here. However, some of this difference could be due to sample variation. Also, while the vinyl tape was essentially impermeable, the taping procedure did not necessarily produce an air-tight seal since some air could leak along the sides. For the rest of this paper we will only present results of the capillary sorption studied for samples taped on the sides.

Sample Curing/Mix Design. Figure 5 shows the sorption data for an exposure period of over 300 days for the two concrete mixtures at different curing times. We first note that there was a moderate difference in the total water taken up for the different curing periods (about 20%). However, there was more rapid sorption in the samples that had been cured in limewater the shortest amount of time. Table 1 shows the sorptivity coefficient obtained from fits of the data in Figure 5 to Equation 1. Clearly the longer the curing period the smaller the sorptivity indicating that the additional curing has reduced the pore size. Previous studies (18) have

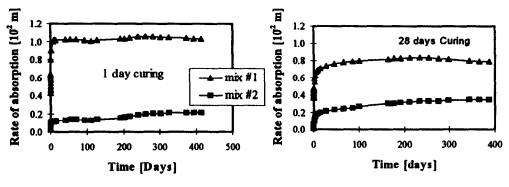


FIG. 5.

Comparison of water sorption for different curing periods and concrete design mix. Mix # 1: normal concrete; Mix # 2: HPC. All specimens were bench dried before exposure to water.

correlated other transport properties like the diffusivity of chloride ions and permeability with curing period. For roughly equivalent curing periods it was found that the chloride diffusivity decreased by about an order of magnitude while the permeability decreased by about two orders of magnitude. Our measured sorptivities were less sensitive to the curing period, decreasing by a factor of about 2 to 3. Scaling arguments may be used to show why permeability decreases much more rapidly with longer curing than sorption does. It has been shown that for cement mortars (18), diffusivity scales as r_c and permeability scales as r_c^3 , where r_c is a critical pore radius based on percolation ideas (18). Sorption in tube models (see appendix) predicts that the sorptivity scales as $r_c^{1/2}$. If effects due to the tortuosity of the porous medium are included, it can be shown that permeability scales as r_c^3 (18). Then sorption should scale more closely with r_c . However, since the initial suction is controlled by the microstructure near the surface it is likely that tortuosity effects are less important explaining why sorption appeared less sensitive to the curing period than diffusivity.

It also appears that the sorption has nearly stopped after 200 days, or so, for the conventional concrete sample. Visual examination of such samples, broken after 400 days of sorption measurements, indicated that they were not fully saturated as the water level was far from the top. However, these samples could have been in equilibrium with the air since they were not

TABLE 1
Sorptivity of Concrete Versus Time Curing. Specimens Were Bench Dried
Before Exposure to Water

	Sorptivity [10 ⁻² m/√days] Time of curing [days] 1 28	
Concrete . Mix		
#1: Conventional #2: HPC	0.67 0.22	0.25 0.12

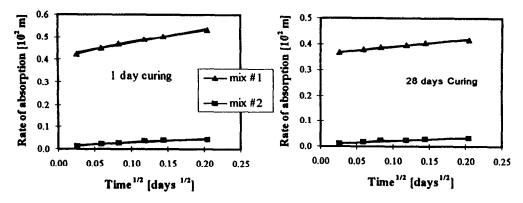


FIG. 6.

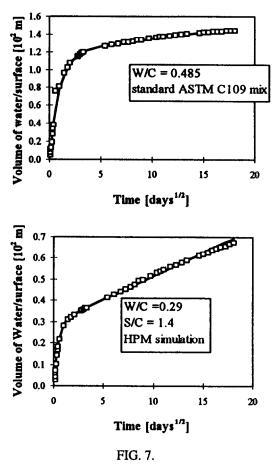
Early time behavior (up to 1 hour) of sorption for different curing periods and concrete design mixtures. All specimens were bench dried before exposure to water.

taped on the top. Such finite size effects will be the subject of further studies. We also note that the amount of sorption can depend on mixture design. For instance, Mixture 2 was designed to produce lower porosity concrete which should result in a lower absorption.

Sorption Versus Time. Let us first consider sorption during initial exposure to water. Figure 6 shows the absorbed water vs (time) $^{1/2}$ for a period of about one hour (for the two concrete mixes). In nearly all cases, we found that the total water absorbed was proportional to $t^{1/2}$ for a period of a few hours. Note that the higher porosity mix is subject to very strong surface effects as the sorption data is offset from zero when t = 0. After a period of about 6 hours, the rate of sorption began to noticeably decrease.

Figure 7 compares sorption data for an exposure period of over 200 days for the oven dried HPM and ASTM mortars. Here, the sorption data is plotted versus $t^{1/2}$. Note that both the short and long time moisture sorptions for the two mortars are consistent with a $t^{1/2}$ behavior but that the sorptivity, S, (slope of the curve) is dramatically different in these regimes, differing by factors of about 30 and 80 respectively. Since $S \sim r^{1/2}$ for a straight tube model, such a difference in sorptivity would correspond to pore sizes differing by a factor of about 900 and 6400 for the HPM and ASTM mortars respectively. Similarly, concrete is noted as having capillary pores of the order of microns and gel pores which may be several orders of magnitude smaller. Simple comparison with sorption theory would then imply that the capillary pores are dominating the sorption process at early times and that at later stages the gel pores limit the rate of flow. However, it is quite possible that, at later stages, the ingress of water may be controlled by moisture diffusion processes (19) as well.

Sorption Function. We now will focus on the issue of mathematically describing sorption as a function of time. In nearly all cases, we found that the water absorbed was proportional to $t^{1/2}$ over short times as described in Equation 1. For periods greater than a day, there was a clear trend away from the $t^{1/2}$ behavior as the rate of sorption decreased. Simple sorption theory based on tube models (see appendix) predicts an exponential decay in the rate of sorption due to gravitational effects. None of our samples exhibited a pure exponential decay. Indeed, the equilibrium height of the water should be tens of meters (see appendix). As a consequence of the large equilibrium height, finite size effects can have an important effect on capillary



Sorption versus square root of days for mortars. The specimens were oven dried until constant weight, just after demolding (1 day curing).

sorption studies concerning concrete. A detailed study of finite size effects will be presented in a future work. Barring finite size effects, the decrease in sorption rate may be due to several factors. First, as mentioned above, as the water invades the pore space it encounters smaller pores hence slowing the rate of sorption. Second, even if the capillary pores form a strongly connected network through the specimen, such as through the interfacial zone (20) around the aggregates where capillary pores may be larger, the ingress of water may still be slowed as the air/water interface relaxes to a stable or metastable configuration in the pore space (Figure 1). Then any further ingress of moisture would be controlled by capillary transport through the gel pores or moisture diffusion in the capillary and gel pores.

It has been recently suggested (14) that as water is absorbed in concrete, calcium hydroxide is dissolved into the pore solution producing a concentration gradient which diminishes the absorption rate. Our own preliminary studies, did not show a significant difference between the sorption of water or the sorption of calcium hydroxide saturated water.

Slow relaxation phenomena and diffusion in complex pore structures having a wide range of pore sizes is often described using the so-called stretched exponential function (21). To model

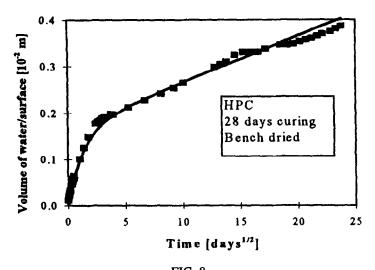


FIG. 8. Fit of equation 13 to HPC data.

the transition from rapid to slow sorption rates we will use the following empirical function which incorporates the stretched exponential function to account for the crossover regime:

$$\frac{W}{A} = C(1 - exp(-St^{1/2}/C)) + S_g t^{1/2} + S_o$$
 (2)

where, as before, W is the volume of water absorbed, A is the cross-sectional area of the water exposed surface, and C is a constant which is related to the distance from the concrete surface over which capillary pores control the initial sorption (and may be most sensitive to finite size effects). The coefficient $S_g << S$ describes the sorptivity in the smaller pores or the effects of moisture diffusion. We constructed this function so that at early stages, in the limit $t^{1/2} < C/S$, expansion of the exponential gives $C(1 - exp(-St^{1/2}/C)) \approx St^{1/2}$ which is the same as Equation 1. At long times, the above equation is dominated by the $S_g t^{1/2}$ term.

Figures 7 and 8 show the fitting of data using Equation 2. Note the good agreement over four decades in time. Reasonably good fits were obtained for all the mix designs as well as for different initial saturations. Table 2 contains some representative values of coefficients for Equation 2 from fits to our data. Note, the effect of the S_o term is negligible when fitting data over very long periods hence we set $S_o = 0$.

One interesting point is that if, instead, the anomalous scaling form $W/A = St^{\alpha}$ is assumed, an anomalous scaling exponent of $\alpha \approx 0.25$ is obtained for the data in Figure 7. However, it appears that this exponent is really due to an initial uptake due to surface effects and the crossover from large to small pore dominated sorption.

At this point it is appropriate to mention a few caveats. First, Equation 2 cannot describe sorption in its entirety in that the additional $t^{1/2}$ term implies the specimen would never stop absorbing water. However, given the slowness of the sorption and the fact that capillary rise in small tubes can reach tens of meters, it is possible that Equation 2 may be usable over very long time periods, up to even years. Second, we were unable to accurately determine all

Bench Dried HPC

Bench dried

28

0

Specimen Curing C S S, S. [10⁻² m] [10⁻² m/√days] [10⁻² m/\days] [10⁻² m] Age [days] 0.4 0.02 0 ASTM mortar 1 0.295 Bench dried ASTM mortar 1 1.2 1.2 0.015 0 Oven dried **HPM** 1 0.295 0.65 0.0221 0 Oven dried 28 0.25 0.009 0 Conventional 0.35 Concrete

0.12

0.01

TABLE 2
Parameters from Equation 13 Fit

the coefficients of Equation 2 over very short periods of measurement (of order a few hours) because the power law term will obviously have a greater impact on predicted sorption at later times. If the effect of the smallest pores (or moisture diffusion) is ignored (i.e., setting $S_g = 0$), simple fits of Equation 2, based on data acquired from the first day, give predictions of sorption within 30% of total sorption values recorded over a period of about one year. To closely predict sorption for long periods (i.e., one year) of exposure, we needed data from ten to twenty days of measurements in order to account for the crossover regime.

0.165

Appealing aspects of Equation 2 include its simplicity and ease of physical interpretation. However, since we did not derive the stretched exponential functional form from basic physical principles, we cannot rule out other "simple" functions that may work as well to describe our data. In addition, it should be emphasized that we have adopted the stretched exponential form to describe the crossover regime in contrast to its typical usage of describing very long time behavior. Further study is needed to determine the accuracy and utility of such a functional form.

Service Life Prediction

Sorptivity tests alone cannot accurately predict the service life of concrete. As we have shown, sorption rates can strongly depend on the degree of saturation and any estimate of service life must make reasonable assumptions about the exposure of the concrete specimen to a variety of weather conditions and wetting-drying cycles. A more general approach may be to consider the capillary diffusivity (5), (22) (see appendix) which relates the rate of sorption to the degree of saturation. Such information may then be used in models to predict moisture transport which account for the environmental exposure of concrete. However, in the determination of capillary diffusivity, we have shown that care must be taken to correctly account for surface effects. Also, estimates of capillary diffusivity made from measurements made over short time intervals will not properly take into account the effect of smaller pores which appear to dominate sorption at long times.

Nevertheless, since the sorptivity of a material should be inversely correlated with its degradability, sorption measurements performed on uniformly prepared concrete and mortar specimens can provide useful information concerning quality control and the determination of which samples are likely to have a longer service life. For instance, sorption measurements could be useful for the determination of frost resistance of concrete by predicting how easily critical saturation is reached.

In addition, our studies indicate that in many cases, sorptivity may be the main controlling factor determining the service life of building materials like concrete. For materials subject to wetting/drying cycles, capillary transport may provide a more rapid means of ingress of chlorides than diffusion and, further, sorption appears to be less sensitive to the curing period than diffusion implying that sorption remains a more robust transport process over time.

Conclusions

A simple empirical fitting form (Equation 2) was suggested that accurately fits experimentally measured sorption data for a variety of mortars and concrete which assumes that pores at two different length scales control the sorption. The anomalous time behavior suggested in some earlier sorption studies may be the result of not taking into account surface effects when the sample is initially exposed to water and the fact that smaller pores probably control capillary suction at longer times. While it is difficult to precisely predict long term trends from measurements taken over very short periods, our data suggests very good estimates, for an exposure period of approximately a year, may be obtained by examining the initial uptake over a period of 10 to 20 days by using Equation 2.

Future studies include the role saturation plays in sorption, the continuation of sorption measurements to check longer time behavior, and the examination of how other transport properties correlate with sorption.

Acknowledgements

The authors acknowledge support for this research by the National Institute of Standards and Technology Program on High-Performance Construction Materials and Systems. We would like to thank John Winpigler for technical assistance in data acquisition, Dale Bentz, Doug Burch, James Clifton, Edward Garboczi, and Ken Snyder for making many useful comments.

Appendix: Capillary Transport in a Tube

When two dissimilar materials, such as two immiscible fluids or a fluid and a solid, are brought into contact with each other, surface tension forces arise due to the energy needed to form an interface. At the point where a fluid-fluid interface meets a solid, a contact angle, θ , is defined by the planes tangent to the fluid-fluid interface and the fluid-solid interface (Figure 9). When the surface tension forces are balanced a static contact angle (16) is obtained such that Young's Equation is satisfied:

$$\gamma_{bs} - \gamma_{as} = \gamma_{ab} cos\theta \tag{3}$$

where γ_{ab} is the surface tension between the two fluids, γ_{as} is the surface tension between fluid a and solid, and γ_{bs} is the surface tension between the fluid b and solid. Surface tension forces can also create a pressure drop ΔP across the interface between two immiscible fluids. This pressure drop is described by Laplace's law:

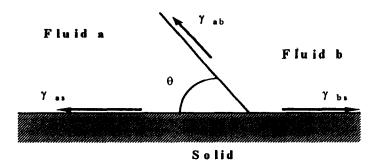


FIG. 9.

A static contact angle θ , defined where the fluid/fluid interface meets a solid surface, is obtained as the results of the balance of surface tension forces.

$$\Delta P = \gamma \kappa. \tag{4}$$

where γ is the surface tension and κ is the average curvature of the interface. In order to pin an interface, which approximately forms a spherical cap, in a tube of radius r, it can be shown that the following pressure difference must be applied (16):

$$\Delta P = 2\gamma \cos\theta/r. \tag{5}$$

Otherwise, capillary transport results from the unbalanced surface tension forces between the fluid-fluid and fluid-solid interfaces.

In general, the average velocity, V, of the fluid, in a porous medium, may be obtained from Darcy's law

$$V = -\frac{K\Delta P}{l\mu} \tag{6}$$

where K is the permeability, μ is the viscosity, and l is the length over which the pressure drop ΔP is measured. For a capillary tube $K = r^2/8$ so that

$$V = \frac{r}{4\mu l} \gamma \cos\theta. \tag{7}$$

where we ignore gravity (assuming a horizontal tube) and effects due to the details of the contact line motion. Since V scales as the tube radius, porous media with smaller pores will absorb a liquid more slowly. Integrating Equation 5, where we take V = dl/dt, we obtain

$$l = \sqrt{\frac{r\gamma cos\theta t}{2\mu}} \equiv St^{1/2} \tag{8}$$

where S is the sorptivity.

For the case of a vertical tube in a gravitational field the meniscus will reach an equilibrium height, h_{∞} , given by $h_{\infty} = 2\gamma_{ab}cos\theta/(r\rho g)$ where g is the gravitational constant. For a tube of radius 1 micrometer (a typical size of the larger capillary pores in many concretes), and $\gamma_{ab} \approx 7.2 \times 10^{-2}$ N/m for a water/air interface at room temperature (16), and assuming water

is perfectly wetting (cos $\theta = 0$), $h \approx 14$ meters. Also a simple analysis based on the Washburn equation (16) shows, at long times, that

$$h \approx h_{\infty}(1 - exp(-\alpha t)) \tag{9}$$

where $\alpha = r^2 g/(8\mu h_{\infty})$.

If one assumes a straight parallel tube model of porous media, then a similar approach may be applied to estimate the water sorption. Here, the permeability of the tubes are replaced with the permeability of the porous medium. Therefore, at early stages, the moisture absorbed should be described by

$$W/A = St^{1/2} + S_0 (10)$$

where W is the volume of water absorbed, A is the sample surface area exposed to water, S is the sorptivity and S_0 is a correction term added to account for surface effects at the time the specimen is placed in contact with the water.

Of course, a random porous material like concrete cannot be accurately modeled as a collection of tubes. In addition, the above theory of capillary suction applies to the case where the porous medium is initially dry. Clearly, the rate of sorption will depend on the degree of saturation of the porous medium. A more general macroscopic description of capillary suction is given by the following equation (5):

$$\frac{d\theta}{dt} = \nabla D \nabla \theta \tag{11}$$

where the water content, θ , is the volume fraction saturated at time t, and D is the capillary diffusivity. Note D must depend in a complicated way on the pore structure and capillary pressure, which in turn depends on the water content. A simple empirical form, commonly used to describe moisture transport in soils and construction materials is

$$D(\theta) = D_0 exp(B\theta_r) \tag{12}$$

where $\theta_r = (\theta - \theta_0)/(\theta_1 - \theta_0)$, θ_0 is the initial saturation, θ_1 is the saturation at the fluid-solid interface, and B and D_0 are empirically determined constants.

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