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# Effect of Wet-Mat Curing Time and Earlier Loading on Long-Term Durability of Bridge Decks: Literature Review

By Sanjaya Senadheera, Randal Scott Phelan, Hector Garcia-Monzon, Aruna Amarasiri, Montasheema Afroze, Hari Aamidala, Sang-Yun Lee, Hassan Ghanem

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By the  
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## **CHAPTER I**

### **INTRODUCTION**

#### **1.1 CURING**

Curing is the practice of maintaining a favorable moisture content and temperature within a concrete for a period of time (Garcia-Monzon, 2006). The duration and effectiveness of a curing treatment affects the development of concrete properties such as strength, permeability, and resistance to freeze-thaw deterioration. Insufficient moisture during curing has been found to produce cracks, compromise strength, and reduce long-term durability (Wojcik and Fitzjarrald 2001). For Portland cements, typically the highest rate of heat generation occurs during the first 24 hours after initial contact between water and cement, and a large amount of heat due to hydration evolves within the first three days (PCA, 1997). To prevent mix water from evaporating due to the heat of hydration and /or ambient conditions and to ensure sufficient moisture is present, concrete should be kept moist or saturated during this critical period.

There are primarily two methods of curing which can be used in the field – water and sealed curing. Water curing supplies additional moisture to the concrete as well as prevents mix water evaporation. Sealed curing does not supply additional moisture but rather relies on the prevention of moisture loss.

##### 1.1.1 Water Curing

Water curing can be accomplished by spraying or ponding water on the concrete surface or applying moist coverings. The use of lawn sprinklers is one method of spraying water on concrete and keeping it saturated. Spraying tends to consume large amounts of water, however, and is not economical when water supplies at the site are limited. If spraying is performed in intervals, drying of the concrete must not be allowed to prevent surface crazing (PCA 1998). Care must also be taken to prevent erosion of freshly finished concrete.

Curing concrete by way of ponding requires maintaining a layer of water on the concrete surface. This is performed by surrounding the perimeter of the concrete with

earth or sand dikes which can sustain a pond of water. Ponding is a good method to prevent moisture loss, provide sufficient moisture, and maintain a constant temperature during concrete hydration. Although ponding may be a good method, it requires a great deal of work.

Moist coverings are another form of water curing and include cotton mats, burlap, and other moisture-retaining fabrics. These coverings should be: (1) applied on top of the concrete as soon as the concrete has hardened sufficiently, (2) saturated with water, and (3) kept continually moist for the duration of the curing period. Periodic supervision is necessary since coverings tend to dry out and therefore need occasional moistening. If water curing is the method of choice, it should be applied as soon as possible to prevent the sealing of capillary pores due to drying. However, it cannot be applied too early due to the possible existence of bleed water, which can increase the water cement ratio of the cement paste at the top surface.

#### 1.1.2 Sealed Curing

Sealed curing can consist of plastic sheeting, waterproof paper or membrane-forming curing compound. Plastic sheeting or waterproof paper should be applied to the surface of the concrete as soon as possible. However, it cannot be placed too soon or marring of the surface will occur. Plastic sheeting traps evaporated moisture within the sheeting. The moisture condenses on the sheeting and redistributes itself over the surface of the concrete. This condensed moisture helps continue the hydration process.

Curing compounds or membrane-forming compounds have become a very popular form of curing as they can be applied much sooner than sheets or mats. Although curing compounds have found wide acceptance, they provide the least amount of curing protection. Also, they do not necessarily prevent complete evaporation of mix water. Instead, they only retard this process, as it is typically impossible to completely seal the entire concrete deck surface with the compound. As a result of an impermeable layer forming on the concrete surface, mix water generally is the primary means for hydration, with some help possible from moist curing if applied later. The use of curing compounds is best after there has been some initial time of moist curing (e.g., sprinkling water, ponding, or saturated covering).

## **1.2 WET MAT CURING IN TEXAS**

The Texas Department of Transportation (TxDOT) allows the use of what is termed “wet mats” to aid in the curing of concrete in Specification 420 (TxDOT, 2004). Fresh concrete in bridge decks is kept continuously wet by maintaining wet cotton mats in direct contact with the fresh concrete for a specified curing time. The specification requirement for wet mat curing is 8 days for decks with Type I cement, 10 days for decks with Type II or I/II cement, and 10 days for decks with supplementary cementing materials. (TxDOT, 2004). The concrete can be opened to all traffic after the specification requirement of 8 – 10 days wet mat curing plus a day for the surface to dry and a day to apply the concrete surface treatment, for a total of 10 – 12 days. The 1995 specification required a minimum of 14 days for construction traffic not to exceed three-quarter ton vehicles and a minimum of 21 days to open to all traffic. The 1982 specification required 14 days before construction traffic was allowed and a minimum of 30 days before opening to all traffic. The longer times required by the earlier specifications were based upon concerns that younger concrete might have more microcracking due to applied loads.

### 1.2.1 Objective

Although concrete mix designs have improved in high early strength and durability capabilities, there is a paucity of quantitative field and laboratory data on the durability properties of early-loaded concrete. TxDOT and the general public would like to open newly-cast concrete bridge decks to full traffic as early as possible to relieve roadway congestion and decrease project costs. The objective of this research program was to collect field and laboratory data leading to a better understanding of the relationships of concrete mix designs across the state of Texas, allowance of early loading, and long-term durability of the concrete bridge decks. Additionally, researchers developed a method named the Strength Durability Index, SDI method, to predict the strength and permeability of concrete. The SDI method can be used as a guideline for terminating wet mat curing and determining when traffic loading can be allowed.

### 1.2.2 Approach

Researchers conducted an extensive literature search, survey of TxDOT districts, and survey of other state Departments of Transportation (DOTs) to determine the state-of-the-art for bridge deck curing, early loading, early age behavior, and durability prediction models (Phelan, undated, Phelan and Senadheera, February 2001). Several concrete mixtures commonly used in regional districts throughout the state of Texas were tested (Garcia-Monzon, 2006). Each concrete mixture was tested under field conditions within its respective climatic region. Field testing and testing of field-collected samples provided information on concrete strength, concrete maturity and permeability. Supplementary laboratory experiments were performed to determine permeability using the salt ponding method (Garcia-Monzon, 2006), and the Rapid Chloride Permeability Test, RCPT, (Afroze, 2002). Researchers used the laboratory tests to correlate results with field-collected samples and concrete strengths. Both field and laboratory test data were compared with existing models for predicting concrete maturity, and a Strength Durability Index (SDI) was developed to predict strength and permeability of concrete for various mix designs and curing methods (Garcia-Monzon, 2006). Core samples from three field sites were examined using petrographic techniques to determine air void contents, calcium hydroxide contents, aggregate/paste interface features, cracks, unhydrated cement grains and other petrographic features (Lee, 2000). Researchers related the variations of petrographic features with wet mat curing duration. Finally, researchers investigated the fracture properties of several medium-strength concrete mixes cured for various durations in order to characterize the extent of cracking that might allow the ingress of chlorides from de-icing salts to the reinforcing bars (Amarasiri, 2003).

### 1.2.3 Purpose of This Report

The purpose of this report is to present results from an extensive literature review completed in the initial stages of the research project. The literature review topics included concrete curing, early loading of concrete bridge decks, early age behavior of concrete, durability prediction models, descriptions of test procedures used in the research and descriptions of test sites. A brief description of concrete composition, hydration, curing, and strength development is first provided as an introduction. In addition, the Rapid

Chloride Permeability Test (RCPT) and ponding test are presented. With these are accompanied the guidelines which assign a permeability classification to the concrete.

### 1.3 COMPOSITION OF CEMENT

Ordinary Portland cement is generally composed of four major compounds: tricalcium silicate (C<sub>3</sub>S), dicalcium silicate (C<sub>2</sub>S), tricalcium aluminate (C<sub>3</sub>A), and tetracalcium aluminoferrite (C<sub>4</sub>AF). The percentages of these compounds can be manipulated to modify properties of cement to achieve desirable qualities. ASTM C150 distinguished five types of Portland cement: Types I, II, III, IV, and V. The characteristics and composition of each cement type are displayed in Tables 1.1 and 1.2, respectively.

**Table 1.1** Characteristics of Portland Cement Types (PCA 1998)

Cement Type	Characteristic
I	Normal cement (general purpose)
II	Moderate sulfate resistance
III	High early strength
IV	Low heat of hydration
V	High sulfate resistance

**Table 1.2** Percentages of Compound Contents in Portland Cement (PCA 1998)

Chemical Compound	Portland Cement Type				
	I	II	III	IV	V
C <sub>3</sub> S	55	51	56	28	38
C <sub>2</sub> S	19	24	19	49	43
C <sub>3</sub> A	10	6	10	4	4
C <sub>4</sub> AF	7	11	7	12	9

Every chemical compound serves a purpose in the composition of Portland cement. If rapid hardening is required, higher concentrations of C<sub>3</sub>S are present in the cement. The rapid strength gain from this compound also generates the most heat. If thermal cracking from high heat of hydration is of concern, then a major portion of C<sub>3</sub>S may be replaced by C<sub>2</sub>S since it releases less heat. For resistance against sulfates attack, C<sub>3</sub>A content is lowered in the cement. C<sub>4</sub>AF is largely responsible for lowering clinkering temperature during the

production of Portland cement and also contributes to the cement's color.

### 1.3.1 Hydration of Cement

The hydration of concrete is an exothermic chemical process. Heat generated from this process is primarily due to the interaction between water and  $C_3S$  within the cement (Mindess et al., 2002). Although other chemicals are present in Portland cement, they generally have minor roles in the production of heat during the hydration process.

When cement first comes into contact with water a period of rapid heat evolution occurs and lasts approximately 15 minutes, followed by a dormant period of inactivity that indicates the plastic state of concrete. Concrete will generally remain in a plastic state anywhere from 2 to 4 hours after mixing.

Following the plastic state, an acceleration period of renewed reaction within the cement occurs. Hydration products consisting of a hydrate layer form around the surface of  $C_3S$  particles and are produced at a high rate. The reaction is accompanied by an increased rate of heat generation (Mindess et al. 2002). As the temperature rises in the concrete, the hydration rate is further accelerated and concrete gains strength rapidly (PCA, 1997). It is at the end of this stage that the maximum rate of heat generation is achieved. The acceleration period lasts for about 4 to 8 hours.

A deceleration period, resulting from the constant growth of the hydrate layer around  $C_3S$  particles, follows the acceleration period. The hydrate layer begins to obstruct the path of free pore water in the concrete from reaching unhydrated  $C_3S$  particles. With increasing pore water path obstruction from growing hydrate layers, the hydration process approaches the steady state, where hydration continues to occur, but at a very slow and steady rate. The steady state period starts about 18 to 36 hours from initial contact between water and cement. Once this stage has been reached, hydration approaches 100% completion asymptotically (Mindess et al., 2002).

### 1.3.2 Supplementary Cementitious Materials (SCMs)

Supplementary Cementitious Materials (SCMs) are siliceous or aluminosiliceous materials with little to no cementitious attributes in themselves. However, SCMs do react with water and calcium hydroxide produced from the hydration of Portland cement. The



use of SCM as a cement replacement can produce a lower cost concrete, since some SCMs can be half the price of cement (Mindess 2002) and concrete with more desirable properties. The properties warranted for a concrete mixture can determine the quantity and required SCM material.

SCMs usually have a slower rate of reduction. This results in lower heats of hydration and reduced early-age strength. Long-term strength, however, is not affected and can be improved with the correct addition of SCM. In order to gain the benefits from the addition of SCMs, a longer period of moist curing is needed to progress the hydration of such material, otherwise it will act as a filler. SCMs primarily for cement replacement include fly ash and silica fume. The benefits of both are discussed in the following sections.

### 1.3.3 Fly Ash

Fly ash is a noncombustible inorganic residue from coal burning in power plants. The two common types of fly ash are class C and F. Class C fly ash is higher in calcium content than class F fly ash. In addition, class C fly ash reacts with water and hardens whereas class F fly ash will remain relatively dormant.

The use of fly ash in a concrete mixture can reduce the amount of heat generated during hydration and thus minimize thermal cracking. Fly ash aids in the placement of concrete by improving workability and reducing segregation and bleeding. Fly ash can reduce concrete permeability and improve long term strength provided a prolonged and sufficient curing duration is used (PCA 1998).

### 1.3.4 Ground Granulated Blast-Furnace Slag (GGBS)

GGBS is primarily a by-product from blast furnace production of iron from ore. The advantages of using GGBS in a concrete mixture include a reduction in heat of hydration, improved workability, and reduced permeability with a period of adequate curing. A negative effect of GGBS is the potential of increased bleeding after concrete placement (PCA 1998).

### 1.3.5 Silica Fume

Silica fume is produced from the oxidized vapor resulting from the manufacture of silicon or ferrosilicon alloy. Silica fume can lessen segregation and bleeding of a concrete mixture and is very effective in reducing permeability with appropriate curing. However, concrete mixtures containing silica fume generally required more water to produce the same slump as in a concrete without silica fume (PCA 1998). Thus, workability may be reduced if mix water is not increased.

## **1.4 STUDIES OF CONCRETE CURING**

### 1.4.1 Studies of Curing Regimen Effects on Concrete Temperature

Curing method can affect and/or control the temperature rise in concrete slabs. Findings by Cable, Wang, and Ge (2003) have shown moist-curing to be the most effective method to minimize the variation in concrete surface temperatures due to diurnal atmospheric conditions when compared to utilizing only a curing compound or nothing at all. Sections receiving the curing compound treatment had better surface temperature control with respect to the section with no cure coverage. Moreover, Khan, Cook, and Mitchell (1998) have found cure treatment to affect peak temperature. They subjected 4-inch thick concrete slabs to three different cure treatments under laboratory conditions of 22 °C (71.6 °F) and relative humidity of 50%. The cure treatments used were moist (wet burlap), sealed (covered with polyethylene), and air cured. Both the moist and sealed cured concretes produced relatively high peak temperatures (approximately 120 to 127 °F) at 21 hours when compared to the air-cured slabs (95 °F at 24 hours). Moist and sealed curing would be beneficial during cold weather concreting since the increase in peak temperature would help progress hydration.

### 1.4.2 Studies of Curing Regimen Effects on Concrete Strength

The factors affecting concrete strength development, other than mixture composition, are primarily temperature and moisture. Findings from other researchers (Soroka and Baum 1994, Aïtcin et al. 1994, Nassif and Suksawang 2002, Conroy-Jones and Barr 2003) consistently reveal very low compressive and tensile strengths for air-cured (no protection against moisture loss) specimens when compared to specimens with either water

or sealed curing. These studies support the fact that moisture is an important factor for proper hydration and strength development.

With proper hydration during curing, early age compressive strength may be accelerated by increasing curing temperature. Of course, this increase in temperature can cause lower ultimate strengths when compared to curing at normal temperatures (Topcu and Toprak 2005, Klieger 1958, Chanvillard and D'Aloia 1997). If a high early age compressive strength is desired, engineers must decide on an acceptable degree of strength acceleration without sacrificing ultimate strength.

#### 1.4.3 Studies of Curing Regimen Effects on Concrete Permeability

Nassif and Suksawang (2002) reported lower permeability from concrete samples that were moist-cured with wet burlap as opposed to no curing. Permeability was further reduced with increased cure duration. Cable, Wang, and Ge (2003) discovered that the top concrete of a slab was affected by the type of concrete treatment. Slab sections treated with either a double application of curing compound or moist covering had lower permeability when compared to uncured slabs. They found, however, concrete at the bottom of the slabs to have similar permeability irrespective of the cure treatment used.

Therefore, the structure of the top layer concrete is of major concern during curing. Assuring adequate protection against drying reduces porosity (Alsayed 1994) and results in a tighter and less permeable matrix.

### **1.5 METHODS TO DETERMINE CONCRETE PERMEABILITY**

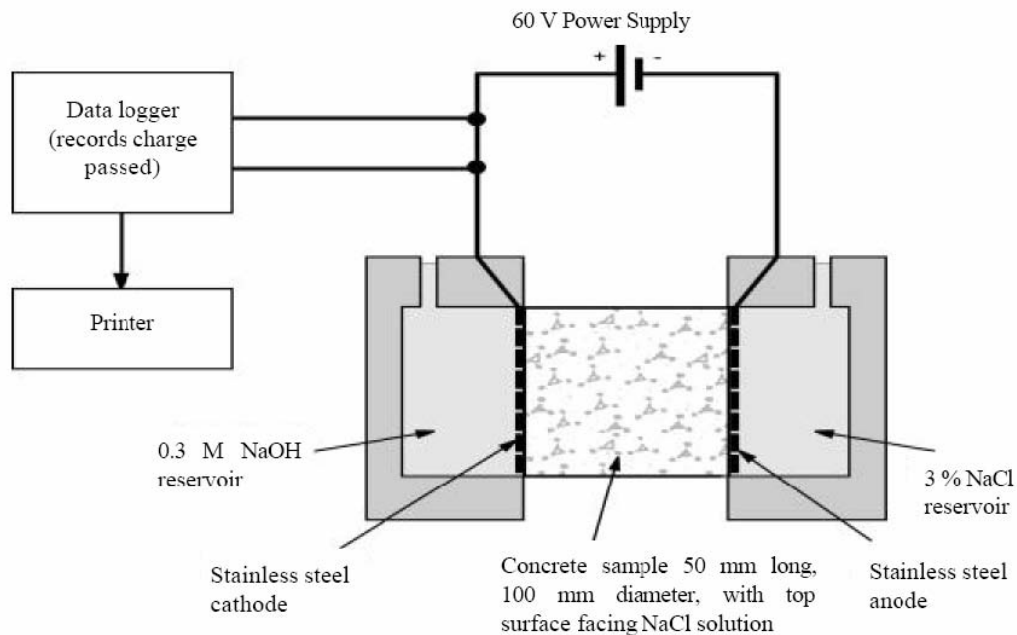
Concrete strength is sometimes used as an indirect durability measure. This parameter alone is not sufficient to dictate the level of durability but should be coupled with additional parameters. The level of concrete permeability has long been an accepted measure of durability. A strong durable concrete would be characterized as having low permeability. Concretes with low permeability have a high penetration resistance towards harmful liquids or gases, such as chlorine ions. This high resistance helps deter damaging reactions which may occur from these harmful materials. Conversely, high permeable concretes (low resistance to penetration) offer little protection from such intrusion. These unsafe agents can lead to the breakdown of the concrete matrix by creating internal

pressures from the formation of rust on reinforcement steel.

A number of tests are available to determine concrete permeability. Some of these test methods measure chloride ion penetrability directly while others measure it indirectly. Of the test methods available, the Rapid Chloride Permeability Test (RCPT) and the Test for Resistance of Concrete to Chloride Ion Penetration (hereafter referred to as ponding test) are the most popular. Both these methods have desirable qualities as well as shortcomings, which are discussed in the following sections.

### 1.5.1 Rapid Chloride Permeability Test (RCPT)

RCPT measures permeability indirectly by determining the electrical resistivity of concrete. This is achieved by subjecting a 2-inch by 6-inch diameter specimen to a 60-volt current for a period of 6 hours. The surface of the specimen corresponding to the top slab surface is exposed to the 3% NaCl solution. The other end is in contact with a 0.3 M NaOH solution. Detailed testing procedures can be found in AASHTO T 277 or ASTM C 1202. A schematic of a typical RCPT setup is illustrated in Figure 1.1.



**Figure 1.1** Typical RCPT Setup (Stanish, K.D. et al., 1997)

At the conclusion of the test, the coulombs passing through a sample is determined by plotting the recorded current over the 6-hour period. The area under the curve formed

by the plotted data is the total coulombs and can be determined by using the trapezoidal rule. These coulomb values can then be used to interpret chloride ion penetrability based on coulomb ranges set forth by ASTM C 1202. Table 1.3 lists permeability potential based on coulombs passed.

**Table 1.3** Concrete Permeability Based on Charge Passed

Charge Passed <i>a</i> (coulombs)	Chloride Ion Penetrability
> 4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
< 100	Negligible

*a* Taken from ASTM C 1202

The above permeability classifications were first proposed by Whiting (1981) from a study utilizing a limited number of specimens. Although the above classification guidelines are commonly accepted in practice, they can be misleading if other variables such as aggregate type and size, cement content, and concrete density are not considered (Whiting 1981). Additionally, current measurements are related to the movement of all ions (not just chloride ions) and can be influenced by increasing specimen temperatures resulting from the test (Stanish, K.D. et al. 1997). Even with the many variables which could affect RCPT results, this test method is appealing since it is relatively inexpensive and quick to perform.

Although this test has been adopted as a standard test, it has a number of drawbacks:

1. The current that passes through the sample during the test indicates the movement of all ions in the pore solution (that is, the sample's electrical conductivity), not just chloride ions. Therefore, supplementary cementitious materials (such as fly ash, silica fume, or ground granulated blast-furnace slag) or chemical admixtures (such as water reducers, superplasticizers, or corrosion inhibitors) can create misleading

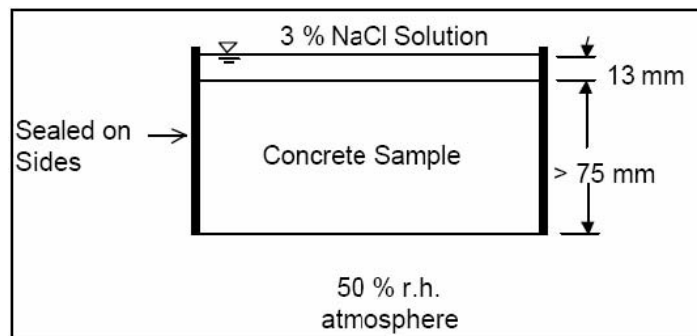
results largely due to the chemical composition of the pore solution, rather than from the actual permeability. As a result, some researchers do not recommend the RCPT to evaluate the chloride permeability of concrete containing these materials (Shi et al., 1998).

2. The conditions under which the measurements are taken may cause physical and chemical changes in the specimen, resulting in unrealistic values (Feldman et al., 1994). For example, the high voltage applied during the test increases the temperature of the sample, which can accelerate hydration, particularly in younger concretes.
3. The test has low inherent repeatability and reproducibility characteristics. As stated in the ASTM procedure, a single operator will have a coefficient of variation of 12.3%; thus the results from two properly conducted tests on the same material by the same operator could vary by as much as 42% (ASTM C1202.97). The multilaboratory coefficient of variation has been found to be 18.0%; thus two properly conducted tests on the same material by different laboratories could vary by as much as 51%. For this reason, three tests are usually conducted and the test results averaged, which brings the multilaboratory average down to 29%.
4. Another difficulty with the RCPT test is that it depends upon the conductivity of the concrete being in some way related to the chloride ion penetrability. Thus, any conducting material present in the concrete sample will bias the results, causing them to be too high. This would be the case if any reinforcing steel is present, if conductive fibers are used (e.g. carbon or steel), or if a highly ionic conductive pore solution is present (ASTM C 1202). This pore solution effect may be noticed if calcium nitrite is included as a corrosion inhibiting admixture, and other admixtures may also have this effect (ASTM C1202). Because these conductors all influence the results, a higher coulomb value than would otherwise be recorded may be determined. Nevertheless, the method still can serve as a quality control test. It can qualify a mix, but not necessarily disqualify it (Ozyildirim, 1994). If an acceptably low rating is achieved, it is known that the concrete is not worse than that, at least within the precision of the test method.

### 1.5.2 Ponding Test

The ponding test directly measures chloride ion concentration at different depths of a concrete sample. This procedure is performed on concrete specimens that have a minimum top surface area of 300-mm by 300-mm (12-in. x 12-in.) and at least 75-mm (3-in.) in height. Concrete samples are cured for 14 days and stored for 28 days as outlined in AASHTO T 259. Some variations to the curing and storage procedure can be made if experimental work seeks to investigate non-standard laboratory conditions, as is the case for this study. Alterations to the standards are discussed in more detail in subsequent chapters.

Once concrete specimens have undergone prescribed curing and conditioning, they are sealed on all sides, and the top and bottom surfaces are exposed. A dike assembly is constructed on the top surface of the sample. A 3% NaCl solution is continuously ponded at a depth of 13-mm (0.5-in.) on the surface for a period of 90 days and the specimen is stored in a 50% R.H. environment. A schematic of a ponded concrete sample is shown in Figure 1.2



**Figure 1.2** Ponding Test Setup (Stanish, K.D. et al., 1997)

After the 90-day ponding period, concrete powder samples are collected. Powder samples are taken over a 0.5-inch interval down to a depth of 1.5-inches as suggested by AASHTO T 259. Powder samples are then chemically tested to determine the average amount of chloride concentration for a particular depth. Results from this test present an approximate profile of the chloride ion penetration and are not interpreted easily since no known standard exists which classifies concrete permeability, (e.g. “high”, “moderate” or “low”), based on chloride concentration (Stanish, K.D. et al., 1997). There are, however, chloride concentration thresholds and some suggested classifications from Whiting’s

(1981) previous work on RCPT development, which are discussed in the following section.

The ponding test has several limitations including:

1. It takes at least 132 days from the time the samples are made to complete the test, requiring the concrete samples be cast at least five months before job site casting to evaluate the chloride permeability of a specific concrete.
2. A ponding period of 90 days is often too short to differentiate between the chloride permeability of different high performance concretes. A longer ponding time, however, extends the lead time necessary.
3. The .433 in. - and .511 in. thicknesses of the chloride samples do not provide a fine enough measurement to allow for determination of a profile of the chloride penetration. The test method allows an option - specifying other thicknesses - which many researchers exercise.
4. The ponding test provides a crude one-dimensional chloride ingress profile, but this profile is not just a function of chloride diffusion. Since the specimens have been left to dry for 28 days, there is an initial sorption effect when the slabs are first exposed to the solution. Salt solution is drawn quickly into the pores of the concrete. Also, the exposure of the bottom face to a 50 percent relative humidity environment during the test causes chlorides to be drawn into the concrete through a mechanism other than pure diffusion. There is vapor transmission from the wet front in the concrete to the drier atmosphere at the external face, causing more water to be drawn into the concrete and bringing chloride ions with it. This effect is called wicking (Stanish et al., 1997).
5. Although all these transport mechanisms may be present in a structure, the relative importance of each is not necessarily reflected by this test procedure. The test overemphasizes the importance of sorption, and to a lesser extent wicking. The relative amount of chloride pulled into the concrete by capillary absorption to the amount entering by diffusion will be greater when the test is only 90 days than when compared to the relative quantities entering during the lifetime of a structure. Also, if wicking is occurring in the concrete element of interest, the relative



humidity gradient will likely be less, at least for part of the time, than that which is set up during the test (Stanish et al., 1997).

### 1.5.3 Relating Integral Chloride and RCPT

Whiting’s (1981) study of rapid chloride permeability determination led to the accepted chloride penetrability classifications presented in Table 1.3. While establishing this coulomb-based classification system, Whiting determined chloride concentrations for the same concrete mixtures in the study. Whiting presented this parameter as total integral chloride and defined it as the chloride concentration versus unit depth of 0.2-inch increments as opposed to actual depth. Whiting believed this approach to be best since “sufficient results were not available on the lateral distribution of chloride within the test slabs” and “an integration using the actual depth values would only indicate how much chloride was contained in the particular drill hole sample, not in the slab as a whole” (Whiting 1981).

Cross-referencing results between ponding specimens and electrical resistivity tests performed on slab specimens, Whiting (1981) determined mean integral chloride values for corresponding permeability classifications. The integral chloride was calculated as a percentage of concrete sample weight. Plotted data correlating coulomb and integral chloride did not completely lie on a line of best fit, therefore Whiting included 95% confidence limits to encompass all data. Table 1.4 lists the mean and range values for given classifications of concrete chloride permeability.

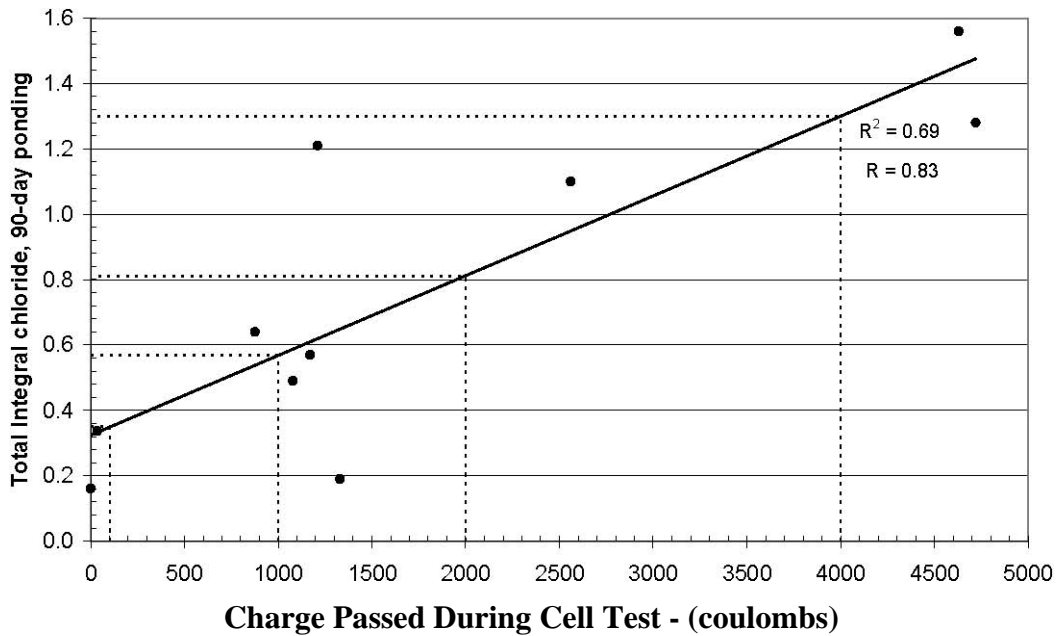
**Table 1.4** Chloride Penetrability Based on Integral Chloride Range

Chloride Ion Penetrability Classification	Calculated 90-Day Total Integral Chloride	Range of 95% Confidence Limit
High	1.08 %	0.89 - 1.27
Moderate	0.65 %	0.50 - 0.80
Low	0.37 %	0.18 - 0.56
Very Low	0.24 %	0.02 - 0.46

It should be noted that the penetrability classification from the previous table was derived from electrical resistivity tests performed on slab specimens with a 12-inch by 12-inch surface area and not the customary 4-inch diameter samples used in current practice. Confidence limits from Table 1.4 show the high end of the “very low” category encompasses a large portion of the “low” category and the “low” category slightly includes a portion of the “moderate” category. Whiting (1981) concludes the overlapping integral chloride ranges are the result of a broad confidence limit at low permeability.

The correlation between electrical resistivity from 4-inch diameter cores and integral chloride from ponding samples has less agreement (correlation coefficient,  $R$ , of 0.83) when compared to the relationship using slab specimens for both test method ( $R$  of 0.92). Although the comparison using electrical resistivity from slab specimens is better, a comparison utilizing 4-inch diameter specimens is desirable since it is the easiest to perform of the two.

Results from Whiting’s (1981) study correlating coulombs from the cell test (i.e. 4-inch diameter cores) and integral chloride are shown in Figure 1.3. The figure illustrates there is little agreement for low values of coulombs and somewhat better agreement with increasing values. Based on the guidelines for RCPT in Table 1.3, range values for integral chloride can be inferred. Vertical lines are drawn from the limit values on the abscissa upward to the linear regressed line. Horizontal lines are then provided from the intersection at the linear line to the ordinate. The values on the ordinate approximate the integral chloride for particular coulomb values when using 4-inch diameter cores. The corresponding ranges of coulombs and integral chloride for a permeability classification are displayed in Figure 1.3 on the following page.



**Figure 1.3** RCPT and Integral Chloride Correlation (Whiting 1981)

**Table 1.5** Concrete Permeability Based on RCPT and Ponding

Charge Passed <i>a</i> (coulombs)	Chloride Ion Penetrability	Integral Chloride <i>b</i> Content per 0.2-in.
> 4000	High	> 1.30
2000-4000	Moderate	0.80 to 1.30
1000-2000	Low	0.55 to 0.80
100-1000	Very Low	0.35 to 0.55
< 100	Negligible	< 0.35

*a* Taken from ASTM C 1202

*b* Deduced from findings by Whiting 1981

Although the correlation shown in Figure 1.3 is not remarkable, the guidelines set forth in Table 1.5 will be used to determine the permeability classification of concrete.



## **CHAPTER II**

### **DURABILITY OF CONCRETE**

#### **2.1 DURABILITY OF CONCRETE**

The durability of concrete usually is measured by the number of years' service it provides. If a correct prediction can be made of the conditions to which the concrete will be subjected (including applied loads), there is no reason for a properly proportioned concrete not to last for decades without significance maintenance (Nielsen, 1985). With the knowledge and experience currently available to protect concrete from aggressive agents, the selection of sound constitutive materials and the production of high quality concrete have become more attainable. However, economic pressure to reduce initial costs of construction and the desire for rapid construction often prevent the desired outcome. High durability concrete can be perceived to be more expensive to produce and sometimes more difficult to place than normal concrete. Also, its benefits are mostly evident in the long term. Life cycle cost analyses usually indicate that for many structures, the final cost of repairing avoidable damage is much greater than the additional cost to prevent problems from occurring. However, predictions from these analyses are not always needed.

In many cases, damage in concrete structures begins many years before any visible signs are observed. Once the material is compromised, concrete becomes vulnerable to many degradation mechanisms. Thus, damage occurs exponentially and concrete that has apparently survived for fifteen years may need to be replaced several years later.

Degradation of concrete can be divided into chemical attack and physical attack as shown in Table 2.1 (Young et al, 1998). One of the most widespread forms of concrete deterioration is cracking and spalling due to corrosion of the steel reinforcement, particularly when promoted by chloride salts. A more detailed explanation on the cause of corrosion and its mechanisms is presented in section 2.6.

**Table 2.1** Forms of Degradation in Concrete (Young et al. 1998)

<b>Type of Degradations</b>	<b>Description</b>	<b>Cause</b>	<b>Component involved</b>	<b>Symptoms</b>
Chemical	Alkali - aggregate	Reaction of siliceous aggregate by alkali ions	Aggregate	Coarse “map cracking” with viscous fluids erupting
	Sulfate attack	Reaction of paste components with sulfates	Paste	General cracking and softening
	Acid attack	Dissolution by acids	Paste (aggregate)	General etching of surface
	Rebar corrosion	Rusting of steel	Reinforcement	Cracks with rust stains above location of reinforcement
Physical	Frost attack	Freezing of water in pores	Paste	General scaling and spalling at surface
	D cracking	Freezing of water in pores	Aggregate	Fine crack pattern roughly parallel to joints in pavements
	Fire damage	Decomposition of hydration products and development of internal stresses	Paste (aggregate)	Cracking and spalling
	Thermal cracking shrinkage	Internal stresses from restrained contractions	Paste (aggregate)	Localized cracking

### 2.1.1 Permeability of Concrete

Permeability is a measure of how easy it is for water, air and other aggressive media to enter concrete. Concrete is a porous material, and therefore fluid movement inside concrete can occur by flow, diffusion, or sorption. Larger pores allow easier entry, while smaller pores decrease the rate at which these substances enter the concrete.

By definition, diffusion is the net movement of molecules from an area of high concentration to low concentration. This is a spontaneous process, requiring no input of energy (Neville, 1996). If a membrane separates the regions of high and low concentrations, diffusion occurs across the membrane from the region of higher concentration to the region of lower concentration, as long as the membrane is permeable to that substance. This is called passive transport, because it requires no energy to make it happen. Much of the movement of molecules across cell membranes occurs this way. By comparison, active transport goes against the concentration gradient, and requires the input of energy.

The coefficient of diffusion depends on the degree of packing of molecules relative to each other. The more closely packed the molecules are in the substance, the less space they have to maneuver, and therefore diffusion will be much more difficult. This is the case of solid substances that are composed of particles packed tightly together.

Sorption is the result of capillary movement in the pores open to an ambient medium. Capillary suction takes place only in partially-saturated concrete. Thus, there is no sorption of water in either completely dry or completely saturated concrete.

### 2.1.2 Concrete Porosity

In properly consolidated, good quality, hardened concrete, fluid movement occurs through the hardened cement paste and through the interfacial zone between concrete “macro components” (e.g., aggregates, reinforcing materials, fibers.) The paste-aggregate interfacial zone is known to be different from the bulk cement paste. It is usually more porous, richer in calcium hydroxide, and is more prone to microcracking than the rest of the paste matrix (Asbridge et al., 2001). The interfacial zone is normally in the order of 50µm in thickness, and can occupy 30 to 50% of the total volume of cement paste in concrete. In comparison to the bulk hydrated cement paste, the paste-aggregate interfacial zone is

weaker, more soluble due to the presence of calcium hydroxide, and can be a less resistant path for migrating moisture and other harmful substances.

It should be noted that although aggregates are porous, their pores are normally discontinuous in a concrete matrix, usually being completely enveloped by cement paste. Discrete voids or pores in concrete, including entrained air bubbles, do not contribute significantly to concrete permeability.

Concrete porosity is usually expressed in terms of percentage by volume of concrete. It is the interconnectivity of pores, rather than total porosity that determines a concrete's permeability. A concrete with a high proportion of disconnected pores may be less permeable than a concrete with a much smaller proportion of connected or continuous pores. It is the overall nature of the matrix pore structure that ultimately affects its permeability, sorptivity, and diffusivity. The size, distribution, interconnectivity and shape of pores are all determining factors in the overall permeability of a concrete matrix (Asbridge et al., 2001).

Completely waterproof or watertight Portland cement concrete is not attainable. Therefore, the goal in design mixture and formulation of durable concrete mixtures is to slow down, or minimize the potential for and rate of fluid ingress and movement.

### 2.1.3 Steel Corrosion

Low permeability concrete can help reduce the potential for reinforcing steel to corrode when exposed to chlorides by limiting the permeation of those chlorides into concrete. When reinforcing steel comes into contact with plastic concrete, a chemical reaction occurs between the steel and the concrete that causes a protective layer, also known as the passivation layer to develop around reinforcing steel. This passive layer protects against corrosion of the reinforcing steel (González et al., 1980).

Concrete can be exposed to salts – either after hardening by the use of de-icing salts, or prior to hardening by the addition of salts to the concrete mix, most often as an accelerating admixture. These salts can migrate down to the reinforcing steel through small pores in the concrete. Over time, the chlorides in these salts react with the reinforcing steel, breaking down the passivation layer and causing the steel to corrode. When reinforcing steel in concrete corrodes, the product of that corrosion (rust) takes up more volume than



the original steel, and causes the concrete to expand crack (Smith, 2001). After cracks develop, the deterioration accelerates as chlorides are allowed fairly easy ingress to the reinforcing steel. Deterioration of both the concrete and reinforcing steel compromises the integrity of the structure. This deterioration typically reduces the load-bearing capacity and the overall service life of the structure.

## **2.2 CHLORIDE ATTACK AND CARBONATION**

The main and frequent cause of corrosion of reinforcement in reinforced concrete structures is chloride attack and carbonation. Chlorides come from several sources. They can be cast in concrete but often they can diffuse into concrete as a result of sea salt spray and direct seawater wetting. Further, they can diffuse into concrete due to the application of chloride de-icing salts and from the storage of chloride substances in concrete tanks, as an example.

### 2.2.1 Classification of Chloride in Concrete

Chloride in concrete is classified into two categories:

- external or internal chloride
- bound or free chloride

#### *2.2.1.1 External Chlorides*

Exposure to chlorides can occur in areas that experience freezing temperatures so that de-icing salts are applied to the bridge deck and/or concrete pavement. Reinforced concrete bridge decks are at a high risk of experiencing deterioration from chloride penetration. The problem of external chloride penetration does not end at the roadway. Chlorides in solution may adhere to cars and pedestrians transporting these salts and affecting parking garages, walkways, and even building entrances that may not be directly exposed to weather.

Chloride penetration can also be a problem in marine environments. Concrete docks and piers are exposed to the high chloride content of salt water. However, corrosion is seldom a problem in structures that are continuously submerged. This is apparently due to the lack of diffused oxygen available. The concrete will allow the penetration of chlorides

and water, but without the presence of oxygen, corrosion will not occur (Berke et al., 1988). In this case, the concrete cover over the rebar typically provides significant protection.

#### *2.2.1.2 Internal Chlorides*

In some cases, chlorides are added to the concrete during mixing, whether intentionally or unintentionally. These internal chlorides also lead to corrosion of the rebar. Some aggregates contain traces of chlorides within pores, which become free ions when water is added to the mixture. Certain chemical admixtures contain chloride compounds, which may ionize, thus aiding the corrosion process. Calcium chloride is an accelerating admixture which may increase the amount of free chlorides available for corrosion. The severity of chlorides added by admixtures is under some debate, because these chlorides may remain in compound form, and therefore would not contribute to corrosion (Berke et al., 1988).

#### *2.2.1.3 Bound and Free Chloride*

Chlorides in cementitious materials have free and bound components. The bound components exist in the form of chloro-aluminates and appear on the adsorbed phase on the pore walls, making them unavailable for free transport. It has been reported that the amount of bound chlorides is dependent on the binder material, electric potential of the pore wall, and the pH level in pore solution. In contrast, free chlorides are dissolved in the pore solution. They can migrate to reach the reinforcement in the concrete. Typically, only the free chloride ions cause the degradation of reinforced concrete structures by causing corrosion of steel.

Chloride binding in cementitious systems is dominated by the content of tricalcium aluminate (C<sub>3</sub>A) and tetracalcium aluminoferrite (C<sub>4</sub>AF) no matter the chloride source. Both C<sub>3</sub>A and C<sub>4</sub>AF form Friedels salt, even with sodium chloride (Justnes, 2001). The sulphates in the cement form stronger bonds than the chlorides, so only a fraction of the original content of C<sub>3</sub>A and C<sub>4</sub>AF is accessible for chloride binding. Chloride sorption is dominated by the amount of CSH gel (Justnes, 2001).

Calcium chloride can in addition be bound through the formation of compounds with calcium hydroxide. Such compounds are not formed to any significant extent by

sodium chloride. Replacement of cement or addition of fly ash and ground blast furnace slag increases the chloride binding since these mineral additives form additional calcium aluminate hydrates in their reaction, while silica fume replacements will decrease the chloride binding (Justnes, 2001).

Bound chlorides can again be released if the cement paste at a later stage is carbonated or intruded by sulphates. Fewer chlorides are bound from seawater than the corresponding concentration of sodium chloride from fresh water if intermixed, since the sulphates from the sea water will be bound first and occupy sites otherwise available for chloride.

### **2.3 METHODS OF CHLORIDE ION TRANSPORT**

Related to durability issues, there are three fluids which can enter the concrete: water, aggressive ions in solution, carbon dioxide and oxygen. They can move through the concrete in different ways, but all transports depend primarily on the structure of the hydrated cement paste.

Capillary absorption (sorption), hydrostatic pressure (permeation) and diffusion are the ways by which chloride ions penetrate concrete. The most familiar method is diffusion, the movement of chloride ions under a concentrated gradient. For this to occur the concrete must have a continuous liquid phase and there must be a chloride ion concentrated gradient (Thomas, et al., 1995).

The second mechanism for chloride penetration is permeation, driven by pressure gradients. If there is an applied hydraulic head on one face of the concrete and chlorides are present, they permeate into the concrete.

The most common method for chloride penetration is absorption. When concrete is exposed to external conditions, it will undergo wetting and drying cycles. When water (generally containing chlorides) encounters a dry surface, it is drawn into the pore structure through capillary suction. Absorption is driven by moisture gradients. Typically, the depth of drying is small, and this transport mechanism alone will not bring chloride to the level of the reinforcing steel unless the concrete is of extremely poor quality and the reinforcing steel is near the top surface. It does, however, serve to quickly bring chlorides to some

depth in the concrete and therefore reduce the distance that they must diffuse to reach the rebar (Thomas, et al., 1995)

It is rare for a significant hydraulic head to be exerted on the structure, and the effect of absorption is typically limited to a shallow cover region. In the bulk of the concrete, the pores remain saturated and chloride ion movement is controlled by concentration gradients. Thus, diffusion is the primary transport mechanism described that can bring chlorides into the concrete to the level of the rebar.

## **2.4 EFFECT OF THE PORE SYSTEM ON CHLORIDE ION TRANSPORT**

The aspect of the structure of hardened cement paste relevant to permeability is the nature of the pore system both within the bulk of the hydrated cement paste and in the zone near the interface between the cement paste and the aggregate (Larbi, 1993). The interfacial zone occupies as much as one-third to one-half of the total volume of hardened cement paste in concrete and is known to have a different microstructure from the bulk of the hardened cement paste. The interface is also the location of early microcracking. For this reason, the interface zone contributes significantly to the permeability of concrete (Young, 1988).

As stated above, the penetrability of concrete is obviously related to the pore structure of the cement paste matrix. This will be influenced by the water-cement ratio of the concrete, the inclusion of supplementary cementitious materials which serve to subdivide the pore structure (McGrath, 1996), and the degree of hydration of the concrete. Generally, the older the concrete, the greater the amount of hydration that has occurred and thus, generally the more highly developed pore structure. This is especially true for concrete containing slower reacting supplementary cementitious materials such as fly ash that require a longer time to hydrate (Tang and Nilsson, 1992; Bamforth, 1995).

Another influence on the pore structure is the temperature at the time of casting. High-temperature curing accelerates the curing process so that at young concrete ages, a high-temperature cured concrete will be more mature and thus have a better resistance to chloride ion penetration than a normally-cured, but otherwise identical, concrete at the same age. However, at later ages when the normally-cured concrete has had a chance to hydrate more fully, it will have a lower chloride ion diffusion coefficient than the high-

temperature-cured concrete (Detwiler, et al., 1991; Cao and Detwiler, 1995). This finding has been attributed to the coarse initial structure developed in the high-temperature-cured concrete due to its initial rapid rate of hydration as well as the possible development of initial internal microcracking.

The rate of chloride penetration into concrete is affected by the chloride binding capacity of the concrete. Concrete is not inert relative to the chlorides in the pore solution. A portion of the chloride ions reacts with the concrete matrix, becoming either chemically or physically bound, and this binding reduces the rate of diffusion. However, if the diffusion coefficient is measured after steady-state conditions have been reached, all the binding can be presumed to have taken place and this effect will not then be observed. If a steady state condition has not been reached, then not all of the binding will have occurred and this will affect test results. The chloride binding capacity is controlled by the cementing materials used in the concrete. The inclusion of supplementary cementing materials affects binding, though the exact influence is unclear (Byfors, et al., 1986; Rasheeduzafar, et al., 1992; Sandberg and Larsson, 1993; Thomas, et al., 1995). Also, the  $C_3A$  content of the cement influences its binding capacity, with increased  $C_3A$  content leading to increased binding (Holden, et al., 1983; Midgely and Illston, 1984; Hansson and Sorenson, 1990).

The pores relevant to permeability are those with a diameter of at least 120 to 160 nanometers. These pores must be continuous. Pores that are ineffective to permeability are the discontinuous pores and the pores which contain adsorbed water.

After intensive research, Sato and Agopian (2001) found that pores with dimensions larger than 0.1 micrometers contribute to the mass transport by diffusion, ionic migration and capillarity, while the smaller pores influence only the process of gaseous diffusion and sorption and also of ionic diffusion and migration. They also observed that dried concrete when put in contact with salt solutions, the transport of water due to capillary action prevails only in the superficial layers that present open and connected pores.

Although the pores may be connected to the deep interior of the concrete, the capillary transport takes place only in the superficial layers of the concrete as the pore walls provide resistance to the flow of liquid. The degree of this resistance depends on pore dimensions, with smaller pores presenting larger hydraulic resistance than larger pores (Sato and Agopian, 2001).

## **2.5 EFFECT OF CRACKS ON CHLORIDE PENETRATION**

In the case of reinforced concrete structures, the penetration of chlorides depends not only on concrete transfer properties but also on the load applied, on the state of strains, macroscopically characterized by the presence of cracking.

In concrete structures, cracks act as interconnecting channels for the penetration of potential aggressive agents, mainly chloride ions. The effect of cracks on the corrosion development of the reinforcement has long been a controversy among researchers. Danilecki (1969) found that the cracks were directly responsible for the start of the corrosion. However, Shiessl (1988) has found that the width of the crack does not play an important factor as the cracks only accelerate the corrosion initiation.

Additional research conducted by Francois and Arliguie (1999) concludes that the development of the reinforcement corrosion is not influenced by the width of the cracks or by the existence of the cracks themselves. However, it was clear that the load applied to the concrete played a significant role in the penetration of aggressive agents and then in the corrosion of the reinforcement. This was due to the damage of the paste aggregate interface. This damage will consequently reduce the service life of the reinforced concrete.

## **2.6 CORROSION MECHANISMS**

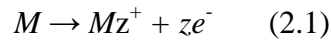
Corrosion is defined as the degradation of a metal by an electrochemical reaction within its environment (Uhlig, 1948). According to the thermodynamic laws, there is a strong tendency for high energy states to transform into low energy states. It is this tendency of metals to recombine with elements present in the environment that leads to the phenomenon known as corrosion. All interactions between elements and compounds are governed by the free energy changes commonly referred to as “ $DG$ ” available to them. For a spontaneous reaction to occur,  $DG$  must be negative. At room temperature most chemical compounds of metals have lower values (more negative) of  $DG$  than the uncombined metals; therefore, most metals have an inherent tendency to corrode.

### **2.6.1 Mechanism of Electrochemical Corrosion**

In electrochemical corrosion, there are two reactions which occur at the metal/liquid interface: the electron producing reaction which is an anodic reaction (oxidation) and the

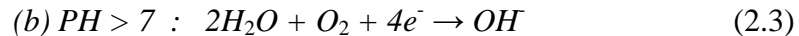
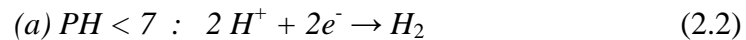
electron consuming reaction which is a cathodic reaction (reduction). For a basic corrosion cell, there are four essential components involved:

a. The anode. The anode usually corrodes by loss of electrons from electrically neutral metal atoms to form discrete ions. These ions may remain in solution or react to form insoluble corrosion products. The corrosion reaction of a metal  $M$  is usually expressed by the simplified equation:



in which the number of electrons taken from each atom is governed by the valency of the metal. For iron,  $z$  equals two.

b. The cathode. The cathode reaction must consume the electrons produced by the anode process. There are two basic reactions which occur at the cathode depending on the pH of the solution:

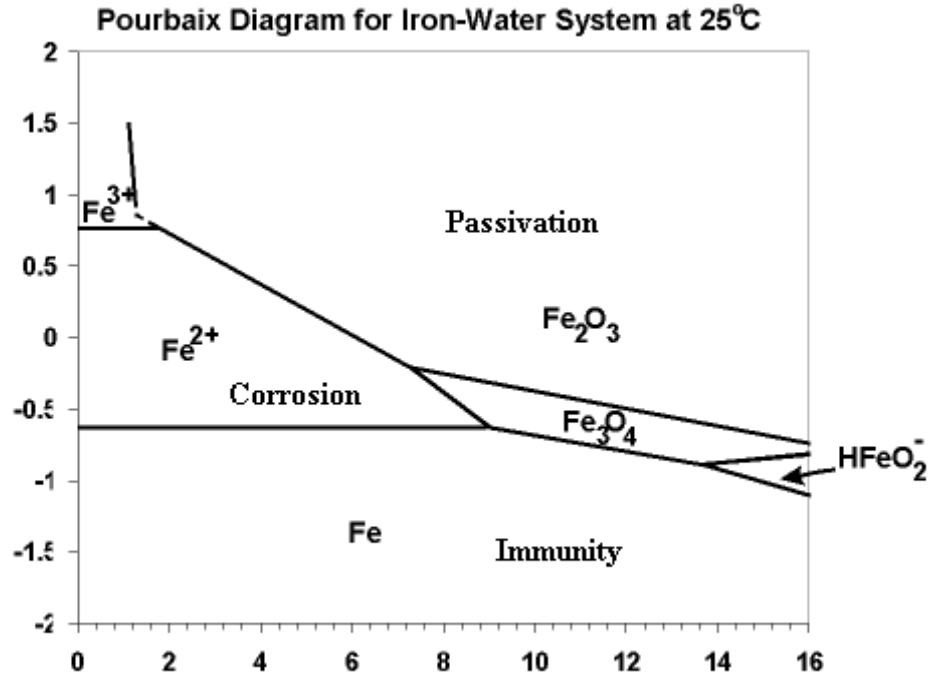


c. An electrolyte. This is the name given to the solution, which must of necessity conduct electricity. In the solution cations can move from anodic to cathodic regions. Anions move in the opposite direction.

d. Electrical connection. The anode and cathode must be in electrical contact for a current to flow in the corrosion cell. The removal of any one of the four components of the simple corrosion cell will stop the corrosion reaction.

### 2.6.2 Pourbaix Diagrams

Based on thermodynamic data on reactions between metal and water, Pourbaix (1976) developed potential versus pH diagrams which indicate thermodynamically stable phases as a function of electrode potential and pH. The Pourbaix diagram for iron is shown in Figure 2.1.



**Figure 2.1** Pourbaix Diagram for the FeO-H<sub>2</sub>O System at 77°F (25°C) for 10<sup>-6</sup>M Activities of All Metal Ions (Pourbaix (1976))

There are three general regions described as regions of corrosion, passivity and immunity. A soluble product is formed under a range of acidic conditions (3<PH<5) and under a narrow range of very alkaline conditions (12<PH<13). These are regions of corrosion. Between these two regions an insoluble film is formed, and that region is referred as passive region. The third region, immunity, shows that metal is thermodynamically stable and no corrosion will occur. Pourbaix diagrams provide a strong thermodynamic basis for understanding corrosion reactions. There are two main limitations on use of diagrams. One arises from a lack of kinetic data and the other comes from the purity of environment. In practice, corrosion processes are involved in contaminated environments such as footing subjected to waste water from the ground.

### 2.6.3 Polarization

The difference between the potentials of an electrode with and without current is called electrochemical polarization.



There are three kinds of polarizations which may act separately or simultaneously, namely concentration, resistance (ohmic) and activation polarization.

Concentration polarization is caused by the concentration on the electrode surface from that of the bulk solution. An example of this would be depletion of oxygen at the cathode. The rate of oxygen diffusion through the concrete to the reinforcement determines the rate of corrosion (Evans, 1960).

Resistance (ohmic) polarization is due to an ohmic resistance in a film, e.g. an oxide film on the electrode surface, causing an ohmic potential drop.

Activation polarization occurs due to a certain slow step in the electrode process requiring activation energy for overcoming the reaction hindrance (Evans, 1960).

#### 2.6.4 Passivity

Passivity occurs when the corrosion product is insoluble and adherent and results in the formation of an ultra-thin protective film on the surface of the metal. Passivity can be either chemical or mechanical.

*Chemical Passivity.* This type of passivity is due to an invisible thin but dense and semi-conducting oxide film on the metal surface, displacing the electrode potential of the metal strongly in the positive direction.

*Mechanical Passivity.* This is due to the precipitation of solid salts on the metal surface. The cause of strongly reduced corrosion rate for mechanical passivity is a thick but essentially porous salt layer, usually non-conducting in itself.

The maintenance of passivity needs certain electrochemical environmental conditions. The breakdown of passive film is usually brought about by changes of the electrochemical environmental conditions or mechanical forces (Young et al., 1998).

#### 2.6.5 Concrete as an Electrolyte

The steel corrosion process in concrete is generally considered electrochemical in nature, and basic mechanisms of electrochemical theory of corrosion developed for liquid electrolytes apply (Page, 1979; Cabrera, 1996). However, electrochemical corrosion of iron in concrete has a number of characteristic differences that are determined by the peculiarities of electrochemical processes in the complex “concrete electrolyte,” the

properties of which are affected by the microporous structure of the concrete and service exposure conditions.

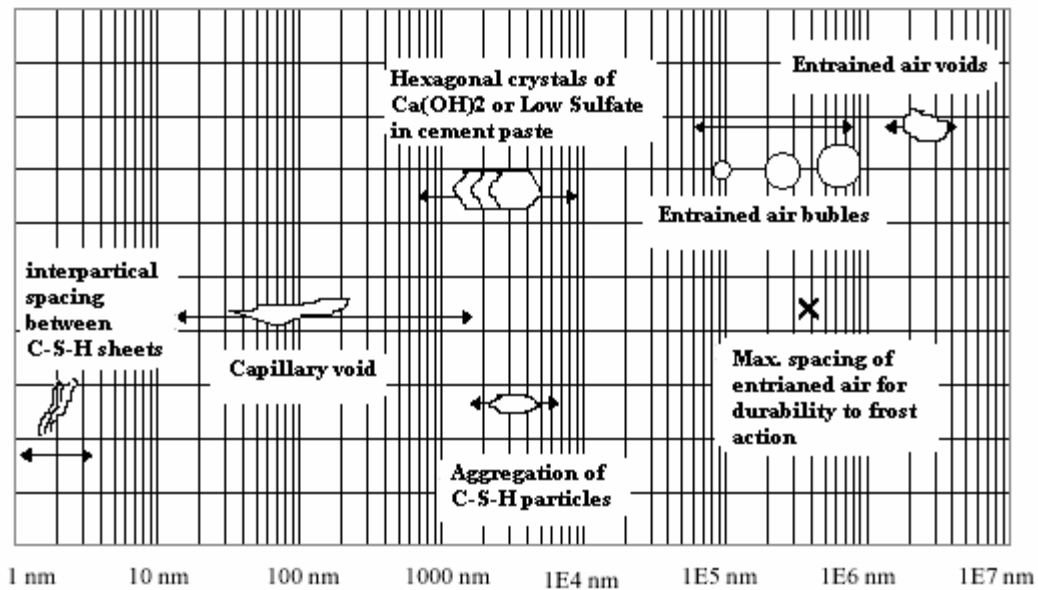
#### 2.6.6 Structure of Concrete

Concrete is a highly heterogeneous and complex structure, which contains a heterogeneous distribution of different types and amounts of solid phases, pores, and microcracks (Mehta, 1993). In addition, the structure of concrete is also subject to change with time, environmental humidity and temperature. A large amount of water can exist in the hydrated cement paste, depending on the environmental humidity, porosity and pore size distribution of the hydrated cement paste. The presence and transport of the corrosion reactants (water, oxygen and various ions), the corrosion products, and the passage of the ionic current necessary to support corrosion are normally dependent on the cement paste pore solution and the structure and distribution of pores.

The composition of the pore solution is the decisive factor in determining whether embedded steel will be passivated or whether it will actively corrode. Research on the influence of a number of factors concerning the composition of pore solution (Byfors et al., 1986, Hansson et al., 1985) has shown that the presence of sodium and potassium oxides in the cement, as well as calcium hydroxide produced in the hydration reactions of cement components can give the pore solution of ordinary Portland cement a pH of about 13 while the pH of blended cement is somewhat lower. The range of high pH values of typical concrete is within the pH domain in which insoluble oxides of iron are thermodynamically stable to maintain a passive film on steel surface. Unfortunately, the pH value of concrete can be reduced by carbonation and by leaching.

The structure, pore size distribution and pore connectivity in the cement phase determine the availability of oxygen and moisture at the steel surface, both of which are necessary for the maintenance of a passive film. They also determine the penetration or diffusion rate of chloride ion and carbon dioxide which, as mentioned above, are the two most common causes in the corrosion of embedded steel in concrete.

The typical sizes of both the solid phase and the voids in hydrated cement paste are shown in Figure 2.2 (Mehta, 1993). Pore size distributions are mainly affected by the water/cement ratio, and the degree of hydration.



**Figure 2.2.** Dimensional Range of Solids and Pores in a Hydrated Cement Paste  
(Mehta 1993)

### 2.6.7 Concrete Electrolyte

The concrete pore system filled with pore water and air provides a path for corrosive elements and the electrolyte. In addition to vapor empty or partially water-filled voids, water can exist in the hydrated cement paste in several forms:

- a. Capillary water. This is the water present in voids larger than about 50 nm.
- b. Adsorbed water. This is the water close to the solid surface; that is, under the influence of attraction forces, water molecules are physically adsorbed onto the surface of solid in the hydrated cement paste. A major portion of the adsorbed water can be lost by drying the hydrated cement paste to 30 percent relative humidity.
- c. Interlayer water. This is the water associated with the C-S-H structure strongly held by hydrogen bonding. The interlayer water is lost on strong drying (i.e., below 11 percent relative humidity).
- d. Chemically combined water. This is the water that is an internal part of the structure of various cement hydration products which is not lost on drying.

It is important to note that concrete is an ionic conductor of electric current with the exception of its very dry condition, and it can be considered to be corrosive electrolyte. However, it is quite different from the usual liquid electrolyte, because of its physicochemical and electrochemical properties.

The electrochemical properties of the concrete vary within very wide limits, depending not only on its internal structure but also on its location, and seasonal weather condition. Therefore, concrete can vary considerably in electrical conductivity during its service life.

These properties of concrete as an electrolyte will influence the character of the electrochemical reactions significantly by changing the conditions required for cathodic and anodic processes. The most fundamental characteristic is the difference in mechanism and the rate of oxygen supply under different corrosion conditions: through the liquid electrolyte (corrosion of metal in solution), through a thin film of electrolyte (such as atmospheric corrosion), or through a solid microporous electrolyte (such as steel corrosion in concrete). In solution, access of oxygen to the corroding surface of the metal is dependent primarily on diffusion; in the atmosphere, on the moisture thickness; and in concrete, on its structure (pore size distribution, porosity and pore connectivity), degree of saturation and cover depth. The corrosion process (or rate of corrosion) in concrete also is dependent on the conductivity of concrete electrolyte.

#### 2.6.8 Principles of Steel Corrosion in Concrete

Corrosion of steel in concrete is an electrochemical process. The corroding system consists of an anode in which steel is corroded, a cathode, an electrical conductor, and an electrolyte (concrete pore solution). The potential difference between anode and cathode is the driving electrical force for steel corrosion.

Usually, the process can be divided into primary electrochemical processes and secondary processes.

##### *2.6.8.1 Primary Electrochemical Processes*

For steel in concrete, as the passive film is degraded by chloride ions or the pH level is reduced by carbonation, the metallic *Fe* at the anode is oxidized to form ferrous ions

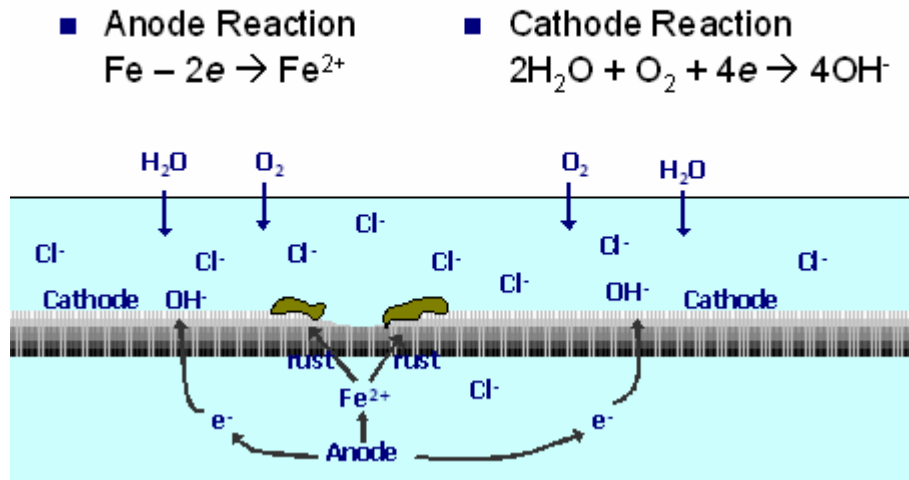
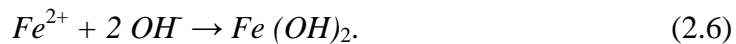
( $Fe^{2+}$ ):



The electrons released at the anode flow through the steel to the cathodic areas, as illustrated in Figure 2.3 (Mehta, 1993). The above reaction is initially balanced by cathodic reaction of dissolved oxygen ( $O_2$ ) to hydroxyl ions ( $OH^-$ ):



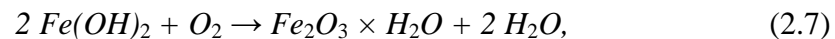
The anodic product  $Fe^{2+}$  reacts with the cathodically formed hydroxyl ions to produce a ring of a white precipitate of ferrous hydroxide ( $Fe(OH)_2$ ):

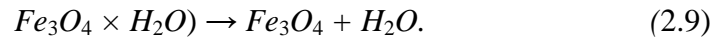
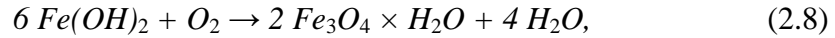


**Figure 2.3** Mechanism of Corrosion of Steel in Concrete (Mehta 1993)

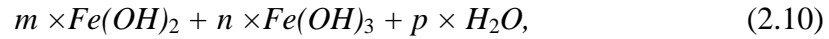
#### 2.6.8.2 Secondary Processes

The  $Fe(OH)_2$  can be further converted to hydrated ferric oxide ( $Fe_2O_3 \times H_2O$ ), also known as ordinary red-brown rust, and black magnetite ( $Fe_3O_4$ ) preceded by the formation of green hydrated magnetite ( $Fe_3O_4 \times H_2O$ ):



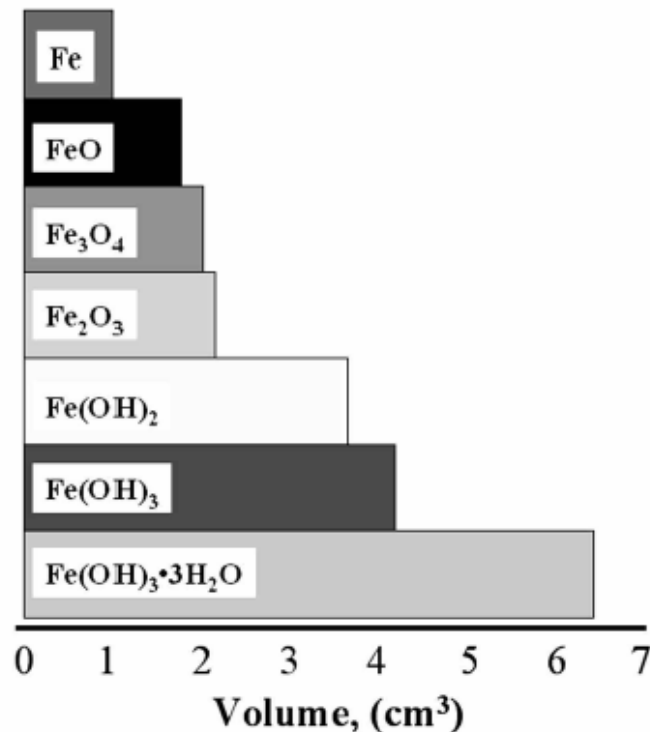


The composition of rust on iron may be expressed as a general formula:



where the values of  $m$ ,  $n$  and  $p$  vary considerably depending on conditions such as pH of the solution, the oxygen supply and moisture content.

Since the volume of rust products is much higher (about 4 to 6 times) than that of the iron as shown in Figure 2.4 (Nielsen, 1985), the formation of rust products will lead to cracking and spalling of the cover concrete when expansive stress exceeds the tensile strength of the concrete, and reduction of steel reinforcing cross section may lead to structure failure.



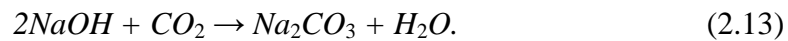
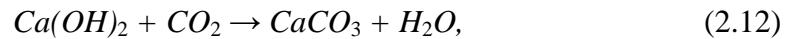
**Figure 2.4** Relative Volumes of Iron and Its Corrosion Reaction Products (Nielsen, 1985)

### 2.6.9 Initiation of Steel Corrosion in Concrete

The high alkaline environment of good quality concrete forms a passive film on the surface of the embedded steel which normally prevents the steel from further corroding. The maintenance of passivity of steel in concrete requires a high pH and presence of both water and oxygen. Two major causes of steel corrosion in reinforced concrete and consequent initiation of active corrosion are carbonation-induced corrosion and chloride-induced corrosion.

#### *2.6.9.1 Carbonation-Induced Corrosion*

Concrete structures are constantly affected by  $CO_2$  in the atmosphere. In the presence of  $CO_2$  which play the role of a weak acid in an aqueous solution, the different hydrates in cement paste such as portlandite ( $Ca(OH)_2$ ) and  $CSH$  can react with  $CO_2$  and become carbonated as shown in Equation 2.12 and 2.13.



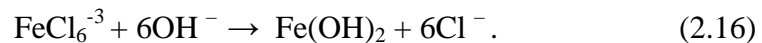
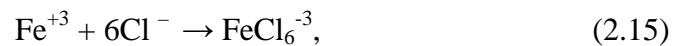
The results of carbonation lowers the pH value (Parrott, 1987), and the protective film covering the steel surface which is maintained in a high pH environment is dissolved. Therefore, corrosion of steel occurs.

The carbonation rate is mainly determined by the quality of concrete, which is a function of cement type, water/cement ratio and proportion of cement. The degree of saturation of the concrete is also a decisive factor in determining the carbonation rate as the  $CO_2$  permeates the concrete most rapidly in the gas phase while carbonation reaction takes place in the liquid phase. In a completely dry concrete or a completely saturated concrete, the carbonation reaction rate is very slow. When the pores have a layer of moisture on the walls but are not completely saturated (50 to 80 percent relative humidity), the  $CO_2$  can rapidly reach the vicinity of the pore walls and have enough water to be able to react (Parrott, 1987).

### 2.6.9.2 Chloride-Induced Corrosion

Researchers (Mehta, 1993; Venuat, 1977) show that the presence of chloride ions in reinforced concrete can cause the steel to corrode if sufficient oxygen and moisture are present to sustain the reaction. The chloride-induced corrosion is the most prevalent and damaging cause of corrosion of steel in concrete and this is the focus of this thesis.

Once in contact with the metal surface, chloride ions favor hydration of metal ions and increase the ease in which metal ions go into solution. Hime and Erlin (1987) showed that a reaction between the chloride ions and the ferrous and hydroxyl ions, as shown in Equations 2.14 through 2.16, removes ferrous ions from the lattice to produce rust and at the same time releases chlorides ions for further reaction with the ferrous ions:



## 2.7 FORMS OF CORROSION

Five types of corrosions occur in steel reinforcement (Khan, 1991):

1- General Corrosion: Rusting is the most familiar form of steel corrosion. It can be considered a uniform corrosion process. In atmospheric exposures, oxygen in the air is the usual oxidizing agent, and water necessary for the reaction is readily available in the form of rain, condensation or humidity (water vapor in the air). In the rusting of ordinary steel, the corrosion product (rust) does not form an effective barrier to further corrosion, but permits reactants to penetrate to the steel surface beneath and continue the rusting cycle.

2- Pitting corrosion: this is a non-uniform, highly localized form of corrosion that occurs at distinct locations where deep pits form. (A pit is a small electro-chemical corrosion cell, with the bottom of the pit acting as the anode.) Pitting is considered more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Chloride-induced corrosion is of this type and can be seen frequently in structures exposed in coastal areas. Pitting is initiated by:

- a. Localized chemical or mechanical damage to the protective oxide film;  
water chemistry factors which can cause the breakdown of a passive film are



acidity, low dissolved oxygen concentrations (which tend to render a protective oxide film less stable) and high concentrations of chloride (as in seawater)

- b. Localized damage to, or poor application of, a protective coating
- c. The presence of non-uniformities in the metal structure of the component, e.g. nonmetallic inclusions.

3- Galvanic corrosion: when two metals of different electrochemical potential are joined or coupled electrically in the presence of moisture or an aqueous solution, one will act as the anode and corrode; the corrosion of steel in contact with copper is a familiar example.

4- Stress Corrosion: under stress, corrosion processes proceed much faster and can lead to brittle failure as corrosion tends to be localized.

5- Crevice Corrosion: it occurs when moisture and contaminants retained in crevices accelerate corrosion.

## **2.8 THRESHOLD CHLORIDE CONCENTRATION**

To initiate corrosion, a threshold concentration of chloride (minimum concentration of chloride necessary to destroy the passive film) is required in excess of the amount immobilized by reaction with tricalcium aluminate in cement (i.e. bounded). Many researchers (Schiessel and Raupach, 1991) believe that only freely dissolved chloride ions in the concrete pore water can be involved in the corrosion reactions.

The threshold concentration of chloride ions to initiate corrosion is controversial between researchers as it depends on several factors, including the pH value of concrete, the water content, the type of cement, the proportion of water-soluble chloride, the sulfate content and the temperature (Schiessel, 1990; Clear, 1983).

The results of previous studies on threshold chloride ion concentration determination are presented in Table 2.2 (Miki, 1990). A level of 0.71 to 0.89 kg/m<sup>3</sup> is usually considered a threshold level for bare steel in regular reinforced concrete bridge decks (Miki, 1990). According to AASHTO, a concentration less than 1.42 kg/m<sup>3</sup> are acceptable for bridge decks; however, deck replacement should occur when the level of chlorides reaches 2.8 kg/m<sup>3</sup> (Miller et al., 1993).

**Table 2.2** Threshold Chloride Ion Concentrations of Previous Researchers (Miki 1990)

Researchers	Year	Kg/m <sup>3</sup>
Lewis	1962	0.7
Hausmann	1967	0.2-0.8
Berman	1972	0.7
Clear and Hay	1973	0.6 – 0.9
Clear	1974	0.66
Stratfull, Jaukovich and Spellman	1975	0.66
Cady	1978	0.6 – 1.3
Browne	1982	1.33
Pfeifer, Landgren and Zoob	1986	0.5 – 0.9

Hansson (1990) found that critical chloride threshold values based on total chlorides from 15 different publications varied from 0.17 to 0.78 wt. % of the cement. Values from actual structures varied from 0.17 to 0.93 by wt. % of the cement. Concrete samples exposed outside exhibited ranges from 0.32 to 0.6 wt. % of the cement, while laboratory samples exhibited threshold values from 0.5 to 2.5 by wt. % of the cement. In all cases, values vary significantly.

A practical value of chloride threshold level for corrosion initiation, based on practical experience with structures in a temperate climate, is 0.25 % by weight of cement or 1.4 pounds per cubic yard (0.83 kg/m<sup>3</sup>) for typical mixture of normal weight concrete (density 2300 kg/m<sup>3</sup>) (West and Hime 1985).

Field experience and research (Daily, 1997) have show that on existing structures subjected to chloride ions, a threshold concentration of about 0.026% (by weight of concrete) is sufficient to break down the passive film and subject the reinforcing steel to corrosion. This equates to 260-ppm chloride or approximately 1.0 lb/yd<sup>3</sup> of concrete.

The American Concrete Institute (ACI) recommends the following chloride limits in concrete expressed as a percent by weight of cement as shown Table 2.3. The threshold chloride content for water soluble chloride in different units is presented in Table 2.4.

**Table 2.3** Chloride Limits for New Construction (ACI 2002)

Type of member	Maximum water soluble chloride ion (Cl) In concrete, % weight of cement
Prestressed Concrete	0.06
Reinforced concrete exposed to chloride in service	0.15
Reinforced concrete that will be dry or protected from moisture in service	1.00
Other reinforced concrete construction	0.30

**Table 2.4** Threshold Chloride Content (Water Soluble)

Threshold chloride content (water soluble)				
0.15 % by weight of cement	0.023% by weight of concrete	0.9 lb/yd <sup>3</sup>	0.53 kg/m <sup>3</sup>	230 ppm by weight of concrete

## 2.9 EFFECT OF POZZOLANS AND OTHER SUPPLEMENTARY CEMENTITIOUS MATERIALS ON CONCRETE PROPERTIES

By definition, pozzolans are materials that have little or no cementitious properties of their own; however, they act as hydraulic cement when mixed with water in the presence of calcium hydroxide. Pozzolans contain high quantities of silicon dioxide and may also contain significant amounts of aluminum oxide and iron oxide (Neville, 1996). Hydration of a pozzolan, when compared with hydration of silicates in Portland cement, is a slow reaction and is characterized by low heat of hydration and slow strength gain. Hydration of silicates in Portland cement results in the formation of C-S-H and calcium hydroxide (CH). In pozzolanic reactions, pozzolan reacts with CH from the Portland cement hydration, and water, and forms C-S-H. The C-S-H produced in the pozzolanic reaction has a lower

density than that formed from the Portland cement hydration. However, since the reaction is much slower, the products of the pozzolanic reaction fill the already existing capillary spaces in the cement paste. Thus, it improves strength properties and reduces permeability (Alhozaimy et al., 1996).

Bentz and Garboczi (1991) in the research that they conducted found that the pozzolanic mineral admixtures do not eliminate the capillary porosity, but reduce it by significantly lowering the volume fraction of CH and at the same time increasing the total amount of C-S-H.

Mineral admixtures with very fine particle sizes are known to increase the water requirement in almost direct proportion to their amount present, so if the normal consistency of the mixture is desired at an unchanged w/c ratio, a water reducing admixture may be required (Mehta, 1984). Typically, such admixtures are required for pozzolanic mixtures.

Pozzolans used in concrete include both natural and by-product materials. Natural materials include volcanic glasses and tuffs, and calcined clays or shales. Natural pozzolans require processing such as crushing, grinding, and size separation. The process may also involve thermal activation. Major sources of by-products are power plants and metallurgical furnaces producing cast iron, ferrosilicon alloys and silicon metal. The benefit of using industrial by-products is that they may not require processing before being used in concrete, thus resulting in cost and energy savings.

### 2.9.1 Fly Ash

According to ASTM C 618, “Cement and Concrete Terminology,” fly ash is “the finely divided residue resulting from the combustion of ground or powdered coal which is transported from the firebox through the boiler by flue gasses.” The combustion of coal is used to raise steam for power generation in power plants.

Fly ash used in concrete is mostly a byproduct of coal-fired electric generating plants. Coal-burning electric power plants became available in quantity in the 1930s. In the United States, the study of fly ash in concrete began about that time (Mielenz, 1983). The major breakthrough in using fly ash in concrete was the construction of the Hungry Horse Dam in Montana in 1953, utilizing 120,000 metric tons of fly ash.

Fly ash (0.1µm to 0.1 mm, with an average of 15 µm) is generally finer than Portland cement (1µm-100µm). The main constituents include silica, alumina, and oxides of calcium and iron. Its physical and chemical properties depend on the degree of coal pulverization, flame temperature, oxidation condition and system of collecting and storing of fly ash.

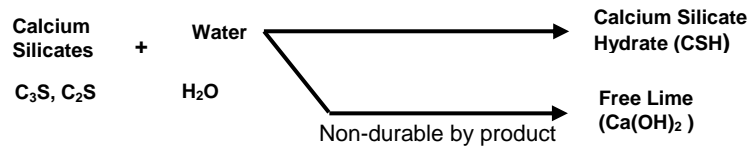
ASTM C 618 defines two classes of fly ash; Class C and Class F. Class F fly ash is usually produced by burning anthracite or bituminous coal while Class C fly ash is produced by burning sub-bituminous coal or lignite. Bituminous and anthracite coals generally contain a smaller amount of calcium mineral proportion than sub-bituminous coals. The separation of fly ash into two classes by their compositions reflects differences in cementitious and pozzolanic properties. Class C fly ash usually reacts with water by itself and shows cementitious properties while Class F fly ash is rarely cementitious when mixed with water alone. The reason for this is the higher calcium oxide (lime) ingredient in Class C fly ash.

The chemical composition of fly ash is very similar to that of Portland cement. Table 2.5 (Neville, 1996) illustrates the basic comparison of ingredients of fly ash and Portland cement.

**Table 2.5** Typical Chemical Compounds in Fly Ash and Portland Cement  
(Neville 1996)

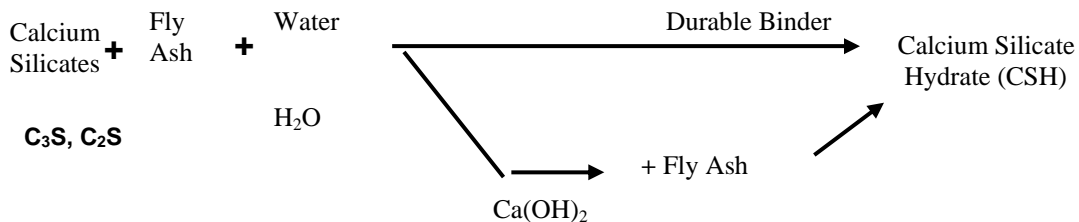
Chemical Compound	Fly Ash Type		Portland Cement
	Class F	Class C	
SiO <sub>2</sub>	54.90	39.90	22.60
Al <sub>2</sub> O <sub>3</sub>	25.80	16.70	4.30
Fe <sub>2</sub> O <sub>3</sub>	6.9	5.80	2.40
CaO	8.7	24.30	64.40
MgO	1.80	4.60	2.10
SO <sub>3</sub>	0.60	3.30	2.30
Na <sub>2</sub> O & K <sub>2</sub> O	0.60	1.30	0.60

The setting of Portland cement is related to the hydration of the silicate components,  $C_3S$  and  $C_2S$  as shown in Figure 2.5:



**Figure 2.5** Hydration of the Silicate Components in Concrete

Calcium silicate hydrate gel (C-S-H) comprises about 60% of hydrated cement volume and it is the most important hydration product that provides strength and bond to the cement paste (Neville, 1996). The other component of hydrated cement is  $Ca(OH)_2$  (calcium hydroxide) which forms 20% of hydrated cement volume and does not contribute to strength.  $Ca(OH)_2$  can react with siliceous and aluminous materials in fly ash to form strong and durable cementing compounds, no different than those formed during hydration of ordinary Portland cement. This reaction is shown in Figure 2.6:



**Figure 2.6** Hydration of Fly Ash and Silicate Components in Concrete

The advantages of using fly ash in concrete are numerous (Jerzy, 1998):

- a. Improved workability
- b. Lower heat of hydration
- c. Lower cost concrete
- d. Improved resistance to sulfate attack
- e. Improved resistance to alkali-silica reaction

- f. Higher long-term strength
- g. Opportunity for higher strength concrete
- h. Equal or increased freeze thaw durability
- i. Lower shrinkage characteristics
- j. Lower porosity and improved impermeability

The main disadvantages of fly ash are that concrete mixtures take more time to attain the required strength and thus increase the importance of curing, and the high carbon content in certain fly ash products absorbs some air entraining agents (which controls the freeze-thaw durability) reducing the amount of air produced in the concrete frost damage.

The addition of fly ash to concrete changes both the microstructure and the pore solution composition of the concrete, resulting in a finer pore structure in both the cement paste matrix and the paste aggregate interface in concrete (Liu and Beaudoin, 2000).

Class F fly ash reduces permeability at low level of cement substitution (10 % by weight). In class C fly ash, twenty to thirty percent by weight is required to produce any significant reduction in permeability. Work done by Alhozaimy et al (1996) showed Class C fly ash gives higher permeability than class F, except for a 30 % substitution level at 28 day testing, although Class C effectively reduces water demand.

### *2.9.2 Slag Cement*

Slag is a by-product from the production of copper. During metal production, liquid slag is rapidly quenched from a high temperature by immersion in water (Mehta, 1993). The slag is a glassy, granular, non-metallic product that consists “essentially of silicates and aluminosilicates of calcium and other bases” (Klieger et al., 1994). It is also known as granulated blast furnace slag (GBFS). Slag, in addition to pozzolanic properties, and unlike Class F fly ash and silica fume, also has cementitious properties. With regard to strength, there are three grades of slag: Grade 80, Grade 100, and Grade 120. Each number corresponds to a minimum 28-day compressive strength ratio of a mortar cube made with only Portland cement and a mortar cube made with 50% Portland cement and 50% slag. Because of cementitious properties, particles smaller than 10  $\mu\text{m}$  contribute to early strength, while particles larger than 10  $\mu\text{m}$  and smaller than 45  $\mu\text{m}$  contribute to later

strength. Since particles greater than 45  $\mu\text{m}$  are difficult to hydrate, slag is mostly pulverized to particles with diameters less than 45  $\mu\text{m}$  (Mehta, 1993).

When used in concrete, slag provides the following benefits (Lewis, 1985): high ultimate strength with low early strength, high ratio of flexural to compressive strength, resistant to sulfates and seawater, improved alkali-silica reaction resistance, low heat of hydration and decreased porosity and permeability.

Substitution of cement materials with ground granulated slag increases the chloride binding since these mineral additives form additional calcium aluminate hydrates in their reaction - which is not the case for silica fume, chloride binding increases. Bound chloride can be released again if at a later stage, cement paste is carbonated or attacked by sulfate (Afroze, 2002).

Sato and Agopian (2001) also proved that the addition of slag to a mix directly affects its porosity and its pore structure. They found that concrete without slag had 61 % of its pores larger than 0.12 micrometers in diameter (larger pores) while the concrete with slag, of the same mixture proportions presented only 39 % of these larger pores.

## **2.10 ION AND MASS TRANSPORT IN CONCRETE MIXES DURING RCPT**

The permeability of concrete depends on the pore structure of concrete, while electrical conductivity or resistivity of concrete is determined by both pore structure and the chemistry of the pore solution. Factors that have little to do with the transport of chloride can have great effect on the electrical conductivity of concrete. Thus, the electrical conductivity or resistivity of concrete mixtures cannot always be used as an accurate indication of its permeability. However, the electrical conductivity or resistivity can be used as a quality control indicator when the particular concrete mixtures have similar components and mixing proportions.

The RCPT has been used to evaluate the chloride permeability of hardened cement mortars and concretes made with special cements or supplementary cementing materials (Ozyildirm et al., 1988). Unfortunately, the use of RCPT in some studies has resulted in some invalid or misleading conclusions. In one study (Roy et al., 1987), it was found that the inclusion of sands or Class F fly ash decreases chloride permeability significantly, while their effects on water permeability are much smaller. In another study (Alhozaimy, 1996), a



replacement of 10% cement with Class F fly ash can significantly reduce the chloride permeability of cement mortars at 7 days. Shi (1996) used RCPT to test Portland cement and three alkali-activated slag mortars and found that although sodium silicate-activated slag cement mortar showed the lowest pore porosity and water permeability among the four cement mortars, it gave much higher passed coulombs than the other three mortars due to the high concentration of conductive ion concentration in the pore solution.

### 2.10.1 Specific Electrical Conductivity of Concrete Pore Solution

For a strong electrolyte, its equivalent conductivity,  $\lambda_i$  decreases with the square root of equivalent concentration  $C_i$  (Adamson, 1973):

$$\lambda_i = \lambda_{i,0} - (0.2289 \times \lambda_{i,0} + 60.19) \sqrt{C_i} \quad , \quad (2.17)$$

where  $\lambda_{i,0}$  is the equivalent conductivity at infinite concentration. Table 2.6 lists the equivalent conductivity of aqueous ions commonly identified in concrete pore solution.

**Table 2.6** Equivalent Conductivity of Aqueous Ions at Infinite Concentration at 25°C (Adamson, 1973)

Ion	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	OH <sup>-</sup>	Cl <sup>-</sup>
Equivalent Conductivity $\lambda_0$ (m <sup>2</sup> .mol <sup>-1</sup> .ohm <sup>-1</sup> )	0.00501	0.00735	0.00595	0.00798	0.0198	0.00763

For a given temperature, the specific conductivity of a solution can be expressed as follows (Adamson, 1969):

$$\rho = \rho_{water} + \sum C_i \lambda_i / 1000, \quad (2.18)$$

Where:

$\rho$  = specific electrical conductivity of aqueous solution (m<sup>-1</sup>.ohm<sup>-1</sup>)

$\rho_{water}$  = specific electrical conductivity of water ( $=10^{-5} \text{ m}^{-1} \cdot \text{ohm}^{-1}$ )

$C_i$  = equivalent electrical concentration of ion I ( $\text{equiv} \cdot \text{m}^{-3}$ )

$\lambda_i$  = equivalent electrical conductivity of ion I ( $\text{m}^2 \cdot \text{equiv}^{-1} \cdot \text{ohm}^{-1}$ )

Appreciable concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{OH}^-$ ,  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  from the cement components enter into the mixing water during concrete mixing. After setting and early hydration, the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  diminish to negligible values, leaving a solution composed essentially of dissolved alkali hydroxides. In most cases, the concentration of alkali hydroxides in concrete pore solution is less than 1 Molar. Thus, the specific electrical conductivity of concrete pore solution can be calculated with satisfactory accuracy based on the concentrations of  $\text{OH}^-$ ,  $\text{Na}^+$  and  $\text{K}^+$  using the above equations.

#### 2.10.2 Effect of Supplementary Cementitious Materials on Specific Electrical Conductivity of Concrete Pore Solution

The use of supplementary cementitious materials such as ground blast furnace slag, silica fume, metakaoline (type of pozzolan), coal fly ash and natural pozzolan can have a very significant effect on the pore solution chemistry of concrete, depending on the dosage and composition of these materials (Shehata et al., 1999). Supplementary cementing materials with low alkali content will incorporate more alkalis into hydration products than they release to the pore solution, which results in a lower alkali concentration or lower pH value in the pore solution (Duchesene et al., 1994). This is one reason for the use of supplementary cementitious materials to decrease the alkalinity of pore solutions in concrete materials to a level that will suppress the alkali-aggregate expansion of concrete.

In their study, Shi et al., (1998) found that a 50 % ground granulated blast furnace slag replacement reduces the specific conductivity of the pore solution by 3.25% at 28 days. This reduction increases with time and reaches 24% at 730 days.

Also in that study, Shi et al., (1998) found that a 60% fly ash replacement shows a reduction of 3.8% at 28 days. The reduction increases to 28.7% at 90 days and does not show a significant change thereafter. They also show that a 25% silica fume replacement reduces the electrical conductivity of the pore solution by 70.6% at 28 days. The reduction increases slightly at 730 days. Finally, the study showed that a combination of 15% silica

fume and 42.5% slag have a similar effect to 25% silica fume replacement. The summary of their findings is tabulated in Table 2.7.

**Table 2.7** Specific Conductivity of Pore Solutions in Different Hardened Cementing Materials (Shi et al 1998)

Cementitious materials	Specific conductivity, $\text{ohm}^{-1}$				Relative specific conductivity, percent			
	28 d	90 d	365 d	730 d	28 d	90 d	365 d	730 d
PC	5.85	6.02	6.23	6.08	100	100	100	100
PCBFS (50%)	5.66	5.52	5.53	4.62	96.75	91.69	88.76	75.99
PCFA (60%)	5.63	4.29	4.63	4.42	96.24	74.26	74.32	72.7
PCSF (25%)	1.72	0.65	0.49	1.48	29.40	10.80	7.87	24.34
PCBFSSF (42.5%, 155)	1.49	0.75	0.87	0.98	25.47	14.46	13.96	16.11

As stated on the previous page, supplementary cementitious materials may have a significant effect on the chemistry or electrical conductivity of the pore solution, depending on the alkali content of the supplementary cementing material, replacement level and age, which has little to do with the chloride permeability.

Asbridge et al., (2001) found that the electrical conductivity of concrete decreases with an increased volume of aggregate in concrete due to the dilution effect of conductive ions in the pore solution and the adsorption of alkalis on the surface of the aggregates. Some conductive ions can be extracted from the aggregate into the pore solution, thereby, increasing the electrical conductivity of concrete.

From this it can be said that the transport of ions in concrete depends on the pore structure of the concrete, while the electrical conductivity of concrete or RCPT results depend on both the pore structure characteristics and the electrical conductivity of the pore solution, which is determined by the composition of the pore solution. Thus, it may not be correct to use electrical conductivity of concrete or RCPT results to rank the rapid chloride permeability of concrete containing supplementary cementing materials.

## **2.11 ION AND MASS TRANSPORT IN CONCRETE MIXES DURING PONDING TESTS**

Ionic and molecular diffusion are the two main modes of chloride transport during the ponding test. Concrete mixtures containing silica fume, fly ash or slag attain a higher resistance against chloride penetration than a control mixture as the development of a dense pore structure due to the pozzolanic reaction. This reaction transforms the calcium hydroxide into calcium silicate hydrate, resulting in a refinement of the pore structure through the transformation of the larger pores into smaller ones. Owing to the net reduction in calcium hydroxide content in the mix due to the pozzolanic reaction, the volume of continuous capillary pores will be proportionally decreased. The microstructure becomes relatively more dense, tortuous and discontinuous in comparison with the control mixture. These properties of the pore structure affect the resistance of concrete to chloride penetration (Wee et al., 2000).

The filler effect in concrete with silica fume, due to its ultra fine particle size (0.1 to 0.2 $\mu$ m) allows the silica fume to fill the voids: i) in the cement paste and also ii) between the cement paste and the coarse aggregate particles. This allows a denser microstructure to develop. Therefore, for mixtures with mineral admixtures, the activation energy for chloride diffusion is high compared to the control mixtures (Afroze., 2002).

In addition to the pore refinement (in the case of silica fume and slag concrete) and filler action (in the case of silica fume), the chemical interaction between the diffusing chlorides and the cement phases ( $C_3A$  and  $C_4AF$ ) lead to chloride binding. The electrical double layer formed on the pore wall surface may also restrict the depth of chloride penetration. As a result of chloride binding, the voluminous chloride binding phases such as Friedel's salt tend to deposit into the coarser pores (greater than 60 nm in diameter) causing a greater degree of pore constriction and tortuosity and thereby partially blocking the subsequent chloride from penetration through the concrete. The aggregate cement paste zone, however, supports the higher depths of chloride penetration through the early ages (3 days curing) but its influence is negligible in well-cured concrete (28 days) mixtures. In contrast, the aggregate cement paste transition zones in silica fume concrete are generally considered to be denser due to the filler action of the silica fume and hence may not allow

the chloride penetration even in the early age concrete. So, the diffusion of chloride through concrete is dependent on the microstructure of the concrete (Afroze., 2002).

The ionic diffusion of chlorides during the ponding test depends on the nature and extent of chemical interaction such as chloride binding, electrical double layer between the chlorides and the pore wall surfaces. Consequently, the subsequent chloride diffusion during the ponding test experiences a greater degree of resistance from the pore structure. (Afroze., 2002).

In their recent study Wee et al., (2000) tried to find a correlation between the charge-passed data derived from the rapid chloride permeability test (RCPT) and the chloride penetration coefficient  $K$  derived through a 90-day soaking test for the concrete containing mineral admixture. For this purpose, concrete specimens containing varying proportions and fineness of mineral admixtures, such as ground granulated blast-furnace slag (GGBS) and silica fume (SF), were moist-cured for different periods (3, 7 and 28 days) and were subjected to both a 90-day soaking test and an RCPT. To supplement the results, the electrical resistivity and compressive strengths of the concrete mixtures were also evaluated.

Wee et al., (2000) found that for the majority of mixtures containing SF and GGBS, the chloride penetration coefficient  $K$  and the charge-passed data followed different trends. The coefficient  $K$  was derived from empirical equations and the steps of AASHTO T259/260 were not followed. Thus, comparison is not available between the ponding results from this research project and the findings of Wee et al., (2000). i.e., when the moist curing period was extended (3 to 28 days), the amount of reduction in the magnitude of charge passed through the mixture was significantly higher than the corresponding reduction in  $K$ . This also suggests a greater influence of the extended curing period (3 to 28 days) on the quantity of charge passed through the concrete compared to that on  $K$  and that the charges passed and  $K$  are the independent properties of concrete controlled by different factors. The charge passed depends on the microstructure and the pore fluid conductivity (especially  $\text{OH}^-$  ions) of the concrete, while  $K$  depends primarily on the microstructure of the concrete. Further, the charge passed through SF and GGBS concrete was shown decreasing exponentially with increasing electrical resistivity of the mixture. Thus, the charge passed through the concrete mixture containing SF and GGBS can only be used as a measure of

the overall conductivity of concrete rather than as a measure of the resistance of concrete to chloride penetration.

## **2.12 EFFECT OF THE INTERFACE ZONE AND AGGREGATE TYPE ON PERMEABILITY OF CONCRETE**

In the past, concrete has been considered a two-phase material, consisting of aggregate particles dispersed in a cementitious matrix. For such a material, the mechanical and transport properties are assumed to depend partially on the w/cm ratio and on the type of aggregate. However, recent research (Nielsen, 1993) has shown that concrete should be modeled as a three phase system: the cement paste, the aggregate and the transition zone between the aggregate and the cement paste. The transition zone develops where the hydration cement system comes in contact with the aggregate and which determines the strength of the cement/aggregate bond.

The resistance of concrete to aggressive agents including chloride ions depends mainly on the strength and densification of the transition zone which provides channels for chloride ions to penetrate through the concrete. The microstructure of the hydrated cement paste in the immediate vicinity of coarse aggregate differs significantly from that of the bulk of the cement paste, because dry cement particles are unable to become closely packed against the relatively large particles of aggregate during mixing. Therefore there is less cement present to hydrate and fill the original voids. In consequence, the interface zone has a much higher porosity than the hydrated cement paste further away from the coarse aggregate.

The microstructure of the interface zone is as follows: the surface of the aggregate is covered with a layer of calcium hydroxide about 0.5  $\mu\text{m}$ . Beyond this calcium hydroxide layer, there is a layer of calcium silicate hydrate (C-S-H) of about the same thickness. Moving further away from the aggregate lies the main interface zone, some 50  $\mu\text{m}$  thick, containing products of hydration of cement with large crystals of calcium hydroxide but with no unhydrated cement.

The strength of the interface zone increases with time in consequence of a secondary reaction described above between the calcium hydroxide and the pozzolans.

Although the interface zone of primary interest is that at the surface of the coarse aggregate, such a zone is also formed around the fine aggregate particles. In this case, the thickness of the interface zone is smaller but the surface effects originating from the fine particles interfere with those of the coarse aggregate and thus affects the overall extent of the interface zone.

The mineralogical characteristics of the coarse aggregate also affect the microstructure of the transition zone; in the case of limestone, there is a chemical reaction between the limestone and the cement paste and consequently a dense interface zone is formed (Monteiro et al., 1985). The result is a lower permeability of concrete. However, this is not the case when siliceous gravel is used during mixing.

### **2.13 CORRELATION BETWEEN PONDING RESULTS AND RAPID CHLORIDE PERMEABILITY TESTS**

Specifying concrete directly on the basis of performance rather than indirectly by strength requires a suitable durability test measure that is simple and reliable. While accelerated durability tests exist, they are costly, time consuming, and limited to laboratory use. On the other hand, correlations between permeability and durability have long been justified and studied.

As described in Section 1.6 of this report, the two tests most often used to determine concrete permeability are AASHTO T-277, Rapid Chloride Permeability Test (RCPT), and T-259, Resistance of Concrete to Chloride on Penetration (ponding test). The AASHTO T259 test has long been favored among concrete corrosion specialists for assessing the chloride penetration of concrete. In contrast, with a growing need for a faster and less expensive indicator of chloride permeability, AASHTO T 277 is becoming more popular among owners and specifiers. Today, the rapid 6-hour test (T277) is a common requirement in construction projects specifications where engineers are specifying low values between 700 and 1000 coulombs to ensure durable concrete. The following sections discuss the original correlation developed between these two tests by previous researchers and investigate the correlation between the two tests for the seven sites studied during this research.

The original report, “Rapid Determination of the Chloride Permeability of Concrete” (Whiting, 1981) included the results of a research program undertaken by the FHWA. David Whiting outlined the development of a test procedure for a rapid assessment of the permeability of concrete to chloride ions (rapid 6-hours test method). He conducted a test program that included the concrete mixtures listed in Table 2.9 and established a correlation (Figure 2.7) between the 6-hour test method and AASHTO T 259, the 90-day ponding test as shown in Table 2.11. The correlation was based upon tests conducted on a single core of each of the concrete mixtures. None of the concrete mixtures tested contained mineral admixtures.

**Table 2.8** Charge Passed versus Total Integral Chloride (Whiting, 1981)

<b>Charge Passed (Coulombs)</b>	<b>Chloride Permeability</b>	<b>Type of Concrete</b>	<b>Total Integral Chloride to 40.6 mm (1.6 in) Depth after 90 day Ponding Test</b>
> 4000	High	High water cement ratio, conventional (>0.6) PCC*	>1.3
2000-4000	Moderate	Moderate water cement ratio conventional (0.5 to 0.5) PCC*	0.8 to 1.3
1000-2000	Low	Low water cement ratio, conventional (<0.4) PCC*	0.55 to 0.8
100-1000	Very Low	Latex modified concrete, internally sealed concrete	0.35 to 0.55
<100	Negligible	Polymer impregnated concrete, polymer concrete	< 0.35

\* Portland cement concrete



**Table 2.9** Concrete Mixtures Used in the FHWA’s 1981 Study (Whiting, 1981)

Concrete Type	Water to Cement Ratio by Weight
Conventional Portland cement Concrete, PCC	0.60, 0.50, 0.40
Latex Modified, LMC	0.24
Internally Sealed Wax Bead, WBC (Heated and not Heated)	0.55
Polymer Impregnated Concrete, PIC	0.5
Iowa Low Slump, IOWA	0.33
Polymer Concrete, PC	N.A.

Whiting introduced the parameter of “Total Integral Chloride,  $I$ , which is a dimensionless value representing the integral of chloride concentration versus unit depth increments of 5.1 mm (0.2- in) rather than actual depth. “ $I$ ” was used to represent the results of the 90 days ponding test in only one value. In equation form the total integral chloride is represented by:

$$I = \frac{\text{Total area under the line representing chloride content vs. Depth}}{5.1\text{mm (0.2in) Depth Increments}} \quad (2.19)$$

Using a linear regression analysis, Whiting developed a correlation between the 90-day ponding test and the rapid 6-hour permeability tests with an  $R^2$  coefficient of 0.708. The linear regression line of his data is reproduced in Figure 2.7 where it can be seen that the data shows a poor correlation in the 700 to 1300 coulombs range. Whiting (1981) also concluded that polymer concrete and polymer-impregnated concrete had negligible chloride permeability based the 6-hour test. Yet, these same concrete mixtures showed  $I$  values of 0.16 and 0.34 according to 90-day ponding tests. These  $I$  values are relatively high compared with the 6-hour test results.

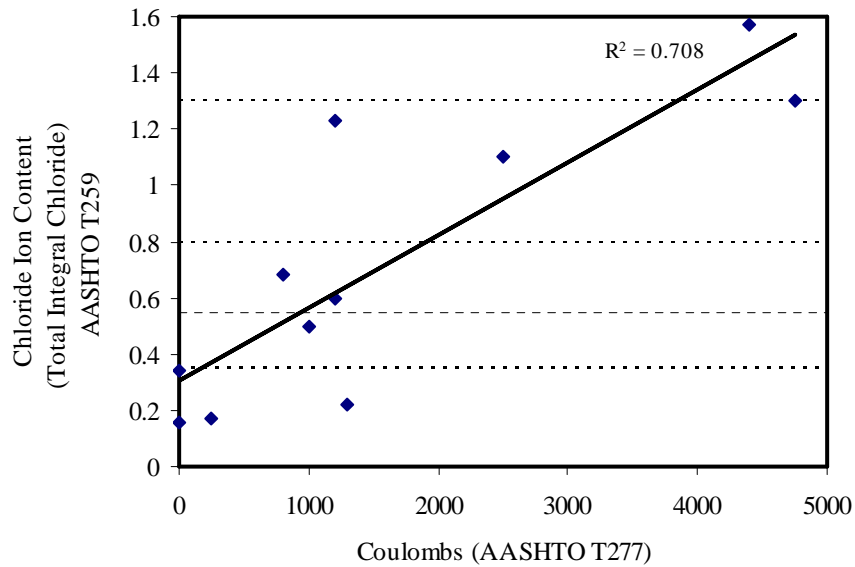


Figure 2.7 Correlation Data of ASTM C1202 Document (Whiting, 1981)

Whiting and Dziedic published “Resistance to Chloride Infiltration of Superplasticized Concrete as Compared with Currently Used Concrete Overlays Systems” in 1989. In it, they discussed the effectiveness of various materials used in bridge overlays at construction sites in Ohio and developed a correlation between the rapid (6-hour) and the 90-day ponding tests. From each of the concrete mixtures listed in Table 2.12, two specimens were tested for AASHTO T277 and a singular specimen was tested for AASHTO T259. Concrete mixtures containing high range water reducers (HRWR) with a silica fume were moist-cured for 42 days and the latex modified concrete (LMC) was moist cured for 2 days then left to air dry for 40 days. Whiting and Dziedic found a correlation coefficient,  $R^2$ , of 0.81 for data from both the rapid 6-hour and the 90-day ponding tests. Long term ponding tests performed on all 22 concrete mixtures resulted in low total integral chloride values,  $I$ , ranging from 0.05 to 0.15. The corresponding coulombs values ranged from 250 to 5000. The latex modified concretes had coulomb values between 700 and 2200, while the HRWR concretes had coulomb values between 250 and 5000 (Whiting and Dziedic, 1989).

In other research, Mitchell and Whiting (1992) stated that results of the AASHTO T277 test are not as reliable as they were thought to be. The authors cited that the

development of the original correlation did not investigate variables such as aggregate type and size, cement content and composition, density, in addition to other factors. In the authors' opinion, the correlation did not represent a large database of concrete, only single cores taken from FHWA original slabs. The authors recommended for individuals using the rapid chloride permeability test (RCPT) to establish their own correlation between charge passed and known chloride permeability for their own particular materials.

**Table 2.10** Concrete Mixtures Used by Whiting and Dziedic in 1989

Concrete Type	Usual w/c	No. of Mixes	Sources of Concrete Mixtures
HRWR modified	0.30 to 0.32	10	2 mixtures from each of 5 sites
Latex Modified	<0.39	10	2 mixtures from each of 5 sites
Silica Fume Modified	0.30	2	1 site

A more recent study conducted in 1994 by Pfeifer, McDonald, and Krauss seriously critiqued the use of the AASHTO T 277 test. The paper included a review of five previous studies that substantiates the use of the ASTM C1202 and several other papers concerned with the application of the rapid RCPT. The authors of the paper calculated and compared total integral values, *I*, from all five studies (Whiting, 1981; Whiting, 1988; Whiting et al., 1989; Ozyildirim et al., 1988; Berke et al., 1988). They concluded that these values exhibit wide variance and no correlation with Table 2.8, originally devised by Whiting in 1981. Results of that comparison are presented in Table 2.11 and show there is no consistency in rating the chloride penetrability of the concrete mixtures tested.

**Table 2.11** Comparison of the Correlations of Chloride Penetrability Based Upon Results from Five ASTM C1202 Studies

Coulombs	Whiting 1981	Whiting 1988	Whiting et al 1989	Berke et al 1988
5000	High	Low	Negligible	Low
2500	Moderate	Very Low	Negligible	Very Low
1500	Low	Very Low	Negligible	Very Low
500	Very Low	Negligible	Negligible	Very Low
<100	Negligible	Negligible	Negligible	Negligible

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## Multidisciplinary Research in Transportation

Texas Tech University | Lubbock, Texas 79409  
P 806.742.3503 | F 806.742.4168