Chloride ion migration/diffusion through concrete and test methods
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Abstract:
In the present day models for the life of concrete structures, the causes of failure have been earmarked and role of chloride ion has been placed at the top, because of comparative ease of Cl⁻ transport in concrete structure and its extraordinary damaging effect on the existing passivating film on the rebar surface. Therefore, diffusion of Cl⁻ ions through concrete media has been given pronounced recognition and various testing techniques for the measurement of ‘diffusion’ of Cl⁻ have been developed and standardized.

Keywords: Diffusion, interdiffusion, diffusion coefficient, Fick’s laws, pore solution, AASHTO permeation test, Nordtest, immersion test.

1. Introduction:
Concrete is a composite cement based material which is multi component, micro-porous and microstructure – sensitive construction material. It provides fluid – flow channels associated with ion transport and this fact causes important phenomena like diffusion of gases, ions (particularly Cl⁻ ions etc.), all of which deteriorate the life expectancy of concrete and also of rebar – embedded concrete. Migration, particularly penetration of chloride ion in the form of diffusion, has become the most important topic because of its role in damaging the concrete structures. Resistance to damage, or in other words, the life of reinforced concrete depends on the effective passivation of the rebar steel, which depends upon the alkalinity (that is OH⁻ ion concentration) of the moist concrete. The effective passivation due to OH⁻ ion is adversely affected by the presence of Cl⁻ ion in particular and carbonation of the concrete which actually reduces the concentration of OH⁻ ion.

In case the OH⁻ ion concentration is lower than 11.5, the adherence of oxide film on the rebar surface is disturbed and become less protective. In the case when the concrete around the rebar is carbonated and the concentration of OH⁻ ion gets reduced in the pore solution, the similar result is observed. It occurs in one or more of the following ways: as the CO₂ molecule penetrate into the concrete it reacts with Ca(OH)₂ with C – S – H gel, with alkali and also with Ca⁺⁺ ions in pore solution, resulting drastic decrease in the alkalinity of the pore solution to the level of about pH 8. Then this carbonation front progresses to the surface of the reinforcing bar, depending on depth of the concrete cover and on the rate of diffusion of CO₂ and time.

It has been noted that films of ferric oxide are more resistant to chloride ion than the ferrous oxide films which are prone to soluble complex formation with Cl⁻

\[
\text{Fe(OH)}_2 + \text{Cl}^- \rightarrow \text{[FeCl]}_x
\]

This means, the presence of Cl⁻ ion in the pore solution will continuously attack Fe(OH)₂ coverage on the reinforcing bar (this is due to auto-catalytic reaction tendency of Cl⁻ ions), which may lead to local pitting due to the continuous and repetitive attack. Actually there could be a competition between passivation process (ferrous oxide film changing to ferric oxide) and ferrous oxide film forming complex with Cl⁻ ion (i.e. deterioration of film). But, a higher OH⁻ ion concentration provides the stability of ferric oxide film. Here the role of dissolved oxygen is in favour of normal passivation route by primarily directing conversion of ferrous to ferric oxide. As a result the zones of low dissolved oxygen content
will suffer pitting attack. The above analysis indicates the role of “hydroxide to Cl ratio” in controlling the onset of pitting corrosion.

Thus the depassivation due to chloride ion is a function of net balance between competing processes – stabilization / repair of the film by OH\(^-\) and disruption of the film by Cl\(^-\) ion. It is expected therefore that there is a threshold (or critical) chloride ion concentration that must be exceeded before depassivation can take place.

The threshold value is a function of \(pH\) (Fig. 1). But most specifications do not address Cl/OH\(^-\) for the purpose of life prediction, these rather refer only to total Cl\(^-\) concentration in the concrete. For example, a recommendation indicates that the chloride content be smaller than 0.2% of the cement content of the concrete [1]. It should be taken into account that it is only the “chloride dissolved in the concrete pore solution” that functions to depassivate the steel.

![Fig.1 Relations between threshold chloride ion concentration and the pH level of the pore solution as suggested by Hausman [2] and Diamond [3].](image)

Now, there may be various sources of ‘chloride’ ordinarily found in concrete e.g., it may come as an admixed component or in chloride contaminated aggregates or mixed water, salt spray salt placed on concrete pavements. In case if chlorides were not incorporated in the original concrete, then penetration of Cl\(^-\) ions to the vicinity of steel rebar is controlled by the concrete cover (i.e. depth of cover) and also by other factors like moisture content, pore structure and the nature of concrete admixtures used. In the similar way CO\(_2\) penetration is affected by the above factors. The concrete cover also plays a role by providing path for ionic current between anodic and cathodic portions of the rebar surface, for continuation of corrosion. For example: (i) if the cover is un-cracked the diffusion and the electrical resistance are controlled by pore structure and the degree of saturation of the pores. Actually the un-cracked concrete cover acts as a barrier to diffusion of Cl\(^-\) ions (and also CO\(_2\) gas and dissolved O\(_2\)). The diffusion of all these species are sensitive to pore structure of the concrete. Whereas chloride diffusion occurs mainly through solution, CO\(_2\) diffuses in the gas phase and oxygen may diffuse either as dissolved molecules in solution or in gas phase. (ii) If the concrete cover is cracked, the width and shape of the cracks control the rate of entry of Cl\(^-\) ions, and also carbonation [4-5]. Summing up these processes, it appears that the fundamental modes of transport of Cl\(^-\) ion in the concrete are diffusion, capillary absorption, evaporative transport and hydrostatic pressure. Movement of chloride ion under a concentration gradient
is known as diffusion, which means Cl\(^-\) ion concentration on the outside surface of the concrete is greater than on the inside, which allows a natural flow of Cl\(^-\) ion from regions of high concentration to low concentration. This is the principle mechanism which drives Cl\(^-\) ions in the pore structure of concrete [6-7]. These pores are interconnected interstitial spaces between the gel particles, occupying about 28% of the total volume of gel. Actually gel pores are much smaller in size than the capillary pores, being in the range of 0.5 – 2.5 nm. The total volume of gel pores increases along with the volume of gel as the hydration proceeds. However the volume of capillary pores decreases with the progress of hydration.

The process of capillary absorption occurs when the dry surface of concrete is exposed to moisture (containing chloride). In this case the solution is drawn into the porous matrix of concrete by the process of capillary suction (like sponge). It may however reduce the distance that chloride ion must travel by diffusion [8]. Concrete being a porous materials, it absorbs water when the water comes in contact, because of the suction in the pores caused by capillary action. This action depends upon surface tension, viscosity, density of the liquid, the contact angle between the water and the pore walls and on the radius of the pore. However the contact angle is small due to the presence of molecular attraction between water and cement paste.

The mechanism of evaporative transport is a result of vapour conduction from a wet surface to a drier surface. This means a body of liquid in the pore structure of the concrete evaporates and leaves deposits of chloride inside.

Permeation is another mechanism of chloride ingress which is driven by the hydrostatic pressure gradient. This gradient provides the required force to move the liquid containing the chloride ions through the internal concrete matrix. For example a constant wave function or retained body of water (in bridges, piers, docks etc.) may give the necessary hydrostatic pressure gradient in marine environment [9].

Among the above methods of chloride ion transport the most familiar method is movement of Cl\(^-\) ion under concentration gradient. For this, the concrete must have a continuous liquid phase having a chloride ion concentration gradient. It may be noted that in the bulk of the concrete the pores remain saturated and the chloride movement is controlled by the concentration gradient.

2. **Factors governing Cl\(^-\) Penetrability (Chloride Penetration into Concrete Structure):**

Chloride ion penetration into Concrete Structure is mainly described in terms of pore structure of the concrete, which at the first instance, is controlled by the raw materials, the actual practice being followed and the age. Thus chloride penetrability can be explained as being influenced by the following factors.

(i) Water-Cement ratio of the concrete: this ratio is affected by the use of supplementary cementing materials which may subdivide the pore structure.

(ii) Aging/degree of hydration: with aging of the concrete, greater amount of hydration can be expected, which result into more highly developed pore structure.

(iii) Use of supplementary cementing materials: there are many such materials (such as fly ash) which require longer time to hydrate, [10-11] affecting the chloride penetration.

(iv) Effect of temperature on pore structure: the effect of temperature (high temperature) during casting/curing of concrete accelerates the curing process. Thus, as the concrete ages, temperature – affected cured concrete will be more matured. As a result this will have better resistance to Cl\(^-\) ion penetration than normally – cured material. However as the normally cured – concrete ages, this has a chance to hydrate more fully. In this case, some research findings have indicated a lower Cl\(^-\) ion diffusion coefficient than the high temperature – cured concrete [12-13]. This conclusion has been attributed to the
coarse structure i.e. initially developed in the high temperature – cured concrete due to its initial rapid hydration as well as the possible development of internal micro-cracking.

(v) Binding capacity: theoretically, concrete is not inert to chlorides in pore solution, a fraction of Cl\(^-\) ion will always react with concrete matrix, in the form of chemically or physically bound, and once bound, it will reduce the rate of diffusion. Therefore the rate of Cl\(^-\) ion penetration into concrete will be affected by the Cl\(^-\) ion binding capacity of the concrete. Again, once the steady state condition is reached, and the diffusion coefficient is measured then all the binding can be presumed to have taken place, and then the “effect of binding capacity” cannot be observed. However, so long the steady state condition has not been reached, the binding capacity will affect the results. The role of supplementary cementing materials on binding capacity have been studied by many [14-16] with no conclusive remarks.

(vi) Role of C\(_3\)A content: the C\(_3\)A content of cement has been found to positively influence the binding capacity i.e. it increases binding as observed by many [17-19].

2.1 Pore Structure:

Among the various factors responsible for the deterioration of rebar/concrete bond, ingress of chloride ion is most important, because (as explained earlier) of its role in the depassivation of the rebar surface. Ordinarily, although under the alkali condition the rebar surface remains passivated, yet the environment inside the concrete remain vulnerable to entry of different species, because the cement paste in its formative hydration period contains pores, which are occupied by evaporable water and during prolong hydration, the products of hydration fill the space, reducing the volume of interconnected capillary system. Thus this volume fraction of capillary pores depends on w/c ratio and degree of hydration. When cement reacts with water, the reaction product has smaller volume than the substance of hydration, which is due to chemical shrinkage. This difference in volume leads to pore formation, and as long as water and unhydrated cement are present, these pores can fill up with cement hydration products: It has been observed that capillary porosity cannot be avoided but capillary discontinuity is achieved after two weeks of hardening for w/c < 0.5, requires six months for w/c = 0.6 and is practically not possible for w/c > 0.7 [20-22].

Pores ranging in size from a few nm to several μm are generally considered capillary pores [23-25]. Interlayerspaces of C–S–Hgel are referred to as gel pores of a few nm [26-27]. In addition, macropores (air voids) also exist in concrete owing to entrapped air bubbles and incomplete compaction (mm in size) [23-25]. In the interfacial transition zone (ITZ) the capillary porosity is generally higher with better interconnectivity and also the hydration products are different [28].

2.2 Pore solution:

For certain specific laboratory tests simulated pore water solution (called pore solution) is prepared in which the rebar is dipped for performing different kind of studies. The pore solution is prepared with 0.002 M Ca(OH)\(_2\) + 0.045 M NaOH + 0.26 M KOH at pH 13.5 [29-31]. Also, there are many other simulated solutions in which experiments can be conducted [32-33].

2.3 Moisture Content:
At a given pore structure, water in the concrete can be present in different forms [34-35], e.g., chemically bound water (combined in hydration products), interlayer water (held in gel pores), adsorbed water (on the pore walls), capillary water (held in capillaries) and water in macropores and air voids. At full hydration (α = 1), the amount of chemically bound water which depends upon degree of hydration is generally at 0.23 – 0.25 g. water / g. cement [26].

When water has evaporated from pores, a layer of adsorbed water is still present on the pore walls regardless of pore size. The thickness of adsorbed layer depends upon the relative humidity in the pores and other related factors like available internal pore surface. It may be noted that capillary pores hold water by capillary forces, which are again dependent upon temperature, relative humidity etc. Macro-pores have no capillary action and thus only fill up when concrete is submerged.

2.4 Permeability and Transport:

The presence of pores may be seen as the efficient system for transport of liquids and gases, which are responsible for deterioration or durability of the reinforced concrete [23, 35]. However, the transport of gel water or adsorbed water is under the effect of surface forces. Transport properties are proportional to the extent of capillary pores and their interconnectivity which was observed in experiments on the coefficient of permeability for stationary water transport in cement paste vs. the volume fraction of capillary porosity. It was found that both pore structure and the presence of capillaries strongly depended on w/c ratio (and also on degree of hydration). This means that the permeability increases nonlinearly with increasing w/c ratio particularly above w/c ≈ 0.5[36-37].

As noted earlier, water sucked into the concrete is the carrier of dissolved Cl⁻ ions. Capillary suction becomes dominant mechanism for concrete in the splash zone during the cyclic wetting and drying process that controls the capillaries, to be filled up or emptied. However, it was observed that absorption by capillary action was faster than water loss by evaporation during drying cycles [34-35].

3.0 Critical Cl⁻ content or Cl⁻ threshold value:

The term critical or threshold (C_{crit}) Cl⁻ means the concentration required to destroy the passive film on the surface of steel embedded in concrete. C_{crit} mainly depends on pH of the pore solution. Thus higher the amount of OH⁻ ions, the amount of C_{crit} to initiate corrosion increases [38], and a critical ratio is Cl⁻/OH⁻ = 0.6 which means, e.g., if the pH is 13 instead of 12, the tolerable Cl⁻ ion concentration is 10 times higher than at pH 12. A high alkalinity of concrete pore solution offers resistance against Cl⁻ induced corrosion. This gives a necessary caution before using puzzolanic material (which lowers the pH) for concrete structures.

C_{crit} is also influenced by the type of steel/concrete interface, e.g., if the interface is covered with solid hydration products (particularly in the case of calcium hydroxide) the C_{crit} increases [39-40]. An easy reference of the role of interface is – a higher Cl⁻ value of C_{crit} is required for steel embedded in concrete as compared of steel immersed in alkaline solution [41-43]. It is also important to note that macroscopic or microscopic defects at the steel/concrete interface are also important factors for C_{crit} value.

4.0 Fick’s laws:

4.1 Historical Development:
The phenomenon of diffusion is perceived as a descriptive term for ‘spreading in all direction from a source’ and as such this term refers to the ‘net movement of matter, attributed to the random movement of molecules, taking place from a region of concentration to one of lower concentration’. It has a classical form and numerous variants of this classical form developed adhoc for specific applications in different disciplines. The notion that diffusion is a physical process (obeying quantitative laws) and explicable in terms of the behaviour of individual molecules can be traced to the work of Dalton at the beginning of the 19th century [44](1808). Another work of Deutrochet (1827) was related to diffusion in liquid systems as a dynamic counterpart, osmosis [45-46]. Another work was produced by Graham (1833) who found that gas diffusion dependent in a simple way to the relative molecular mass of gas molecules and he extended this phenomena to the study of liquids [47-48]. Ludwig and Brücke (1852) recognized the importance of the matter and studied the phenomena with limited success [49]. Another study by Pfeffer (1877) showed measurement of osmosis through semipermeable membrane: Actually, work of Fick confronted this problem in which diffusion and osmosis were conceived in terms of passage through some kind of physical barrier, a porous membrane. However Fick (1855) assumed another kind of model in which he simplified the matter in the form of a mathematical model, giving net rate of solute movement and local curvature of concentration gradient [50]. This work of Fick (1855) is widely acknowledged and have established the law of diffusion, inductively from experimental data. The relationship, known Fick’s law of diffusion gives the rate at which the concentration of the substance at any point ‘x’ in a system is proportional to the curvature of the concentration gradient at that point, and the proportionality constant is the diffusion coefficient or diffusivity (D) in the system. Einstein (1905) and von Smoluchowski(1906) independently found an explanation for Fick’s law in molecular terms [51-52]. Actually these authors were in search of a critical test for kinetic theory, but they arrived at the explanation of the phenomena of Brownian motion [52], and in addition they derived the Fick’s law as a macroscopic diffusion process in terms of molecular kinetic mechanism of Brownian motion in fluid system where there are concentration gradients. Thus we see that the classical theory comparing Fick’s law, the Brownian motion concept and the Einstein – von Smoluchowski model, were developed from a number of scientific advances in 19th and early 20th century physics and physiology, e.g., the study of Brownian motion, osmotic theory, the theory of heat conduction, kinetic theory and the study of “diffusion” per se, the above work of Einstein and von Smoluchowski further assisted (through the theory of stochastic processes) Wiener (1964) to study probability distribution of diffusing particles in order to study an individual particle to pass during a stated interval of time between any two points in a defined space[53]. This Stochastic theory has been influential in quantum mechanics (e.g. Feynman’s path integral method), in mathematics (Functional analysis, differential equation and probability theory) and in several other fields [54].

4.2 The Driving Force for Diffusion:

The diffusion occurs only when a concentration gradient exists for example, in an electrolytic solution. The concentration of an ionic species ‘i’, may be assumed “to vary in the x direction but is constant in the y and z directions” and one can map equi-concentration surfaces which will be parallel to the y z plane (Fig. 2).
The situation pictured in Fig. 2 can also be considered in terms of the partial molar free energy (or chemical potential, $\mu$) of the particular species ‘i’ as:

$$\mu_i = \mu_i^0 + RT \ln c_i$$

(1)

Here $c_i$ is a function of $x$ and the chemical potential also is a function of $x$, i.e., the chemical potential varies along the $x$ coordinate.

Now, if we assume that the species $i$ has an initial concentration $c_I$ at $x_I$ to a final concentration $c_F$ at $x_F$, then the change in free energy (or chemical potential) of the system is (explained in Fig. 3).

$$\Delta \mu = \mu_F - \mu_I = RT \ln \frac{c_F}{c_I}$$

(2)

Fig. 3 Schematic representation of the work done $W$ in transporting one mole of species $i$ from an equiconcentration surface where its concentration and chemical potential are $c_I$ and $\mu_I$ to a surface where its concentration and chemical potential are $c_F$ and $\mu_F$.

This change in free energy is equal to the net work done on the system in an isothermal, constant-pressure reversible process. The work done to transport one mole of species $i$ from $x_I$ to $x_F$ is

$$W = \Delta \mu$$

(3)
The above case is comparable to work done (W) in mechanics in which a mass is lifted from a height \( X_i \) to \( X_f \) at the expense of

\[
W = -F_G (X_f - X_i) = -F_G \Delta X = \Delta U,
\]

Where, \( F_G \) is gravitational force on the body and \( \Delta U = \) gravitational potential energy.

An infinitesimal change in energy – distance relation (in mechanics) will be

\[
F_G = \frac{dU}{dX}
\]

Here the negative of the gradient of gravitational potential energy defines the gravitational force. Similarly the negative of the gradient of electrostatic potential defines the electric force, and therefore the negative of the gradient of the chemical potential would act formally like a force. Again, just as the gravitational force results in the motion of a mass and the electric force results in the motion of a charge, the chemical-potential gradient results in the net motion (or transfer) of the species from a region of high chemical potential to a region of low chemical potential. This net flow of the species idown the chemical-potential gradient is called diffusion, and therefore the gradient of chemical potential may be looked upon as the diffusion force \( F_D \). Thus, one can write

\[
F_D = -\frac{d\mu_i}{dx} \quad \text{----- (4)}
\]

**4.3 Fick's First Law (Steady-State Diffusion):**

The gradient of chemical potential resulting from a non-uniform concentration is equivalent to a driving force for diffusion and it produces a diffusion flux, \( J \) (i.e. the number of moles of species ‘\( i \)’ crossing per second per unit area of a plane normal to the flow direction).

If diffusion is occurring, the driving force \( F_D \) and the flux \( J \) may reach values that do not change with time (i.e. a steady state), then a relation between the diffusion flux \( J \) and the diffusion force \( F_D \) can be given by a power series

\[
J = A + BF_D + CF_D^2 + DF_D^3 + \cdots \quad \text{----- (5)}
\]

Where A, B, C, etc., are constants. If \( F_D \) is less than unity and sufficiently small, the terms containing the powers of \( F_D \) (greater than unity) can be neglected and

\[
J = A + BF_D \quad \text{----- (6)}
\]

Here the constant A must be zero; otherwise, it will mean that one would have the impossible situation of having diffusion even though there is no driving force for diffusion.

Hence the assumption of a sufficiently small driving force leads to the result

\[
J = BF_D \quad \text{----- (7)}
\]

i.e., the flux is linearly related to the driving force and a value of \( F_D = 0 \) corresponds to an equilibrium situation; but assumption of a small value of \( F_D \) is required to ensure a linear relation (Eqn. 7) between flux and force which is tantamount to saying that the system is near equilibrium, but not at equilibrium.

Now, the driving force on 1 mole of ions being \(-d\mu_i/dx\) (Eqn. 4) then if the concentration of the diffusing species adjacent to the transit plane (Fig. 4), across which the flux is to be studied i.e. \( c_i \) moles per unit volume, the driving force \( F_D \), at this plane, will be \(-c_i(d\mu_i/dx)\). Then the (Eqn. 7) becomes

\[
J_i = -Bc_i \frac{d\mu_i}{dx} \quad \text{----- (8)}
\]

Using

\[
\mu = \mu^0 + RT\ln c_i \quad \text{----- (9)}
\]

and assuming ideal behaviour, eqn. 8, becomes

\[
J_i = -Bc_i \frac{RT}{c_i} \frac{d\ln c_i}{dx} = -BRT \frac{dc_i}{dx} \quad \text{----- (10)}
\]
Thus, the steady-state diffusion flux can be shown to be proportional to the gradient of concentration. This proportionality existed has been empirically known as Fick’s first law of steady state diffusion:

\[ J = -D \frac{dc}{dx} \] 

----- (11)

Where, \( D \) is called diffusion coefficient, and

\[ BRT = D \] 

----- (12)

in which \( B \) is a constant and therefore it may appears that \( D \) also is a constant, but expression (Eqn. 12) was obtained only because an ideal solution was considered, and use of activity coefficients were ignored in Eqn. 1. Thus strictly, diffusion coefficient is not a constant but, if the variation of the activity coefficient is not significant over the concentration difference that produces diffusion, then for all practical purposes \( D \) is a constant. The quantity \( D \) can be understood in a fundamental way only by probing into the ionic movements, the results of which show up in the macroscopic world as the phenomenon of diffusion.

4.4 Fick’s Second Law (Non-Steady-State Diffusion):

The most fundamental differential equation of diffusion in an isotropic medium can be derived from Fick’s First Law (Eqn. 11). So far we have considered steady-state diffusion in which neither the flux nor the concentration of diffusing particles in various regions changes with time i.e the whole transport process is time independent. Now, if a concentration gradient is suddenly produced in the electrolyte initially in a time-invariant equilibrium condition, then diffusion starts, but it will not immediately reach a steady state that does not change with time. It means the distance variation of concentration, which is zero at equilibrium, will not instantaneously reach the final steady-state.

To study the variation of concentration with time, let us consider a Consider a parallelepiped (Fig. 5) of unit area and length \( dx \) through ions are diffusing in through the left face and out through the right face, as a continuous of \( x \). If \( c \) is the concentration of ions at the left face, the concentration at the right face is

\[ c + \frac{dc}{dx} dx \]
From Fick’s law (Eqn. 11), the flux into the left face $J_L$ is

$$J_L = -D \frac{dc}{dx} \quad -----(13)$$

and the flux out of the right face is

$$J_R = -D \frac{d}{dx} \left( c + \frac{dc}{dx} dx \right)$$

$$= -D \frac{dc}{dx} - D \frac{d^2c}{dx^2} dx \quad -----(14)$$

The net outflow of material from the parallelepiped of volume $dx$ is

$$J_L - J_R = D \frac{d^2c}{dx^2} dx \quad -----(15)$$

The term $D \left( \frac{d^2c}{dx^2} \right)$ is the net outflow of ions per unit volume per unit time. This net outflow of ions is variation of concentration with time, i.e., $dc / dt$, and therefore the eqn. 15 can be written as

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad -----(16)$$

Where, the partial differential equation has been used because the concentration depends both on time and distance ($c = f(x, t)$). If the diffusion is one dimensional i.e. if there is gradient of concentration only along the X-axis, eqn. 16 is generally referred as Fick’s second law of diffusion.

### 4.5 Diffusion of Cl− ions in concrete:

Fick’s First Law describes the flow of a substance (e.g. impurity) showing that the rate of diffusion of the substance across a plane is proportional to the concentration gradient across the plane. In case of Cl− ion diffusion into concrete, the diffusion process in one dimensional and Fick’s law (steady state diffusion) is applicable. The rate of diffusion includes the effect of porous matrix of concrete that contains both solid and liquid components. This equation can only be used after a steady state condition is obtained because the equation does not involve the change in concentration in time.

The Fick’s Second Law involves changes of concentration gradient with time in the form:

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \quad -----(17)$$

If the following boundary conditions are assumed: surface concentration of Cl− is constant ($C(x=0, t>0) = Co$), initial concentration in the concrete is zero ($C(x>0, t=0) = 0$) and the concentration at an infinite point far enough from the surface is zero ($C(x=\infty, t>0) = 0$). The equation was reduced (Crank’s solution), [55] as follows:
\[
\frac{c(x,t)}{c_0} = 1 - erf\left(\frac{x}{\sqrt{4Dt}}\right) \quad \text{-------- (18)}
\]

where, \(C(x,t)\) = chloride concentration, measured at depth \(x\) and exposure time \(t\) (% mass)
\(t\) = the exposure time (sec)
\(erf\) = error function (tables with values of the error function are given in standard mathematical reference books).

The Crank's solution to Fick's Second Law of Diffusion [55] can also be presented in the following form:
\[
C(x,t) = C_s - (C_s - C_i)erf\left(\frac{x}{\sqrt{4Dt}}\right) \quad \text{-------- (19)}
\]

Where \(C_s\) = initial chloride-ion concentration of the cementitious mixture prior to the submersion in the exposure solution (% mass). A common method of determining the chloride diffusion in concrete is to expose saturated samples to a chloride solution for a known period of time. The chloride concentrations at varying depths are then obtained and diffusion coefficients and surface chloride concentrations are determined by fitting the profiled data to the non-linear Fick's Second Law of Diffusion solution [56].

5.0 Testing techniques for diffusion of Cl⁻:

Testing techniques have been designed primarily for measurement of diffusivity of chloride ions with aim to simulate practical conditions. Naturally, therefore, depending on outlook of the test the techniques are different. For instance, some tests involve slow migration of chloride ion, whereas some tests carry out the experiments at faster rate. In some cases the migration have been enhanced by application of external voltage, which therefore is no more auto-migration, rather it may be termed as enforced migration. Generally in the measurement of \(D\) (Cl⁻ ion), no difference is underlined between the auto/enforced migration, although there should be a difference to be underlined. There are many national/international specifications for the measurement of \(D\), all of which utilize equations for Fick’s diffusion.

5.1 Interdiffusion study (I & Cl⁻):

This method involves the study of interdiffusion of I⁻ and Cl⁻ ions and the tracer diffusion of Cs⁺ ions in water saturated OPC at 30°C, as a function of w/c ratio (during fabrication) [57].

Fig. 6 Schematic diagram of the diffusion cell [57].

\[
\text{Fig. 6 Schematic diagram of the diffusion cell [57].}
\]
The basic arrangement (Fig. 6) is used to measure intrinsic diffusion coefficient \( D_i \) in which cement sample forms a partition between two sides of the diffusion cell. \( D_i \) at steady state condition is calculated by

\[
D_i = \frac{iV}{AC_1}\frac{dc_2}{dt}
\]

(20)

Where, \( D_i \) is the intrinsic diffusion coefficient (m² sec⁻¹) of the particular species, \( V \) is the volume of the low concentration side of the cell (i.e. \( C_2 \)), \( l \) is the thickness and \( A \) is the cross section area of cement specimen.

Result established:

i) The diffusion of ion is a strong function of w/c ratio

ii) The apparent activating energies for \( D_i \) are significantly affected by irreversible thermally induced changes in the pore structure particularly during the heating part of thermal cycle.

5.2 AASHTO T259 (Salt Ponding Test):

In this test [58] concrete samples (three slabs each of 75 mm thick and 300 mm² surface area) are covered on the sides, the top surface (300 mm²) is kept open where ponding is made with 3% NaCl solutions and the bottom surface is connected to an atmosphere of 50% relative humidity. A schematic representation is given in (Fig. 7).

![Fig. 7 AASHTO T259 (Salt Ponding) test Setup [58]](image)

The concrete slabs were moist cured for 14 days and then stored in a drying room at 50% relative humidity for 28 days. The sides of slabs are sealed. After this conditioning treatment, a 3% NaCl solution is ponded on the top surface for 90 days. During this time the bottom surface is exposed to drying environment (50% relative humidity). After this period the slabs are removed and the chloride concentration is determined in 0.5 inch thick slices parallel to the ponding surfaces.

The salt ponding test was found to be too crude, because it does not give proper chloride ingress profile. Beside there is an initial “sorption” effect when the slabs are first exposed to solution, when salt solution is drawn quickly into the pores of the concrete. Another factor is that the exposure of bottom face to a 50% relative humidity environment during the test causes chloride to be drawn into the concrete through a mechanism other than the diffusion. Another factor by which vapour transmission from wet front in the concrete to the drier atmosphere at external face takes place, which may also carry chloride ions. This effect is called wicking. It was noted that chloride migration by capillary absorption in this test is not comparable to life time chloride diffusion behaviour of the structure.
5.3 Nordtest NT Build 443 (1995) (Bulk Diffusion Test):

This Nordic test [59] was developed to overcome some of the deficiencies of salt ponding test and was based on the immersion test APM 302 [60]. As compared to test method of APM 302, in this case the test specimen is saturated with lime water. This method prevents any initial sorption effect when chloride solution is used. In this test other than the top surface all other surfaces are sealed and the top surface is uncovered and exposed to 2.8 M NaCl solution (Fig. 8). It is left this way 35 days (minimum).

![Fig. 8 Nordtest Setup](image)

For chloride analysis milling of surface at depth increment on the order of 0.5 mm are made and the chloride content of the powder is determined according to AASHTO T260 [61]. The error function solution of Fick’s second law is then fit to the curve and a diffusion value and surface chloride concentration is determined.

\[ c(x, t) = c_s (c_s - c_l) . \text{erf} \left( \frac{x}{\sqrt{4D_{\text{ussd}}t}} \right) \]  

(21)

The test is recommended to be carried out for a period extended to 90 days or longer for higher quality concretes and also for modelling purpose.

5.4 Nordtest NT Build 492 (Non-Steady State Migration Test):

The Nordic standard NT BUILD 492 [62] was based on the CTH Rapid Test [63], with some modifications [64].

The test procedure involves:
- Vacuum – saturating the specimen by using AASHTO T277 [65];
- Mounting the specimen in the migration cell (a silicon rubber tube) and filling the downstream cell with 0.3 N NaOH solution (anolyte);
- Placing the cell in the upstream reservoir (a plastic box) containing 10% NaCl solution (catholyte);
- Applying an external potential of 30 V DC between the two electrodes and adjusting the potential (in a range of 10 to 60 V DC) according to the initial current so as to keep the power consumption of the specimen in most cases less than 2 W;
- After test (usually 24 hours), the specimen is axially splitted into two pieces;
- Spraying 0.1 M AgNO₃ solution on one of the freshly split surfaces of the specimen and, when the white silver chloride precipitation on the split surface is clearly visible (about 15 minutes), measuring the penetration depths across the split surface at intervals of 10 mm to obtain 5 to 7 valid depth readings;
The chloride diffusion coefficient, \( D_{nssm} \), is then calculated from the equation:

\[
D_{nssm} = \frac{R T L}{z F \Delta E} \left( x_d - \alpha \sqrt{x_d} \right) \frac{c}{t}
\]

(22)

Where \( x_d \) is the average value of the penetration depths, \( t \) is the test duration, and \( \alpha \) can be taken as a laboratory constant.

\[
\alpha = \frac{2}{\sqrt{\pi}} \text{erf}^{-1} \left( 1 - \frac{2 c_d}{c_0} \right)
\]

(23)

5.5 Nord Test NT Build 355 (Steady State Migration Test):

The Nordic standard NT BUILD 355 [66] was developed earlier (1980's) and revised in 1990's. This is a steady state migration test, which has following procedure.

- Coating the curved surface of the specimen with epoxy resin;
- Saturating the specimen by immersion in saturated lime water until the weight changes by not more than 0.1% per day;
- Mounting the specimen between the migration cells and filling the upstream cell with 5% NaCl solution and the downstream cell with 0.3 N NaOH solution;
- Applying an external potential of 12 V DC between the two cells and measuring the actual potential drop across the specimen by using two reference electrodes;
- Qualitatively checking the downstream cell for chlorides by using slightly acidified 1 M AgNO\(_3\) solution until a white precipitate can be observed;
- Quantitatively determining chloride contents in the downstream cell at least once a day over at least seven days by using a standardized method;
- Performing linear regression analysis of at least five points of the linear part of the \( c-t \) (concentration-time) curve until a linear correlation coefficient of at least 0.9 is obtained;
- Calculating the chloride flux \( J \) from the slope of the linear regression.

The chloride diffusion coefficient, \( D_{ssm} \), is then calculated using the following equation:

\[
D_{ssm} = \frac{R T L}{z F \Delta E c_1} \frac{J}{V_2} \frac{\Delta c_2}{\Delta t} \frac{m^2}{s}
\]

(24)

Where,

\( D_{ssm} \): chloride diffusion coefficient (steady state migration)

\( R \): gas constant, \( R = 8.314 \text{ J/(K-mol)} \);

\( T \): average value of the initial and final temperatures in the anolyte solution (K);

\( L \): thickness of the specimen (m);

\( z \): absolute value of ion valence, for chloride, \( z=1 \);

\( F \): Faraday constant, \( F = 9.648 \times 10^4 \text{ J/(V-mol)} \);

\( \Delta E \): absolute value of the potential difference between the upstream solution and the downstream solution, measured by using two reference electrodes (v);

\( c_1, c_2 \): chloride concentration in the upstream and downstream cell, respectively.

\( J \): chloride flux, kg/(m\(^2\) s);

\( V_2 \): volume of the downstream cell, (m\(^3\));

\( A \): cross-sectional area of the specimen, (m\(^2\));

\( \Delta c_2/\Delta t \): slope of the concentration-time plot, (kg/m\(^2\) s).

Although this method gives sufficient precision for moderately permeable concrete, yet the reproducibility is poor in case of low permeability concrete.
5.6 AASHTO T277: Electrical Indication of Concrete’s Ability to Resist chloride Ion Penetration (Rapid Chloride Permeability Test) (ASTM C1202):

In this test [67] a water saturated, 50 mm thick, 100mm dia concrete specimen is subjected to 60 V DC voltage for six hours, as shown in (Fig. 3).

![AASHTO T277 Test Set Up](image)

Fig. 9 AASHTO T277 (ASTM C1202) test set up.

The figure shows, that two stainless steel electrode (surfaceperforated) are placed on two sides. On one side a reservoir contains 3.0% NaCl solution (connected to –ve terminal) and on the other side, the second reservoir contains 0.3 M NaOH solution, its electrode is connected to +ve terminal. Originally this test was referred to as the “Rapid Chloride Permeability Test” (RCPT) although this test does not give permeability. Some objections to this test are:

i) the current passed is for all ions (not just for chloride ions)

ii) the measurements are before the steady state migration is achieved, and

iii) a higher voltage may lead to increase in temperature, especially for low quality concretes [68 – 72].

Despite these limitations, many attempts have been made to successfully correlate RCPT values with diffusion coefficients from other tests [73-74].

5.7 Rapid Migration Test (CTH test):

In this test [63] a migration cell is setup with a specimen of 100 mm dia and 50 mm thick and the applied voltage is kept at 30 volt (Fig. 10). Although the experimental setup is similar to other electrical migration test, in this case the chloride concentration of the downstream solution is not monitored and after specified duration of test (8 hrs) the samples are removed and split and the depth of chloride penetration is determined in one half of the specimen using colorimetric technique, in which the AgNO₃ solution is used (i.e. sprayed) as indicator. The chlorides bind with silver to produce whitish silver chloride. In the absence of chlorides, the silver bonds with hydroxides of concrete giving brownish colour. Otsuki 1992 [75] determined that the optimum concentration of AgNO₃ to be used is 0.1N solution that gives a colour change corresponding to the location of a soluble chloride concentration of 0.15% by weigh of cement.
The above experiment examines the total chloride content and the soluble chloride percentage to determine whether the chloride comes from external sources or from initial mixing, the w/c ratio of the concrete.

The depth of penetration can be used to determine Cl\(^-\) ion diffusion coefficient from the Nernst-Einstein equation [63].

\[
D = \frac{RT}{x_F} \times \frac{x_f}{t}
\]

(25)

Where, \(X_f\) is the injection point of chloride ion profile, which is related to the depth given by the colorimetric technique.

This CTH test has been found to be more useful than RCPT related examination of actual Cl\(^-\) ion movement and temperature rise.

5.8 Resistivity Technique:

Another method [76] for assessing the ability of chlorides to penetrate concrete uses electrical resistance and conductivity measurement. The conductivity of saturated porous medium (concrete) is primarily determined by the conductivity of pore solution and is given by a term formation factor (FF).

\[
FF = \frac{\sigma}{\sigma_0}
\]

where, \(\sigma\) is the conductivity of the porous material and \(\sigma_0\) is the conductivity of the pore solution. However the conductivity and the diffusivity in a porous medium are both related to same factors, e.g. tortuosity, constrictivity, pore size and connectivity and are given by,

\[
FF = \frac{D}{D_0}
\]

Where, \(D\) is the diffusivity of the porous medium and \(D_0\) is the diffusivity of the chloride ion in the pore solution [77].

There are two types of test to determine the resistivity value involving direct current or alternating current [76]. The measurement of alternating resistance can be done by placing a test specimen (concrete) between two electrodes and applying an A.C. voltage and monitoring current to determine a resistance value. Direct current resistivity is measured by
applying a voltage between two electrodes with the concrete sandwiched between them (Fig. 11).

Because the concrete conducts electricity as an electrolyte, there is a polarisation effect which causes the actual voltage (causing current) to be reduced by an amount. If the polarisation effect is constant at different applied voltages, this can be accounted for by measuring at two given voltages e.g. for D.C. resistance \[ R = \frac{E_{a1} - E_{a2}}{I_{1} - I_{2}} \] (26)

where, \( R \) is the resistance, \( E_{a1} \) and \( E_{a2} \) are the two applied voltages and \( I_{1} \) and \( I_{2} \) are the relevant currents. From this resistivity can be calculated using,

\[ \rho = R \frac{A}{L} \] (27)

where, \( \rho \) is the resistivity, \( A \) is the cross-sectional area and \( L \) is the length of the specimen.

5.9 Wenner’s in situ Resistivity Measurement:

Fig. 12 shows an array of probes for determining resistivity of concrete in situ (i.e. without removing cores to place between plates). An array of four probes is set at four points, at a constant distance apart ‘a’. Between the two outer points the current a current is applied while between two inner points the potential is measured. This has advantage of eliminating the influence of polarisation as the actual potential is measured in the inner region. When the thickness is much greater than the distance between the points (i.e. a semi-infinite region), the resistivity can be calculated as \[ \rho = \frac{2\pi a P}{I} \] (28)

Where, \( \rho \) is the resistivity, \( a \) is the distance between points, \( P \) is the measured potential, and \( I \) is the applied current.
If the Thickness is not much greater than the distance between the two points, a correction factor may be used [78]. The resistivity tests avoids heating of the concrete (voltage can be low ~10 volt or lower) [77]. The main drawback of this technique is in its determination of conductivity of pore solution (either pore solution must be removed from concrete to get resistivity, or the concrete may be pre-saturated with a solution of known conductivity). Pre-saturation requires drying of concrete. Drying may lead to damage of pore structure due to micro-cracking, which may increase the diffusivity [79]. Another important fact is that the pore solution contains a wide range of ions (alkali hydroxides), which may precipitate if the concrete is dried (as a necessity before pore saturation). The precipitated ions may affect the conductivity. As a precaution a highly conductive solution (5M NaCl), [77] is normally used. In this way, this technique manages to ensure a steady state condition from the start of the testing procedure. For very high quality concretes, it will be difficult to extract the pore solution, which is an important disadvantage [80].

5.10 Pressure Penetration Technique:

In this method [81] the flow of chloride ion into concrete is accelerated by exposing one face of the concrete to a chloride containing solution, which is under pressure. This pressure will drive the chloride ions into the concrete under both conditions of convection and diffusion [81]. The method is similar to determining water permeability using a pressure cell, in which concrete specimen is pre-saturated with water and placed in a permeability cell (with proper sealing to avoid leakage). Fig. 13 shows the chloride containing solution at one face of the concrete on top of which pressure is applied for a given period of time, after which the concrete sample is removed from the cell and tested for chlorides.
The proposed condition governing the convection and diffusion is given by eqn. 16 [81].
\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \bar{V} \frac{\partial c}{\partial x}
\]  
(29)
Where \( \bar{V} \) is the average linear rate of flow which is [81]
\[
\bar{V} = -\frac{k}{n} \frac{\partial h}{\partial x}
\]  
(30)
Where \( k \) is the hydraulic permeability, \( n \) is the porosity and \( h \) is the applied pressure head. The solution to this differential equation is [81].
\[
\frac{c_{ct}}{c_s} = 0.5 \left[ \text{erfc} \left( \frac{x - \bar{V} t}{2\sqrt{Dt}} \right) + \exp \left( \frac{\bar{V} x}{D} \right) \text{erf} \left( \frac{x - \bar{V} t}{2\sqrt{Dt}} \right) \right]
\]  
(31)

The above equation allows the determination of chloride diffusion coefficient, if a chloride profile is known at a specific time, which can be obtained as describe below. The depth of chloride penetration of known concentration of chloride at a specific time can be conveniently determined using a colorimetric technique (such as AgNO\(_3\) spray procedure explained in CTH test) [5.7]. This value can also be used to determine water permeability the [82].
\[
k = \frac{n l \chi_d}{\chi h} 
\]  
(32)
where \( k \) is the hydraulic conductivity, \( n \) is the porosity, \( l \) is the length of the specimen, \( \chi_d \) is the depth of chloride penetration, \( t \) is the time over which pressure was applied and \( h \) is the applied head.

5.11 Sorptivity technique:

The term sorptivity is used as a measure of capillary forces exerted by the pore structure causing fluids to withdrawn unto the body of the material.

For simplicity, the one dimensional flow can be stated as [83].
\[
i = St^{1/2}
\]  
(33)
Where \( i \) is the cumulative water absorption per unit area of inflow surface, \( S \) is the sorptivity and \( t \) is the elapsed time. To determine sorptivity of concrete specimen in the laboratory a simple technique is given in (Fig. 14).
For the determination of sorptivity, the concrete specimen is preconditioned to a certain moisture condition either by drying the specimen for seven days in an oven at 50 °C or by drying for four days at 50 °C and then cooling in a sealed container for three days. The sides of the specimen are sealed with tape. The initial mass of the specimen is taken (time zero) and then it is immersed to a depth 5 – 10 mm in water. At selected times (1, 2, 3, 4, 5, 9, 12, 16, 20 and 25 minute) the specimen is removed from water, excess water blotted out and then the specimen is weighed. It is then replaced in the water and then stopwatch is started again. The gain in mass per unit area over the density of water is plotted vs. square root of elapsed time. The slope of the line gives the reported sorptivity.

While sorptivity tests can avoid many of the difficulties of the RCPT, it does have some limitations, such as the following:

- It is only able to evaluate the surface of the concrete, i.e., sorptivity test involving the time frame will not give any information of the bulk properties of the concrete. Therefore, in case of high performances services where the steels (rebars) are at typical depths, the sorptivity results will not be useful.
- Another difficulty arises in field tests where moisture content varies drastically, making sorptivity data unusable [83].
- Sorptivity is not a constant property over the long term. Therefore, sorptivity (S<sub>i</sub>) obtained at initial exposure, will change (because of additional absorption) to another sorptivity (S<sub>f</sub>) [84].
- Sorptivity is not a familiar term with construction engineers compared to permeability or diffusion.

**Other electromigration techniques:**

**5.12.1 Determination of ‘D’ using Nernst – Planck equation:**

The use of electrical field for the movement (migration) of chloride ion has been utilized in many techniques. Such data can also be collected by measuring, in particular, the actual movement of chloride ion (as opposed to simply measuring the amount of charge passed). Using Nernst – Planck equation [85].
The following terms can be measured [85].

Where,

\( J_i \) = Flux of the ionic species \( (i) \)

\( D_i \) = Diffusion co-efficient of the ionic species \( (i) \)

\( C_i(X) \) = Concentration of ionic species as a function of location \( (X) \)

\( Z_i \) = Valence of the ionic species \( (i) \)

\( F \) = Faraday’s constant

\( R \) = Universal gas constant

\( T \) = Temperature

\( E(X) \) = Applied electrical potential as a function of \( X \), and

\( V_i(X) \) = Convection velocity of ionic species \( (i) \).

According to Andrade 1994 [86], when an electric field is applied in an electrolyte, the ions move due to diffusion (differences in concentration), convection (electrolyte movement) and migration (differences in potential), which is represented in the equation above (Eqn. 34).

Now in such situation, where there is no pressure or moisture gradient (no convection) and assuming that the diffusion is negligible as compared to the electrical migration (which is sufficiently reasonable if the applied voltage is about 10 – 15 volt) the equation (Eqn. 34) becomes [86].

\[-J_i = \frac{Z_iF}{RT} D_i C_i \frac{\partial E(X)}{\partial X} + C_i V_i(X)\] (34)

The following terms can be measured [85].

According to Andrade 1994 [86], when an electric field is applied in an electrolyte, the ions move due to diffusion (differences in concentration), convection (electrolyte movement) and migration (differences in potential), which is represented in the equation above (Eqn. 34).

Now in such situation, where there is no pressure or moisture gradient (no convection) and assuming that the diffusion is negligible as compared to the electrical migration (which is sufficiently reasonable if the applied voltage is about 10 – 15 volt) the equation (Eqn. 34) becomes [86].

\[-J_i = \frac{Z_iF}{RT} D_i C_i \frac{\partial E(X)}{\partial X}\] (35)

Also one can have from above equation

\[ D_{eff} = \frac{J_{Cl}RTI}{Z_iFC_iD_E} \] (36)

Where,

\( \gamma \) = Activity co-efficient

\( I \) = Concrete disc thickness (cm.)

\( J_{Cl} \) = Flux of chloride ion \( (\text{mol/cm}^2\cdot\text{S}) \)

Therefore the above simplification for ‘D’ can be utilized once the chloride ion flux is known and if it is assumed that the voltage drop across the cell is linear.

5.12.2 Determination of ‘D’ using Nernst – Einstein equation:

It has been discussed that Fick’s law can be used to determine diffusion of migrating ion with the help of the standard solution of the equation [17]. However in this diffusion process, the fluxing species must not react with the matrix, and matrix is homogeneous in structure and composition. If the concrete is considered to be a solid electrolyte, the diffusivity of the charged species \( \text{‘i’ in concrete is related to its partial conductivity, as given by Nernst – Einstein equation [87].} \)

\[ D_i = \frac{RT\sigma_i}{Z_i^2F^2C_i} \] (37)

Where,

\( D_i \) = Diffusivity of species \( \text{i (cm}^2\cdot\text{s).} \)

\( R \) = Universal gas constant \( (8.314\text{J/mol. K}) \)

\( T \) = Absolute temperature \( (\text{K}) \)

\( \sigma_i \) = Partial conductivity of species \( \text{i}(\text{S/cm}) \)

\( Z_i \) = Charge of species \( \text{i} \)

\( F \) = Faraday’s constant \( (96500\text{ Coulomb/mol}) \)

\( C_i \) = Concentration of species \( \text{i (mol/cm}^3\text{).} \)
The partial conductivity \( \sigma_i \) is given as,

\[
\sigma_i = t_i \cdot \sigma
\]  
(38)

\( t_i \) = Transference no. of species ‘i’

\( \sigma \) = Conductivity of concrete

Also,

\[
t_i = \frac{Q_i}{Q} = \frac{I_i}{I}
\]  
(39)

Where, \( Q_i \) and \( I_i \) are the amount of charge and current contribution of the species ‘i’ to the total electric quantity \( Q \) and current \( I \), respectively. This means if the diffusivity of an ion is to be determined by the Nernst – Einstein equation, the transference number of the ion must be known, however a simpler approach is to take \( t_i = 1.0 \). This is in agreement with the results obtained from laboratory and field data for ordinary concrete, Portland cement and mortar [88 – 103].

5.12.3 Test method on Nernst – Einstein equation:

5.12.3.1 Method – 1

Page et al [104] studied the effect of cement matrix variables on diffusion of chloride ions in concrete. The principle aims to establish a simple technique for study of chloride diffusion kinetics in mature cement pastes and to explain the effect on diffusion of the following factors.

1. w/c ratio and temperature for specimens of constant cement composition.
2. Curing condition and interfacial segregation for specimens of fixed cement composition and w/c ratio at constant temperature.
3. Variation in cement composition for specimens of fixed w/c ratio at constant temperature.

Experimental Cell: The figure (Fig. 15) below shows a two compartment cell, in which the samples were made from cement paste (with desired w/c ratio in the range of 0.4 – 0.6). The cement paste were cast into cylindrical PVC moulds (dia 4.9 mm and length 75 mm) and compacted by vibration.

![Diffusion Cell Diagram](image)

Fig. 15 Diffusion Cell

A typical set of result is shown in (Fig. 16).
In the experiment, an initial delay ($t_0$) was allowed to establish Cl$^-$ diffusion across the thickness of the specimen disc. It was noted that there was a linear increase with time in the Cl$^-$ concentration ($C_2$) of the solution in compartment 2, while concentration ($C_1$) in compartment 1 was remaining effectively constant over the period of measurement. This condition was noted as quasi – steady state diffusion and it implies that the flux ($J$) is normal to the diffusion direction and the activity (of Cl$^-$) is effectively constant. Therefore the flux can be given by [104]

$$J = \frac{V}{A} \frac{dC_2}{dt} = \frac{D}{l} (C_1 - C_2)$$  \hspace{1cm} (40)

Where, $D$ is the effective diffusivity of chloride ion through the disc in m$^2$s$^{-1}$ (assumed to be independent of concentration), $V$ is the volume of solution in compartment 2 in m$^3$, $A$ is the cross-sectional area in m$^2$, $l$ is the thickness of the disc in m and $C_1$ and $C_2$, the solution concentrations, are assumed to be equal to the surface activities of chloride ion in moles /m$^3$.

The above work also included the values of diffusivity of Cl$^-$ at various temperatures in OPC paste (w/c varying). The results of the data was given as Arrhenius plot, constructed by means of linear regression analysis (Fig. 17) [104] and were found to be reasonably acceptable [Fig. 16 and 17].
5.12.3.2 Method – 2:

**Test method (Two – Chamber Cell):** A two chamber cell utilizes with concrete sample at the division between two chambers is shown in (Fig. 18) [87]. Usually the concrete sample is a disc of 100 mm dia and length 15 – 50 mm. The thickness of the disc will affect the duration of test. However the thickness is important to avoid the influence of aggregate interfaces. If the size of the aggregate is comparable to the thickness, there may exist a weak transition zone around the aggregate, which may provide a faster path to the movement of the chloride ions. To avoid this, the thickness must be sufficiently larger than the maximum aggregate size. The cathode chamber may contain chloride ions and the anode chamber may contain water or lime water. A voltage is then applied, and chloride ion concentration of the downstream (anode chamber) is monitored and the change of chloride ion concentration (vs. time) allows to find the diffusion coefficient. Role of applied voltage is important because it controls the time required to perform the test e.g. a low voltage may avoid the heating of the sample but may prolong the duration of test. A wide variety of voltages are reported in literatures, e.g. 10 – 12 volt range, to avoid heating of sample, but these result in long test duration [77, 105 – 109].

![Fig. 18. Typical chloride migration cell](image)

**6.0 Conclusion:**

Different testing techniques for the study of diffusion of chloride ions which is the primary cause for the deterioration and ultimate failure of rebar metals and concrete structures have been briefly discussed above. Yet, most of the testing techniques have invariably used various effective parameters assuming these as constants or negligible, as a result of which, individually each test is answerable to one particular type of environmental condition. This means if a multitude of factors are observed to be effecting chloride migration, then more than one type of test procedure are to be conducted. Another poignant aspect is that in the Fick’s law there are different possibilities which have been undermined, and these will come up every time a new environmental parameter possesses threat to the concrete structure such as the effect of fatigue (on rebar). A brief review of tests on chloride migration indicates that the techniques involving electro – migration have been given greater share, which is probably
due to the interest of rapid evaluation of the effect of chloride migration. But such data cannot be true representative of the “natural” rate of migration of chloride ions, in spite of arranging tests at lower range of voltage e.g. 1 – 3 volt. In this context it may be noted that there always exist a self – driving force inside the concrete cover which provides path for ionic current between the anodic and cathodic portions of the rebar surface. However to track this natural process is time consuming, beside the fact that such a test would involve year(s) – long tests which may be interrupted or distracted by different other evolving factors during the period of experimentation.

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