Cement & Concrete Composites 26 (2004) 75–79

Cement & Concrete Composites

www.elsevier.com/locate/cemconcomp

An explanation for the unsaturated state of water stored concrete

S. Chatterji *

Carl Bernhardsvej 13B; st. 4, DK-1817 Frederiksberg C, Denmark

Received 21 February 2002; accepted 29 October 2002

Abstract

Concrete technologists generally assume that under-water concrete structures are fully saturated with water. Powers was the first to show that cement paste, which has been stored under water for 220 days, is still unsaturated. Since then, a number of workers have confirmed Powers' observation for cement and concrete using various techniques. However, no explanation of these observations is available. In this paper, the above observations have been explained on the basis of hydrodynamics of water flow through a porous medium. Propagation of the saturation front, within the structure, is proportional to the square roots of pore radius and elapsed time after contact with water. The relevant pore radius is related to the relative humidity within the structure by Kelvin's law. This explanation predicts that a concrete structure with a water/cement ratio of about 0.6 or below will remain unsaturated for a very long time. The implications of this continued unsaturation on freeze-thaw durability; creep under compressive load and the depth of chloride ion penetration in concrete have been discussed.

Keywords: Mass concrete; Unsaturation; Long-term; Hydrodynamics; Properties

> "We shall sing something simple. Something old something new. Something for me something for you".
>
> An old BBC signature tune.

1. Introduction

It is a general assumption in the cement and concrete fields that a properly cured concrete or an underwater concrete is fully saturated [1]. This assumption, implicit or explicit, plays an important part in many evaluations of lifetime performance (cf. Ref. [2]). However, in 1947 Powers showed that 1 × 7 inch neat cement paste cylinders remain unsaturated even when stored under water for 222 days [3]. Powers had also observed that the inner parts of these cylinders were looking dry. These observations seemed to have gone unnoticed for a long time. In 1964, an X-ray diffraction test showed that in neat paste of ground clinker ($w/c = 0.6$) C_4AH_{13} forms instead of C_4AH_{19} [4]. This again indicated that the relative humidity within the ground clinker paste was below 85% and the sample was unsaturated. In recent years a number of reports have been published showing that the relative humidities inside concrete samples are lower than 100% even though the samples were stored under water indicating unsaturated states of concrete [5,6]. Persson gives extensive data on this point [6]. The specimen size used by Persson was 1 m in diameter and 0.1 m thick. Thick layers of epoxy resin sealed the flat surfaces leaving only the peripheral surface for water ingress. The relative humidity was measured at mid thickness at 50, 150 and 350 mm from the exposed surface. The water/cement ratios of the concrete samples varied from 0.55 to 0.22. In these samples, the relative humidity decreased from about 0.98 to 0.77 even after 450 days under water curing. During this time interval, the variation in the relative humidity at 50, 150 and 350 mm from the exposed face is very little. It is of interest to note that the relative humidity decreases with a lowering of w/c ratio i.e. with narrowing average pore sizes within concrete samples.

Chloride ion penetration, from outside sources, within mass concrete also shows a similar unsaturated state of mass concrete. It has been observed that after a comparatively short interval of rapid chloride penetration, the rate drops considerably. This drop in the rate

---

* Tel./fax: +45-3321-0332.

E-mail address: chatterji@get2net.dk (S. Chatterji).

0958-9465/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0958-9465(02)00124-5

has been explained as due to the unsaturated state of mass concrete [7]. A recent Danish investigation on the chloride penetration in existing under water structures also shows a similar trend of initial rapid penetration followed by a very slow rate [8]. In these cases also inside of the structures were unsaturated. The chloride fronts coincided with the water saturation fronts.

This long term unsaturated state of under water concrete needs an explanation. The main object of this paper is to propose an explanation for this long-term unsaturation of mass concrete.

2. Basic considerations for water ingress in concrete

A hardened concrete is a hydrophilic porous material i.e. water wets concrete. At first approximation, the pores in a concrete may be considered as capillary tubes of different radii. These capillaries are convoluted in such a fashion that their free ends coincide with the up-stream and down-stream free ends of the structure. However, the actual lengths of these capillaries are much longer than the nominal depth of the structure. Within the body of the structure, these capillaries may have connections with each other. To examine the rate of water penetration in a concrete structure we need to know (i) the driving pressure, (ii) radii of relevant interconnected pores and (iii) the pore characteristics i.e. interconnected pore volume and the actual path-lengths of the capillaries.

2.1. The driving pressure

Consider a long and narrow capillary of radius r in contact with a large reservoir of water. Water will creep in the capillary forming a water meniscus. Due to this meniscus formation there will be a pressure difference, $\boldsymbol{p}_c$, across the water–air interface within the capillary. The pressure difference, $\boldsymbol{p}_c$, is given by Eq. (1)

$$\boldsymbol{p}_c = 2\gamma \cos\theta / r \qquad (1)$$

where γ is the specific surface energy of water, and θ is the contact angle at the water–vapour interface within the capillary [9]. If $\cos\theta$ is positive then the liquid wets the capillary surface and penetrates the capillary under tension created by the curvature of the air–liquid interface. If $\cos\theta$ is zero or negative then the liquid does not wet the capillary surface and has to be pressed into the capillary. In the water–concrete system θ is zero so $\boldsymbol{p}_c$ is equal to $2\gamma/r$. This pressure difference drives water in any concrete structure. This means that in concrete $\boldsymbol{p}_c$ is, in most cases, higher than externally imposed pressure. It appears that for a good quality concrete an externally imposed pressure equivalent to a 1 m high water column could be neglected. This can be seen from the following. For a capillary of 1 μm radius $\boldsymbol{p}_c$ is $(2 \times 72 \times 10^{-3}/10^{-6})$ or 0.14×10^6 N/m^2 whereas pressure due to 1 m high water column is equivalent to 9.8×10^3 N/m^2 i.e. about 7% of $\boldsymbol{p}_c$. For a narrower capillary, a 1 m high water column will have less significance. In the case of an assembly of capillaries of different radii an average $\boldsymbol{p}_c$, corresponding to an average radius, r, is the driving pressure.

2.2. Estimation of the average radius of the relevant pores in unsaturated concrete

In a hardened concrete the pore sizes vary over a range. When the relative humidity drops within such a system its larger pores are progressively emptied until equilibrium is reached. At this stage, only the pores of the equilibrium size and lower are water-filled. Water transport occurs mainly through the larger water filled pores. In a closed system, like inside a concrete structure, the measured relative humidity and the radii of the largest water filled pores are related by Kelvin's equation (2):

$$-\mathrm{Ln}\, p/p_s = 2\gamma V/RTr \qquad (2)$$

where p_s is the saturated water vapour pressure at temperature T, p is the measured vapour pressure within concrete, γ is the specific surface energy of water, V is the molar volume of water, R is the gas constant, T is temperature in °K, r is the capillary radius.

Thus from the measured relative humidity, p/p_s, the radius of the most important group of capillaries could be calculated. Table 1 shows the relevant range of relative humidity along with the corresponding calculated capillary radius.

Table 1 and Eq. (1) show that when the internal relative humidity is 0.98 the driving pressure, $\boldsymbol{p}_c$, is 2.7×10^6 N/m^2 and the effect of a 1 m high water column is negligible. Knowing the relative humidity within a concrete structure, we know both the driving pressure on water and the average size of the relevant pores.

2.3. Estimation of the pore characteristics

The pore characteristics of a concrete have two components i.e. volume fraction of the interconnected

Table 1
Relationship between relative humidity at temperature 25 °C and radius of capillary

Relative humidity	Capillary radius (nm)
1.00	∞
0.99	102.5
0.98	53.2
0.95	20.4
0.90	10
0.80	4.7
0.70	3

pores, ε, and their actual average length. Only the interconnected pore volume is of importance and not the total pore volume. The actual average length of these pores is normally much longer than the nominal depth of the concrete structure. Now a factor $\boldsymbol{T}$ may be defined as the actual average length of the capillaries/nominal depth of the structure. This $\boldsymbol{T}$ is often termed the tortuosity factor and is a number. Unfortunately, for cement-based materials, at present, there are no direct methods to estimate either of these two components independently. However, it is possible to estimate a composite effect of these two factors from the results of steady state halide ion diffusion through concrete or mortar samples.

2.3.1. Theoretical basis

In a normal steady state diffusion of alkali halides, the diffusivity of halide ion is higher than that of alkali ion and that this difference in the diffusivity increases with decreasing water/cement ratio [10,11]. This difference in diffusivity between the ion types shows that other positive ions, other than alkali ion, diffuse along with halide ion. From this and other diffusion characteristics, it can be shown that halide ions move through the bulk liquid phase and alkali and other positive ions move through the electric double layer that forms round cement hydration products [12]. Thus, only the diffusivity of halide ions is uniquely defined and can be used to evaluate the diffusion path characteristics. Combined diffusion of all the positive ions compensate for charge transferred by the diffusion of halide ions so that the individual diffusivities of positive ions are not well defined.

Combining the Nernst relation between molar conductivity of an ion and its diffusivity and Kohlraushch's law relating molar conductivity and concentration of an ion following relationship can be derived [13].

$$D_{c,i} = D_{0,i} - A\sqrt{c_i} \tag{3}$$

where $D_{c,i}$ is the diffusivity of the ion type i at the concentration c, $D_{0,i}$ is the diffusivity of the ion type i at infinite dilution, c_i is the concentration of ion i, A is a constant. It includes, among others, the effect of co-diffusing counter ion.

Eq. (3) is valid only for diffusion through a solution and for the molar concentration range up to about 0.7. By convention when diffusion occurs through a solution, the cross-section and the diffusion path length are taken as unity. From Eq. (3) it can be seen that $D_{0,i}$ is the characteristic property of the ion i but $D_{c,i}$ is not. $D_{0,i}$ can also be calculated from Nernst relation (4):

$$D_{0,i} = RT\Lambda_{0,i}/F^2|z_i| \tag{4}$$

where R is the gas constant, T is the temperature in °K, F is the Faraday constant, z_i is the valence of the ion i, $\Lambda_{0,i}$ is the molar conductivity of the ion i at infinite dilution.

Most physical chemistry books give the characteristic values of $\Lambda_{0,i}$ for different ions (cf. Ref. [14]).

To apply Eq. (3) to diffusion through a porous matrix like mortar or concrete both porosity and the actual diffusion path length have to be taken into account. The porosity, ε, reduces $D_{c,i}$ to $\varepsilon \times D_{c,i}$. $\boldsymbol{T}$ decreases $D_{c,i}$ by a factor $1/\boldsymbol{T}$. Thus for a porous matrix Eq. (3) takes the form (5a):

$$\boldsymbol{T} \times D_{c,i,m}/\varepsilon = D_{c,i} = D_{0,i} - A\sqrt{c_i} \tag{5a}$$

$$D_{c,i,m} = \iota D_{0,i} - \iota A\sqrt{c_i}, \quad \iota = \varepsilon/\boldsymbol{T} \tag{5b}$$

where $D_{c,i,m}$ is the measured diffusivity through the matrix and calculated in terms of the unit sample thickness and cross-section. Other symbols are already defined. Eq. (5a) states that in a porous medium halide ion diffusivity is reduced by the factor $\varepsilon/\boldsymbol{T}$ compared to that through solution. Ionic diffusion through thick clay barrier follows Eq. (5b) [15]. At infinite dilution of the diffusant, Eq. (5a) becomes (6)

$$D_{0,i,m} = D_{0,i} \times \varepsilon/\boldsymbol{T} \tag{6}$$

and

$$\varepsilon/\boldsymbol{T} = D_{0,i,m}/D_{0,i} \tag{7}$$

Thus from the measured $D_{0,i,m}$ and known values of $D_{0,i}$, it is possible to estimate the pore characteristics i.e. combined factor $\varepsilon/\boldsymbol{T}$.

Recently Bigas et al. have published results on the concentration dependence of chloride ion diffusivity through 10 mm thick mortar samples [16]. The mortar mix had a water/cement ratio of 0.5. Fig. 1 shows a plot of their diffusivity data ($D_{c,Cl,m}$) against $\sqrt{c}$. Fig. 1 also shows a least squares fit of the first four diffusivity data values to Eq. (5a); the fifth concentration used lies beyond the range of the equation. From Fig. 1 it can be seen that for first four concentrations, the measured diffusivity data follows Eq. (5a) with a regression coefficient of 0.999. An extrapolation of the regression line to zero concentration i.e. infinite dilution gives $D_{0,Cl,m}$ as 3.99×10^{-12} m²/s. From data given in Ref. [14], $D_{0,Cl}$

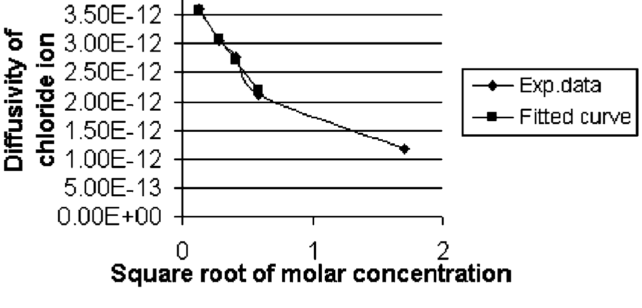

Fig. 1. Concentration dependent chloride diffusivity.

could be calculated as 2.0×10^{-9} m^2/s. These give an average $\varepsilon/\boldsymbol{T}$ for the mortar mix as 0.002. For other water/cement ratios $\varepsilon/\boldsymbol{T}$ could have other values.

2.4. Rate of water penetration through a porous medium

To get an understanding of the physical process involved it will be easier to start with water penetration in a very long, straight capillary of radius r under a pressure difference $\boldsymbol{p}_c$. If the rate of water penetration is slow then the situation is described by the Hagen–Poiseulle's equation (8):

$$Q = v/t = (\pi r^2 l/t) = (\pi/8)(\boldsymbol{p}_c/l)(r^4/\eta) \tag{8}$$

where Q is the volume rate of water penetration in the capillary, v is the volume of water penetrated in time t, l is the length of the capillary filled in time t, η is the viscosity of water.

Eq. (8) on rearranging and noting that $\boldsymbol{p}_c$ equals $2\gamma/r$ gives (9a)

$$l = r^{0.5}(\gamma/4\eta)^{0.5}t^{0.5} \tag{9a}$$

$$l = (r\gamma/4\eta)^{0.5}t^{0.5} \tag{9b}$$

Eq. (9a) shows that the rate of water penetration is proportional to the square roots of time, t, and the radius, r, of the capillary. Eq. (9b) shows that the penetration of saturation front is proportional to the square root of time irrespective of the nature of the fluid and size of the pore. Table 2 shows calculated water penetration through capillaries of different radii in one year.

All the above figures refer to cross-sections fully open to water penetration. In the case of a porous matrix the above figures have to be multiplied by the corresponding $\varepsilon/\boldsymbol{T}$ value. In this case, Eq. (9a) becomes (10).

$$l_m = (\varepsilon/\boldsymbol{T})r^{0.5}(\gamma/4\eta)^{0.5}t^{0.5} \tag{10}$$

where l_m is the depth of saturation front within the matrix at time t.

Thus in a mortar sample with a water/cement ratio of 0.5 and an internal relative humidity of 0.98, the rate of water penetration will be 5.8×0.002 equal to 11.6 mm after one year.

With some assumptions Eq. (11), which is similar in form to (9b), can also be deduced from Darcy's law.

Table 2
Depth of water penetration in the first year

Capillary radius (nm)	Water filled length at one year (m)
102	7.98282269
53	5.81158264
20	3.57002684
10	2.52439018
5	1.78501342
1	0.79828227

$$l_m = (2\varepsilon'\mathbf{K}'_s\boldsymbol{p}'_c)^{0.5}t^{0.5} \tag{11}$$

where ε' is a function related to model porosity, $\mathbf{K}'_s$ is the model hydraulic conductivity, $\boldsymbol{p}'_c$ is the model driving pressure.

These are not true material parameters. Most books on soil physics give this deduction (cf. Ref. [17]). In this case, the effects of pore radius r are included in $\boldsymbol{p}'_c$ and the effects of viscosity η are included in $\mathbf{K}'_s$.

3. Discussion

The above presentation shows that for a long time a large concrete structure, with a water/cement ratio lower than 0.5, will have a comparatively thin water saturated outer layer of a few mm thickness even when constantly in contact with water. The thickness of the saturated layer will not be much affected by the depth of immersion. Unless this state of unsaturation is taken into account all prediction about long-term penetration of chloride or other ions will be highly suspect. This has already been observed in Danish concrete structures. It is expected that this unsaturation will also affect other degrading processes mediated through pore solution.

The above presentation implicitly assumes that the pore characteristics remain unaltered by water ingress during the intervening time. This is an over-simplification. Internal unsaturation lowers the rate of cement hydration. Subsequent water ingress and consequent further cement hydration will reduce the effective pore characteristics i.e. porosity ε and the effective pore radius r will be reduced. The rate of water penetration will also be lowered even though the internal relative humidity may not be much altered. These aspects seem to have not received due attention.

In structures undergoing alternate drying and wetting the situation will be different. Under this condition the pore structure will gradually alter. In some places, micro or/and macro-cracks will form in other places the pore radii will be reduced [18]. Water or an aggressive solution will preferentially enter through the cracks. However, reduced pore radii in the bulk of the structure will hinder water penetration into the bulk of the structure.

Those who are familiar with the Blaine method of determining specific surfaces of cements will recognise the similarity between (9a) and the basis of Blaine's method. Both of them predict that volume flow is proportional to $\sqrt{t}$ and that the finer the material (i.e. the finer the pore dimension) the longer time it takes for the same flow. Both of these have a common basis.

The inferences of this unsaturation have certain bearings on testing of concrete structures for their durability. These implications have not been properly appreciated. In the following three of these are considered.

Consider the ASTM C666 test method for the evaluation of frost resistance of designed concrete mixes. In this procedure the test specimens should be between 76 and 137 mm in diameter and between 356 and 406 mm in length. Testing may start after 14 days water curing. In procedure A of this test method, each specimen is surrounded by a 3 mm water layer while it is being subjected to freezing-thawing cycles. Each specimen with its water layer is kept in a separate container. Note 3 of the test procedure states that both the container and the specimen are subjected to high water pressure during freezing. The pressure could be such that rigid metal containers can be damaged. The required specimen size is such that it could not have been water saturated during 14 days water curing. This means that in each freeze-thaw cycle further water will be pressed into the specimen making it susceptible to frost damage. This has to be contrasted with natural freezing where the sample is not surrounded on all sides by water and at the same time subjected to high water pressure. Thus, in the natural condition the rate of saturation will be much lower and the active service life will be longer than the laboratory results will suggest.

Another example will be the creep of a structure under a compressive load. Due to unsaturation and the consequent presence of empty space within the structure, it will have higher compressibility than a fully saturated companion. If the load is sufficiently high, some internal collapse will occur. The collapsed structure will not recover its old dimensions when the load is removed i.e. there will be irreversible creep.

Penetration of chloride ions in concrete structures is at present a hotly debated topic. The process is diffusion controlled. The penetration depth in a water-saturated structure should be proportional to the square root of time. This expectation is at variance with experience even with under-water structures. As a result, various empirical time dependence relationships have been proposed. However, none of the researchers has investigated the state of saturation within the concrete. Interestingly most of these structures were of the low water/cement ratio type where internal relative humidity is low. The rate of chloride ion penetration beyond the saturation front is very low.

The present explanation is also consistent with the recent observation of Glasser and Zhang [19]. These authors reported “that the self-desiccated state, once achieved, is very difficult to resaturate”. In the main body, the self-desiccated state may persists even more than 10 years of under water service.

References

[1] Lea FM. The chemistry of cement and concrete. London: Edward Arnold; 1988. p. 347.

[2] Boddy A et al. An overview and sensitivity study of a multimechanistic chloride transport model. Cement Concrete Res 1999;29:827–37.

[3] Powers TC, Brownyard TL. Studies of the Physical Properties of Hardened Portland Cement Paste.. Proc J Amer Concrete Inst 1947;43:262.

[4] Chatterji S, Jeffery JW. Reply to the discussion of the paper “A new hypothesis of sulphate expansion”. Mag Concrete Res 1964;16:239–41.

[5] Nilsson LO. Moisture problems at concrete floors. TVBM-3002. Sweden: Lund Institute of Technology; 1980. p. 36–51.

[6] Persson B. Moisture in concrete subjected to different kinds of curing. Mater Struct 1997;30:533–44.

[7] Chatterji S. On the applicability of Fick’s second law to chloride ion migration through Portland cement concrete. Cement Concrete Res 1995;25:299–303.

[8] Nilsson L-O et al. HETEK, A system for estimation of chloride ingress into concrete, Theoretical background. The Danish Road Directorate, Copenhagen, 1996, Report No. 83.

[9] Glasstone S. Textbook of physical chemistry. London: Macmilan; 1966. p. 486.

[10] Chatterji S, Kawamura M. Electrical double layer, ion transport and reactions in hardened cement paste. Cement Concrete Res 1982;22:774–82.

[11] Atkinson A, Nickerson AK. The diffusion of ions through water-saturated cement. J Mater Sci 1984;19:3068–78.

[12] Chatterji S. Colloid electro-chemistry of saturated cement paste and some properties of cement based materials. Adv Cement Based Mater 1998;7:102–8.

[13] Chatterji S. On the non-application of unmodified Fick’s laws to ion transport through cement based materials. Proc. Intern. RILEM Workshop. Chloride Penetration into Concrete. France. 1995. p. 64–73.

[14] Moore WJ. Phys. Chem.. London: Longman; 1978. p. 435.

[15] Achari G, Joshi RC, Bentley LR, Chatterji S. Effect of ion concentration on diffusion through clay. Soil Sci 1997;162: 51–5.

[16] Bigas JP, Lambert F, Ollivier JP. Modelisation globale des interaction physico-chemiques regies par des isotheres non lineariess entre ions chlore et mortier de ciment Portland. Mater Struct 1996;29:277–85.

[17] Young RN, Mohamed AMO, Warkentin BP. Principles of contamination transport in soils. Elsevier; 1992.

[18] Chatterji S. Discussion of the paper “The effect of moisture content upon the elasticity of hardened cement paste”. Mag Concrete Res 1974;25:49–51.

[19] Glasser FP, Zhang L. High-performance cement matrices based on calcium sulfoaluminate-belite composition. Cement Concrete Res 2001;31:1881–6.