CONCRETE PERMEABILITY - A REVIEW OF PROCESSES AND MECHANISMS

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ABSTRACT

The mechanisms and processes by which gases and water containing deleterious substances permeate through the concrete matrix is presented. Capillaries, transition zones and voids, the major pathways of transport are treated from microstructural and morphological view points. Physical phenomena of diffusion, fluid flow and capillary suction are identified as the major mechanisms for transport. Chemical reactions in the form of secondary hydration of cement, chloride binding, acid-base reactions and physico-chemical interactions are seen as part of the events during transport. Chloride profiles obtained from the RCP test directs us to the need for further improvements to the test and even the scope for wider application of the test.

KEYWORDS

capillary, microstructure, transition zone, diffusion, ionic radii, adsorption, chloride binding, attacking agents, matrix proper.

ABBREVIATIONS AND SYMBOLS

Abbreviations and symbols are used in the text to mean the following.

CH	calcium hydroxide	NaCl	sodium chloride
C_3A	tricalcium aluminate	Cl^-	chloride ion
CSA	calcium sulphoaluminates (generic)	SO_4^{2-}	sulphate ion
C_4AF	tetracalcium aluminium ferrite	CO_2	carbon dioxide
CSH	calcium silicate hydrates	H_2CO_3	carbonic acid
C_xA_y	calcium aluminates (generic)	H_2O	water
SO_2	sulphur dioxide (gas)	Na^+	sodium ion
SO_3	sulphur trioxide (gas)	K^+	potassium ion
$MgSO_4$	magnesium sulphate.	N_xO_y	nitrogen oxides (generic)
RCP test	rapid chloride permeability test	H_2S	hydrogen sulphide

H₂	hydrogen	O₂	oxygen

H_2 hydrogen O_2 oxygen

H^+ hydrogen ion O^- oxygen ion

Å   angstrom unit (10^{-10} meter)   nm   nanometer (10^{-9} meter)

INTRODUCTION

A considerable amount has been written about the permeability of concrete and that is because it is a very important aspect in durability control especially towards corrosion prevention of reinforced concrete and maintenance of the structural integrity of concrete itself.

A generic model would consist of an environment with an infinite supply of attacking agents surrounding a finite permeable matrix trying to protect itself and its embedded rebars. In this chain of events, permeability of the concrete will be the rate determining step. (Fig.1.)
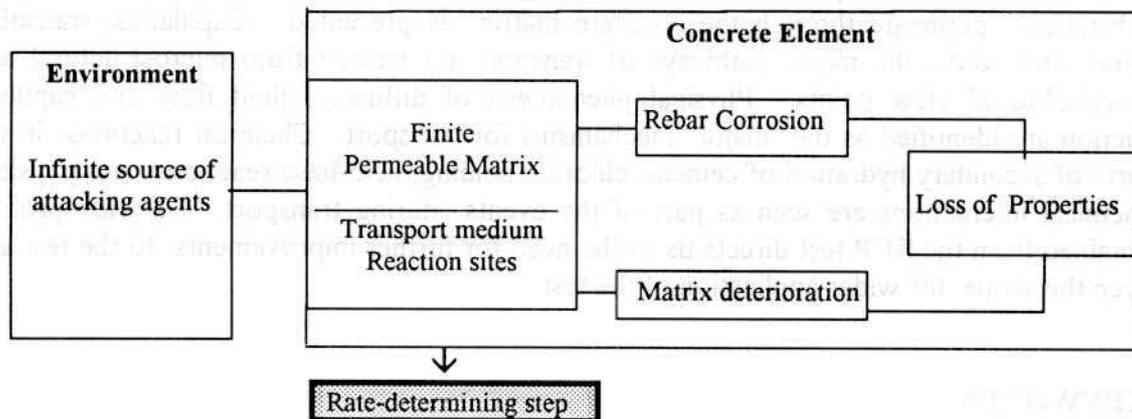

Fig.1 A model of the deterioration system

The transport of water, ions, and gases through the matrix is not a simple phenomena of diffusion or flow. Secondary events and other forces can impede or facilitate transport processes. In order to understand the complexities of the transport processes, we need to consider the nature of the solvent and solute, concrete microstructure, its morphology, and various physical and chemical phenomena that can occur.

ATTACKING AGENTS

The attacking agents, (Table 1.) are in the form of a) water containing ions from dissolved solids and gases and b) gases; though the deleterious effects of gases cannot function without first forming solvated ions. Water is an essential medium as it not only acts as a solvent and carrier but enables chemical reactions and is itself involved in reactions.

| Liquids | Cl^- | SO_4^{2-} | Mg^{2+} | H^+ | Humic acids | water |
| Gases | CO_2 | O_2 | H_2S | SO_2 | SO_3 | N_xO_y water vapour |

Table 1. List of common attacking agents.

TRANSPORT MECHANISMS & PROCESSES

Ionic Transport

Ionic compounds (e.g. Na^+ Cl^-) dissolve easily in polar solvents. Polar solvent molecules (e.g. water) carry small opposite charges (dipole charges) on each molecule. The separation of the positive and negative ions from a solid ionic lattice is facilitated by the dipoles of the water molecule. On dissolution, the anions (negatively charged ions) are separated from the cations (postively charged ions) by a finite volume of water. In the immediate vicinity of the ion it attracts the dipoles of water forming an orientiated sheath-the hydration sheath.

a). Representation of water dipole

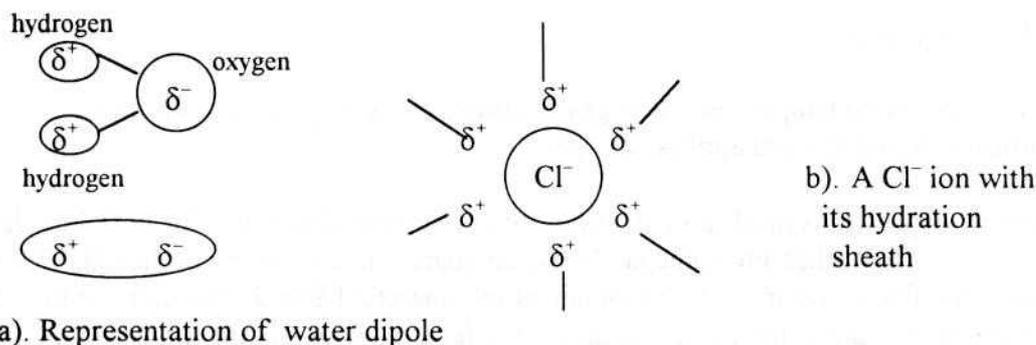b). A Cl^- ion with its hydration sheath

Fig. 2. Water Dipole- Ion interaction producing Hydration Sheaths.

The numerous dipole charges surrounding an ion do not satisfy the large ionic charge as the ionic charges are separated by large distances due to the interjuxtaposition of the water molecules and the attractive or repulsive forces are diminished by the 4th power of the distance.

Ions and water molecules are in constant motion and due to their close proximities collide between themselves causing random changes in directions of travel. Over time they will travel randomly in an ominidirectional manner. This is the force that drives diffusion. Hence a concentration of NaCl in the centre of a sphere of water will eventually be uniformly dispersed throughout the volume of the sphere. When uniformity is reached the equilibrium state or steady state condition is reached. The application of a potential difference (a potential gradient) will cause a rapid directional motion of the ions to their respective electrodes. A pressure gradient on the other hand will cause motion of the entire solution towards low pressure points.

The Diffusion Process

Diffusion is a process whereby different concentrations of atoms, molecules or ions attempt to interdisperse and reach a uniform state of dispersion. It involves random movement and collision of atoms or ions and water molecules as discussed previously.

Transport through capillaries and voids in concrete occurs through diffusion in the absence of other nett physical forces (e.g. pressure or potential gradients). The rates of diffusion are described by Fick's 1st and 2nd Laws, [Eq (1) & (2)].

$$Ficks\ 1st\ Law \quad (for\ steady\ state\ conditions) \qquad J = -D.\,dc/dx \qquad Eq.(1)$$

$$Ficks\ 2nd\ Law \qquad \delta c/\delta t = D.\,d^2c/dx^2 \qquad Eq.(2)$$

where J = rate of permeation of a species through a concentration gradient dc/dx, $\delta c/\delta t$ = rate of increase in concentration at a distance x after time t (when D is independent of concentration) and D = diffusion coefficient.

The diffusion coefficient varies with temperature and is described by an Arrhenius-type equation, [Eq.(3)].

$$D = D_o exp\,(-Q/RT) \qquad\qquad Eq.(3)$$

where T = absolute temperature, R = gas constant, Q = energy of activation and D_o = diffusion factor. D rises approx. 2% per °C.

For concrete, expressions need to be incorporated in the diffusion terms for both liquids and gases to correct for other phenomena. If we compare the diffusion coefficient of 0.05N (3%) NaCl in a free solution with that obtained in concrete[Table 2.] we can see the effect that the concrete matrix has on the degree of difficulty given to the transport of ions. However, even a diffusion coefficient of 10^{-10} may not be sufficient for durable concrete design

D at 25°C in free soln.	= 1.6×10^1 m^2/sec. [Ref 1.]
D in concrete	$\cong 1.0 \times 10^{-10}$ m^2/sec. w:c ratio 0.4
D in silica fume concrete	$\cong 3.0 \times 10^{-12}$ m^2/sec. w:c ratio 0.4

Table .2. Diffusion coefficients in free solution vs concrete

Gaseous Diffusion

Gases also diffuse by the same method of random movement and collisions as liquids. The difference lies in the fact that the kinetic energies of gas molecules are high and therefore mean molecular velocities are much greater. (Note: water vapour is a gas) However in concrete, gases must dissolve in water and form ions before reactions can occur.

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Gas to gas diffusion is more easily expressed by Grahams Law, where the rates of diffusion of two gases into each other is inversely proportional to the square roots of their densities or molecular weight, [Eq.(4)].

Grahams Law $\qquad \dfrac{r_1}{r_2} = \sqrt{\dfrac{d_2}{d_1}} = \sqrt{\dfrac{MW_2}{MW_1}}$ $\qquad\qquad$ Eq. (4).

where for a binary system of gas 1 and gas 2, r = rate of diffusion, d = gas density and MW = molecular weight. Hence O_2 (MW= 32) will diffuse faster than carbon dioxide (MW = 44) by about 20%. Corrections need to be applied as all gases deviate from the theoretical concepts of an ideal gas.

Temperature plays an important role in gas and liquid diffusion. The higher the temperature the greater the diffusion coefficient. This is due to the fact that heat imparts greater kinetic energy to the atoms, ions and molecules and hence their mobilities are increased and hence the collision frequency is also increased causing faster dispersion.

Concentration has a role in diffusion mechanisms. High concentrations produce closer proximities of ions and better probabilities of ion-ion collisions thereby causing interferences to the dispersion process. Hence diffusion coefficients are much higher in dilute solutions than in concentrated ones.

Fluid Flow

Where a pressure gradient exists (e.g. in drying- wetting zones), Darcy's Law is more appropriate.[Eq.(5).]

Darcy's Law (for steady state condition) $\qquad dq/dt \cdot 1/A = K \cdot \Delta h / L$ $\qquad\qquad$ Eq. (5).

where the rate of flow dq/dt per unit area A is governed by the pressure gradient $\Delta h / L$ and K is the coefficient of permeability. In flow under a pressure gradient, the forces that cause diffusion are negated by the pressure gradient. Darcy's Law assumes a laminar flow.

Capillary suction

Where the capillary is dry or partly wet, contact with a solution will cause an immediate suction of the fluid into the concrete, [Fig.(3)]. Capillary suctions increase permeability rates[2] due to a reduction in the diffusion distance. The depth of capillary suction is inversely proportional to the diameter of the capillary pore on the assumption that the capillary is continuous . Transport into dry capillaries by gases does not happen by capillary suction but by gas to gas diffusion as dry capillaries are already occupied by gases, which includes water vapour.

(a) Saturated capillary
Fluid diffusion distance = x

(b) Dry or partially humid capillary
Gas diffusion distance = y
and fluid diffusion distance = x – y
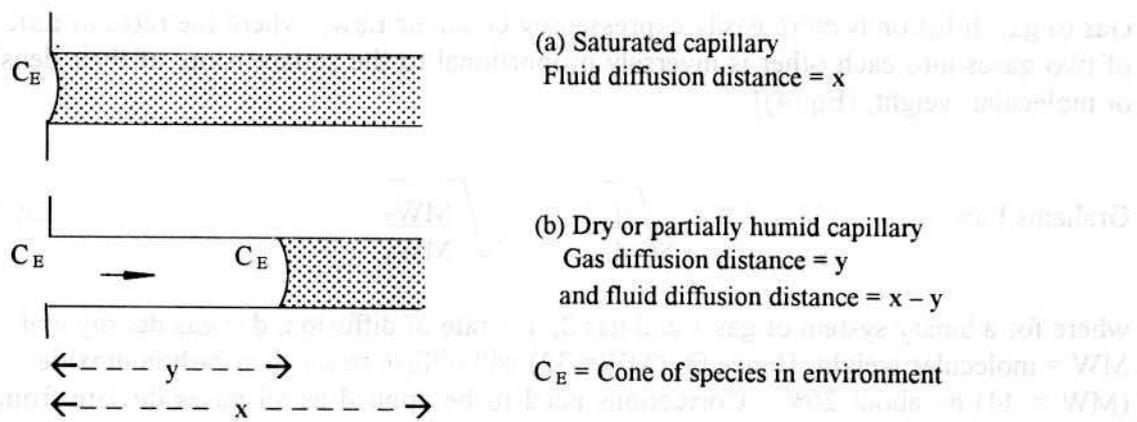
C_E = Cone of species in environment

Fig. 3. Effect of capillary suction in reducing effective diffusion distance.

TRANSPORT PATHWAYS

Concrete Microstructure and Morphology

Hydrated cement is made up of numerous semi-amorphous non-stoichiometric compounds, all of which are probably defect structures together with some stoichiometric crystalline components (e.g CH). Interspersed within the matrix are voids composed of capillaries, gel spaces, entrapped air, bleed water channels and water pockets. In concrete, additional voids in the aggregate-hydrated cement boundaries (the transition zone) are formed. It is the voids that are the major pathways for permeability.

Capillaries

Capillaries are an inevitable consequence by the very method by which hardened concrete forms. They can be visualised as a three-dimensional labryrinth of twisting, tortous, partially networked microtunnels distributed in the hydrated cement matrix. The pore diameters range from 300,000 nm to less than 2 nm³. The internal surfaces of each individual pore is not smooth or uniform along its length. The internal surfaces are covered with protruding deposits of cement hydrates, calcium hydroxide crystals and other crystalline material. The internal diameters vary considerably along its length. Hence its internal surface area is extremely high. Capillaries are one of the major pathways for transport of water, dissolved ions, molecules and gases. It has been reported that pores smaller than 1300A° (130nm) do not transport ions[17]. Judging by the size of ions in water, [Table 2.] there are no reasons for it from a dimensional point of view. It is probable that smaller capillaries are blocked by internal depositions preventing transport or they may have constrictions along their lengths thereby creating greater degrees of difficulties for transport.

Ion	Cl$^-$	SO$_4^{2-}$	Mg^{2+}	H$^+$	Na$^+$	K$^+$	Ca^{2+}	OH$^-$	(H$_2$O)
Radii (Å)	3	4	8	9	4	3	6	3.5	c.1.3

(1 Å = 0.1nm)

Table 2. Approximate effective ionic radii in aqueous solution[4] (25 °C)

Gases can be transported through much smaller capillaries (that are dry or partially dry) due to their smaller sizes and higher kinetic energy (i.e. higher molecular velocities). e.g. the molecular radii of O$_2$ is 0.66 Å. vs molecular radii of H$_2$O which is 1.66Å. (without hydrogen bonding).

The number, size and whether the capillaries are blocked or continuous is determined by concrete design, choice of raw materials, compaction and curing practices[5]. Poor application of the fundamental principles during making and placing concrete leads to a more porous matrix which means higher values in permeability.

The total capillary pore volume in a well hydrated concrete paste (w:c 0.45) is observed to be about 25%[3] . Prof. Neville calculates that capillary pore volumes for a 0.38 w:c ratio cement paste is around 14% by volume of the totally hydrated paste[18]. Hence increases in w:c ratio increases pore volume.

The addition of latent binding agents such as silica fume[6], ggbfs and fly ash causes additional deposition of hydrated products in the capillaries spaces. These depositions are made well after the final set of the concrete and after the capillaries are fully formed. Although the measured total capillary pore volume is roughly the same for concrete with and without the latent binders, the permeabilities of those with the latent binders are extremely low. This implies that latent deposition happens in a way that segments the pores rather than fill it up completely.

The Transition Zone (The Aggregate-Hydrated Cement Matrix Boundary Zone)

The transition zone is observed to contain hydrates that are less dense than the matrix proper. Large well formed CH crystals are also observed to be present[7-12]. The thickness of the zone is observed to be in the range 10,000 to 50,000 nm.

It would appear that w:c ratios at the transition zone are much higher than that of the matrix proper. Circumstantially this implies that in a period prior to the set of the concrete, a water-rich solution appears at the transition zone. It is probable that this happens sometime after the the onset of the bleeding process. Interfacial free energy considerations between the aggregate surface and water system will mean a preferential retention of a boundary layer of the water-rich solution. The presence of very large, near perfect CH crystals is further evidence of a retained water rich solution as large perfect crystal growths require supersaturation and time for growth. The transition zone is absent in compositions containing 10% silica fume where bleed water is absent. In such compositions, CH is deposited as smaller and finer crystals and the hydrates at the aggregate boundary zone are of the same density and structure as that of the matrix proper.
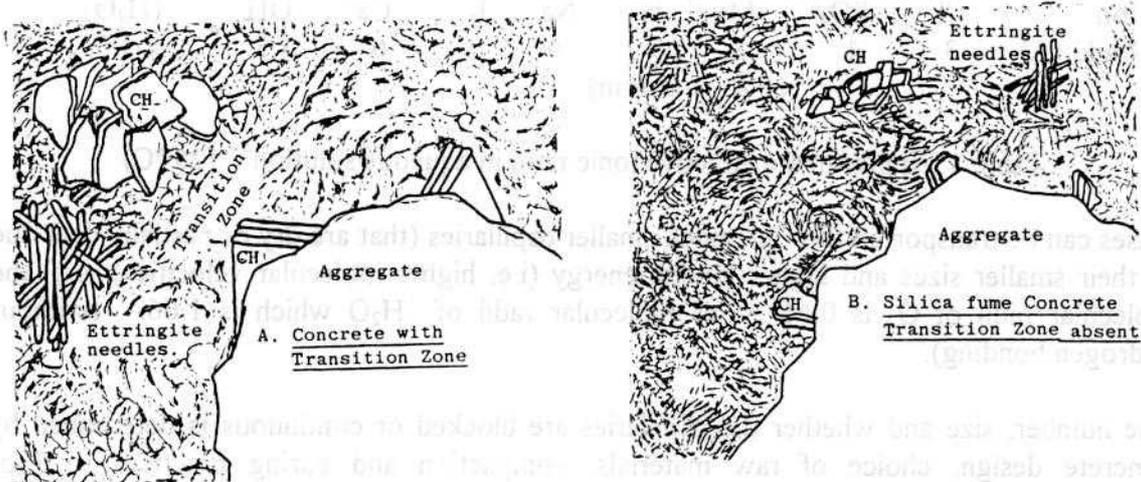
Fig. 4. The Transition Zone Microstructure

If the transition zones are connected to the open capillary system of the matrix then permeability will be high. The transition zone adds to the total pore volume in concrete. This stands to reason as approximately 60% of the paste for a medium cement content (circa. 350Kg/m^3 at 0.4 w:c) concrete is in contact with the aggregate surface.

Gel Pores

These are pores below about 2 nm found as interstitial spaces between and within the disordered lattice structures in the numerous hydrates. Gel pores constitute about 28% by volume of paste for a 0.38 w:c ratio. Diffusion still occurs in the gel pores but the rates are slow. Gel pores in very high w:c ratio concrete contribute significantly to permeability as the lattice structures are seperated by greater volumes of loosely held water molecules.

Other Voids

The presence of entrained air voids caused by poor compaction[5], bleed water channels, water pockets and honeycombs are other contributory causes to high permeability.

Cracks

Microcracks within the matrix if connected to the continuous capillary system of the matrix makes the concrete very highly permeable. Larger width cracks need to be repaired for obvious reasons. Smaller width cracks tend to heal autogenously as the unhydrated cement tends to deposit further in the crack space and block it with the entry of water.

High Temperature Curing

Concrete cured at higher temperatures [13, 14,] e.g. steam cured precasts have higher permeabilities. The microstructure of products formed are coarser and more crystalline than ambient temperature cured concrete.

OTHER PHENOMENA

Adsorption and Chemisorption

There is a tendency for ionic and molecular species to be physically adsorbed on to solid surfaces. Species that form a much stronger bond through attractive forces (chemisorption) are more resistant to displacement.

Electric Double Layer Effects

Positive or negative charges in the solid cause an electrostatic accumulation of oppositely charged ions in the fluid in contact with it. This is the so called electric double layer (Helmholtz double layer). This will cause an attraction or repulsion of a diffusing ion depending on its charge. If we take a negative charged Cl^- ion diffusing for instance, into a postively charged field, the Cl^- ion will be retained in the field and in a negatively charged field the Cl^- ion will be repelled [Fig 5.]. Hence the existence of electric double layers [15,16] in the capillaries can hinder the free passage of ions and especially in narrow capillaries and gel spaces by forming additional diffusion layers. The diffusion layer (δ) is of the order of 0.001 cm to 0.05 cm (1×10^4 nm to 5×10^5 nm). The charge across the double layer develops a potential difference - the zeta potential.

Negative Ion arriving at a negative charge field is repelled.

Negative ion ariving at a positive charge field has additional barrier of diffusion.
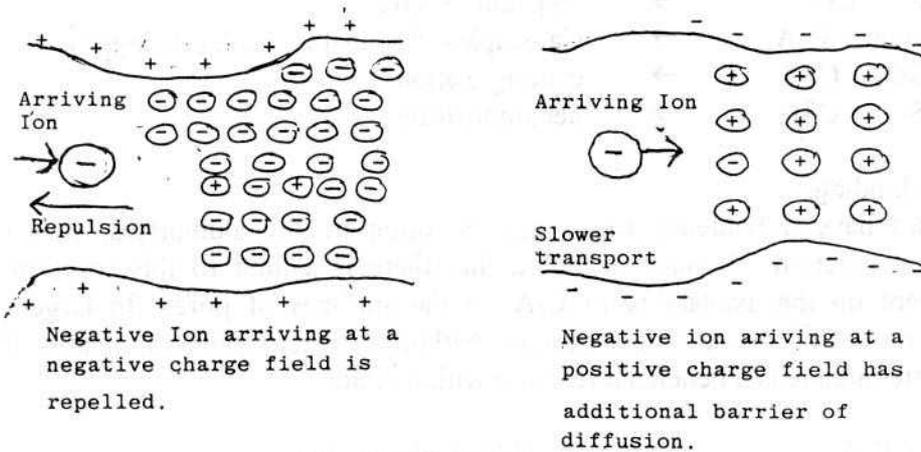
Fig. 5. Representation of Electric Double Layers and their effects on ions.

Ion- Ion Interactions

In concentrated solutions, (which concrete pore water is: pH circa 13.0) the closer proximity of ions cause attractions or repulsions depending on the ionic charges involved producing, hindrances to diffusion processes. Hence equivalent conductivities and diffusion coefficients are higher in dilute solutions than in concentrated solutions due to the larger separation of charges in dilute solutions.

Reactions

Numerous chemical reactions can occur between the water and dissolved species and the compounds already present in the concrete. It must be noted that the reactions outlined here mainly occur at the internal surfaces of pores and where the reacting species have first contact. Attack deeper into the matrix occurs once the surfaces have been made more permeable or destroyed by fragmentation or conversion into other byproducts. The significant reactions are.
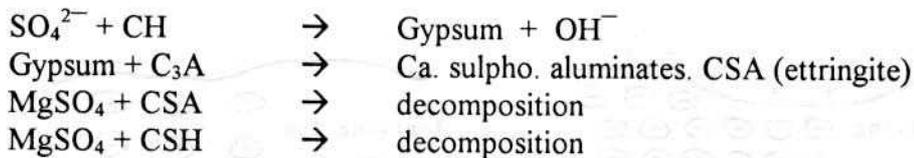
1. Hydration of Unreacted Cement.

   Further hydration of unreacted cement occur[5] and this time probably with the incorporation of other species present in the solution e.g. Na^+, K^+, Cl^-, $Mg.^{2+}$ SO_4^{2-} Secondary depositions usually happen in capillary and other void spaces. Such depositions will effectively reduce capillary and void diameters or even block it by segmentation and decrease permeability further. This effect is quite obvious with the presence of latent binders such as silica fume, ggbfs and flyash. Secondary hydration of concrete with clean water is a beneficial processes.

2. SO_4 attack.

   Sulphates form Ca.sulphoaluminates (ettringites) with expansive consequences. Sulphates such as $MgSO_4$ can continue to attack the Ca. Sulphoaluminates or CSH causing fragmentation, cleavage and formation of soft byproducts.

   $$SO_4^{2-} + CH \rightarrow \text{Gypsum} + OH^-$$
   $$\text{Gypsum} + C_3A \rightarrow \text{Ca. sulpho. aluminates. CSA (ettringite)}$$
   $$MgSO_4 + CSA \rightarrow \text{decomposition}$$
   $$MgSO_4 + CSH \rightarrow \text{decomposition}$$

3. Chloride binding.

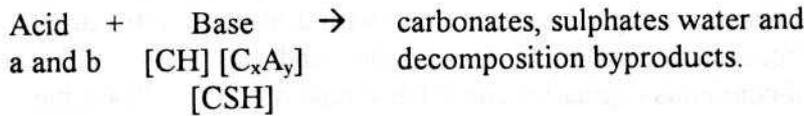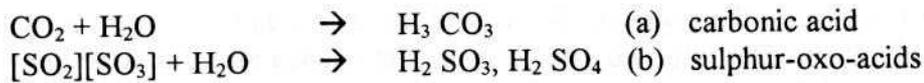   Chlorides have a tendency to be reacted upon by the aluminates, C_3A being the dominant reaction. It must be noted that there is a limit to this reaction which is dependent on the availability of C_3A on the surfaces of pores. In large capillaries considerable Cl^- ions can flow through without contacting the aluminates. Chloride - aluminate binding is a beneficial reaction within limits.

   $$Cl^- + C_3A \rightarrow \text{Ca. chloro. aluminates}$$
   $$Cl^- + C_4AF \rightarrow \text{Ca. chloro. Al. Ferrites.}$$
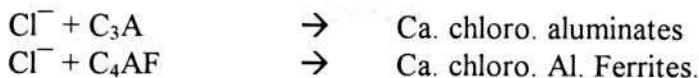
   The predominant reaction here is that of C_3A

4. Acids of carbon dioxide and sulphur oxides

   Since the hydrated compounds in cement are basic, any acid (proton H^+ containing fluids) will produce a decomposition reaction. Carbonation of concrete (an acid-base reaction) is a major consideration especially in the high temperatures and intermediate humidities in the Gulf. Efflorescence is special a case where the dissolved CH is transported externally to the concrete element and then undergoes carbonation.

$$CO_2 + H_2O \quad \rightarrow \quad H_3CO_3 \qquad \text{(a)} \quad \text{carbonic acid}$$
$$[SO_2][SO_3] + H_2O \quad \rightarrow \quad H_2SO_3, H_2SO_4 \quad \text{(b)} \quad \text{sulphur-oxo-acids}$$

$$\begin{array}{llll}
\text{Acid} \quad + \quad \text{Base} & \rightarrow & \text{carbonates, sulphates water and} \\
\text{a and b} \quad [CH] \, [C_xA_y] & & \text{decomposition byproducts.} \\
\qquad\qquad [CSH] &
\end{array}$$

5. Effect of embedded organic molecules.

There are many organic compounds (short or long chained C-C backboned polymers) that are claimed to be of benefit in permeability reduction. It is important to take cognizance of the fact that most organic molecules do not have the same life span that concrete is expected to have. Tests for hydrophobicity, water repellence or permeability reduction in the short term e.g. after 28 days or 1 year will bear little resemblance to its longer term condition than that given by non-organic binders. Most organic materials even under ideal storage conditions will deteriorate within a few years.

RAPID CHLORIDE PERMEABILITY TEST - SIGNIFICANCE

Many test methods and formulae have been devised for permeability testing. The AASHTO T277 (or ASTM 1202) RCP test has gained popularity in the last decade. It uses an electrochemical cell to transport Cl^- ions rapidly into the sample. An electrochemical cell is in fact the most effective and quickest method of driving ions into a permeable medium as ionic mobilities under sizeable potential gradients are large.

CHLORIDE PROFILE
After AASHTO T277 test

Results of chloride tests as per BS 1881 ; Part 124 ; 1988

| | A | B |
Depth (mm)	Control	Microfume
	Chloride,% as Cl,by weight of dry concrete	
0 – 10	0.311	0.043
10 – 20	0.113	0.035
20 – 30	0.059	0.035
30 – 40	0.047	0.035
40 – 50	0.035	0.021

Cement Content 385 Kg.m^3
W:C ratio 0.4

2376 COULOMBS

626 COULOMBS

Cl % by wt.

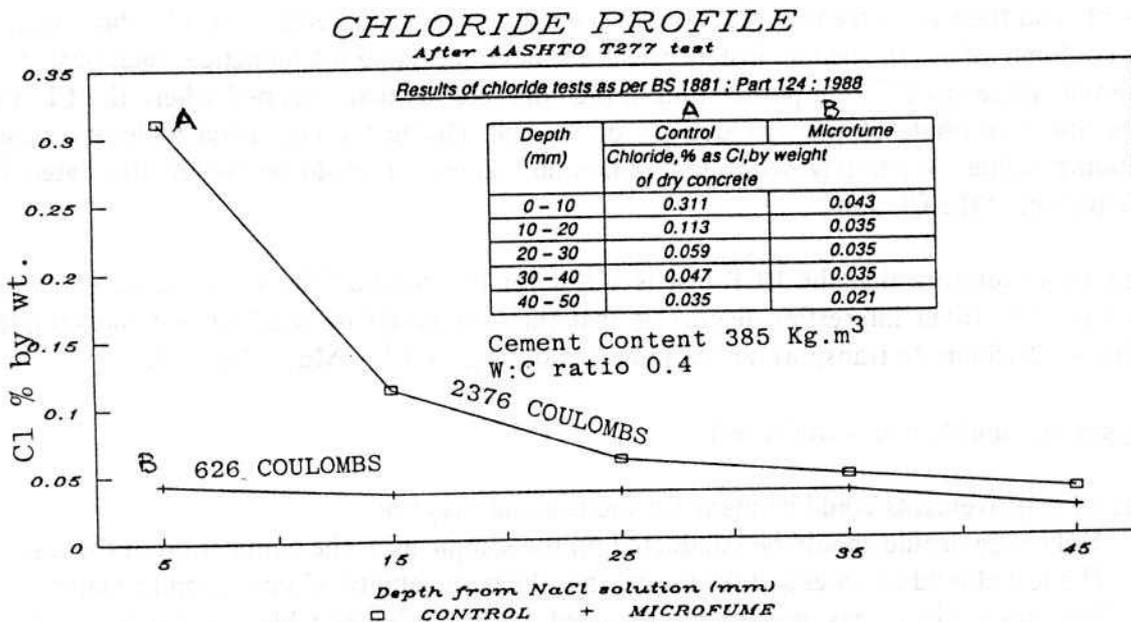Depth from NaCl solution (mm)
□ CONTROL + MICROFUME

Fig.6. Chloride profiles after the RCP Test.

The test, in fact, measures the ability or disability of the specimen to transport ions. In this analysis, the chloride profiles into two samples were determined after the RCP test [Fig.6]. They are of identical formulation except that one sample has the addition of 10% silica fume. The data shows that even a good concrete (A) with a low w:c ratio of 0.4 has the capacity to transport considerable amounts of Cl^- ions and this shows that there are considerable amounts of continous capillaries and other pathways. The silica fume concrete sample shows that there are no easy continuous pathways for ionic migration. This reinforces Whiting's original classification that values below 1000 coulombs constitute impermeable concrete. The data also shows that despite the strong electrochemical pressure, the bound chloride has not shifted from its original values for both the samples. This agrees with many authors views that the paste matrix proper is impermeable or that the chlorides are strongly bonded to the aluminates.

Although the test is called the Rapid Chloride Permeability Test, the data shows that the Cl^- ion does not contribute to the conductivity of the cell for these samples. Conductivity is probably provided by the high concentration of OH^- ions and other coulombic charge transfers at the electrodes which may include hydrolysis of water [Eq.6], recombination of hydroxyls [Eq.7] and corrosion at the anode (Cu^{2+} and Zn^{2+} for brass electrodes) and deposition at the cathode.

$$\text{cathode} \quad H_3O^+ \rightarrow H_2O + H^+ \qquad\qquad 2H^+ + 2e \rightarrow H_2 \qquad \text{Eq. (6)}$$

$$\text{anode} \quad 2OH^- \rightarrow H_2O + O^- \qquad\qquad 2O^- - 2e \rightarrow O_2 \qquad \text{Eq. (7)}$$

It also raises the interesting proposition that in highly porous concrete where the chloride does migrate out of the sample and into the anodic cell, the conductivity will be raised sharply and the charge transfer reactions at the anode will be increased considerably. Hence the coulomb values in such an instance will not have the same mathematical relationship of coulomb values to Cl^- ion penetration in the concrete as that obtained where the Cl^- ion does not contribute to the conductivity of the cell. Hence we may need to look at high coloumb values separately from low coloumb values to evaluate better the rates of penetration of the Cl^- ion.

It follows therefore that the RCP test is a test for the conductivity (or resistance) of the sample. The other interesting feature is that this test could be used to test the samples ability or disability to transport any cation or anion. e.g. SO_4^{2-} , Mg^{2+} , Na^+ , K^+

Suggested improvements to the test.

Certain improvements could be made for the test and they are
1. A chloride profile should be conducted on the sample after the completion of the test.
2. The test should be extended for measuring the permeability of any cation or anion.
3. The brass electrodes should be replaced with non-corrodable electrodes such as platinum on porous porcelain or titanium alloy mesh. Corroding electrodes consume current and increase resistances.
4. Reduce the number of tasks performed in specimen preparation as demonstrated by Detwiler et al [17]. Two examples would be to premould the specimen to its exact diameter by omitting the extra tasks of coring and omit the vacuuming and resaturation process for samples that are already saturated.

5. There are no reasons why calcium nitrite containing samples should be excluded from this test as chloride permeability will be of considerable significance in such samples. There is nothing stopping the diffusion of chlorides from the external environments into nitrite or other inhibitor containing samples. The amount of inhibitor required is proportional to the total amount of chlorides passing through the specimen throughout its expected life.

CONCLUSION

In conclusion, we can therefore see that taken holistically, permeability is a complex process and attempts at discovering an empirical formula for permeability is made difficult by the existence of large numbers of dependent and independent variables. Nevertheless, the major factors influencing permeability such as the presence of continuous capillaries, the transition zones and other voids are easily apparent and whilst we await an empirical formula, control of permeability is possible from a practical point of view by good design, appropriate choice of materials, appropriate interpretation of test results, proper application of compaction and curing procedures and timely maintenance.

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