CHLORIDE ION TRANSPORT IN BRIDGE DECK CONCRETE
UNDER DIFFERENT CURING DURATIONS

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ABSTRACT

The durability of concrete is usually measured by the number of years of maintenance- free service it provides. If a correct prediction has been made of the environmental conditions to which the concrete will be subjected to, concrete can be made to last for its intended service life. The durability of concrete is closely related to its permeability. The permeability dictates the rate at which aggressive agents can penetrate the concrete and attack the steel reinforcement.

During winter, ice accumulates on the top surface of concrete slabs and bridge decks. For the purpose of removing the snow and ice, de-icing agents, such as sodium chloride and calcium chloride, are applied. These salts migrate down to the reinforcing steel through small pores in the concrete. Over time, the chlorides in these salts can react with the reinforcing steel, breaking down the passive layer and causing the steel to corrode.

In Texas, the specification requirement for wet-mat curing is 8 days for decks with Type I and III cements and 10 days for decks with Type II and I/II cements and for mix designs with fly ash. Once the concrete is cured sufficiently, the deck is allowed to dry for one day. An additional day is typically allowed for any required surface treatment. The main objective of the research is to explore the possibility of opening the bridge decks earlier than 10 to 12 days by decreasing the number of wet mat curing days. For this reason, concrete mixtures typically used in Texas bridge deck were evaluated using numerous tests such as the Ponding test, the Rapid Chloride permeability Test, and the Abrasion Test.

This research focuses on the effect of curing on the chloride ion permeability of different mix design. It is expected that the knowledge gained through this work can be used to optimize the number of curing days and age required before full traffic can be allowed on bridge decks in Texas.

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CHAPTER 1

INTRODUCTION

1.1 General

Portland cement concrete plays a critical role as a structural material for the infrastructure in our society, as it is currently the most commonly used construction material (Neville, 1996). However, due to premature deterioration of existing concrete structures built in the last century, the durability of concrete structures has recently become a key issue for concrete technologists.

This thesis results from a research project sponsored by the Texas Department of Transportation (TxDOT) entitled “*Effects of Wet Mat Curing and Earlier Loading on Long-term Durability of Bridge decks*”. The main objective of the research is to explore the possibility of opening bridge decks earlier than the currently required 10 to 12 days by decreasing the number of wet-mat curing days.

For this reason, concrete mixtures with varying water to cementitious (w/cm) material ratios were subjected to the chloride permeability tests.

Permeability tests were performed according to AASHTO T 259-80: *Resistance of Concrete to Chloride ion penetration*, which also is known as the Ponding Test or the Soaking Test. It is expected that the knowledge gained through this work can be used to optimize the number of curing days and the concrete age required before full traffic can be allowed on bridge decks in Texas. This optimization is expected to be performed for particular concrete mixtures. Thus, determination of the effect of wet mat curing time on the long-term durability of concrete bridge decks using ponding tests is the focus of this thesis.

1.2 Curing Practice in Texas

In Texas, the specification requirement for wet-mat curing is eight days for decks with Type I and III cements and 10 days for decks with Type II and I/II cements and for mix designs with fly ash (TxDOT, 1993). According to the 1993 TxDOT Standard Specifications, at least 14 days should be given after the last slab concrete has been in place prior to allowing initial construction traffic on the structures. This initial construction traffic is limited to a $\frac{3}{4}$ - ton vehicle. Similarly, 21 days are required prior to allowance of other construction traffic and/or for the full traffic (TxDOT, 1993).

However, increased traffic congestion during the construction and/or repair work on highways has led to the need for earlier opening of bridge decks to traffic. Research conducted by TxDOT has led to incorporation of the *Special Provisions to Item 420 – Concrete Structures* into standard practice (TxDOT, 1998). These special provisions, adopted in 1998, allow the opening of the bridge deck to full traffic much sooner than the 21 days previously discussed as required by the 1993 specifications. According to the 1998 special provisions, once the concrete is cured sufficiently, the deck is allowed to dry for one day to let it prepare for the surface treatment and an additional day typically is allowed for any required surface treatment (TxDOT, 1998). Once the design compressive strength is attained and the required curing period is completed, the bridge deck is opened to full traffic. In general, the compressive strength is determined using site cast concrete cylinder specimens.

As a result, bridge decks in Texas currently are opened to full traffic in 10 to 12 days after the concrete is placed, representing a significant decrease in the time of curing required by the 1993 specifications. Although this current practice reduces the

number of days before full traffic load is allowed on bridge decks compared to the 1993 specifications, it does not reduce the number of wet mat curing days. This thesis is particularly aimed at investigating the effect of different curing durations on concrete permeability by assessing the resistance of concrete to chloride ingress. It is hoped that many durability problems can be prevented-specifically corrosion of reinforcement. At the conclusion of this study, a better understanding of the effects of curing on long- term durability of bridge decks is expected.

1.3 Permeability Tests

Many methods have been developed in the last twenty years to measure the permeability of concrete, specifically the chloride penetration into concrete. Each method has its own advantages and its drawbacks. The most famous method is the Ponding Test (or the Soaking test), which simulates exactly what is happening in nature. The second method developed is The Rapid Chloride Permeability Test (RCPT), which is well known as a short- test method. In the last couple of years, other methods have been developed recently to overcome some of the deficiencies of the previous ones. From these, The Rapid Migration Test (CTH Test), Electrical Migration Techniques, and Resistivity Techniques are the most famous.

1.4 Organization of the Thesis

This thesis is focused on determination of the effects of different parameters on the chloride permeability of a given concrete mix. The particular concrete mixture, the amount of pozzolanic materials, the age of concrete, and the number of curing days all affect the overall permeability of a concrete bridge deck. This thesis presents

an analysis of results for concrete mixtures used at seven Texas sites located in Houston, Harlingen, San Antonio, Lubbock, Fort Worth, Atlanta, and El Paso.

Chapter 2 reviews the existing literature relevant to the current study of the chloride permeability. It includes a complete review of the different factors affecting concrete permeability, mechanisms of steel reinforcement corrosion, other existing permeability tests methods, and the literature relevant to the correlation between AASHTO T 277 and AASHTO T290.

Chapter 3 describes the tests conducted (AASHTO T 259) including the modifications performed by TTU researchers to reduce the testing time. Also described is the experimental procedure including the mixtures, test specimens, instrumentation, setup and testing procedures for the specimens.

Chapter 4 presents the analysis and interpretation of the results. A discussion of the effect of curing duration on the concrete permeability is also presented.

Chapter 5 presents a comparison between AASHTO T259/260 and AASHTO T277 in three different ways. A comparison between ponding tests results and literature is also presented.

Chapter 6 summarizes the knowledge gained through the research and discusses the conclusions made. Recommendations for more durable concrete bridge decks also are suggested.

CHATER 2

LITERATURE REVIEW

2.1 Durability of Concrete

The durability of concrete usually is measured by the number of year's service it provides. If a correct prediction can be made of the conditions to which the concrete will be subjected to (including applied loads), there is no reason for a properly proportioned concrete not to last for decades without significance maintenance (Nielsen, 1985). Nowadays, with the knowledge and experience that people have to protect concrete from aggressive agents, the selection of sound constitutive materials and the production of high quality concrete have become more attainable. However, ignorance and economic pressure to reduce initial costs of construction often prevent the desired outcome. High durability concrete is typically 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 indicates that for many structures, the final cost of repairing avoidable damage is much greater than the additional cost that would have prevented the problems. 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 a later section.

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

Type of Degradations	Description	Cause	Component involved	Symptoms
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 fluids such as 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 that are tightly packed together.

Sorption is the result of capillary movement in the pores that are open to an ambient medium. Capillary suction can take 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 50 μm 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 least 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 the 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 admixtures. These salts can migrate down to the reinforcing steel through small pores in the concrete. Over time, the chlorides in these salts can 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_3A) and tetracalcium aluminoferrite (C_4AF) no matter the chloride source. Both C_3A and C_4AF 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_3A and C_4AF 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. Less 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 that is experienced 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, 1996). This finding has been attributed to the coarse initial structure that is 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, then 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, 1986; Rasheeduzafer, 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 have to 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. Their effects on the corrosion development of the reinforcement always have been a controversy among the researchers. Danilecki (1969) found that the cracks are 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, 1971). 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-H₂O system at 77°F (25°C) for 10⁻⁶M 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 vary 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 the diagrams. One arises from 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 Polarization. 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 is of two kinds, chemical and mechanical passivity.

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 as the following states.

- a. Capillary water. This is the water present in voids larger than about 50 nm.

b. Adsorbed water. This is the water that is 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 which is 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. The 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 Eq 2.12 & 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

There are five types of corrosions that occurred 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 nonuniform, 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 to be 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 when it is 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/m³ 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/m³ are acceptable for bridge decks; however, deck replacement should occur when the level of chlorides reaches 2.8 kg/m³ (Miller et al., 1993).

Table 2.2. Threshold chloride Ion concentrations of Previous Researchers (Miki 1990)

Researchers	Year	Kg/m ³
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, which is 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/m³) for typical mixture of normal weight concrete (density 2300 kg/m³) (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/yd³ 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 ³	0.53 kg/m ³	230 ppm by weight of concrete

2.9 Existing Permeability Tests

Many methods have been developed in the last twenty years to measure the permeability of concrete. Each method has its own advantages and drawbacks. The Rapid Chloride Permeability Test (RCPT) is well known as a short duration test method. In contrast, the AASHTO T259/260 Ponding Test (or Soaking test) is considered a long term method. Others methods have been developed recently to

overcome some of the deficiencies of the previous tests. From these, the Rapid Migration Test (CTH Test), Electrical Migration Techniques and Resistivity Techniques are the more favored.

2.9.1 Rapid Chloride Permeability Test

For specification and quality-control purposes in projects, researchers and practitioners prefer a test that is simple to conduct and that can be performed in a short time period. The rapid chloride permeability test meets these goals. First developed by Whiting in 1981, RCPT has had results that correlate partially with results from the classical 90-day salt ponding test.

Standardized testing procedures are in AASHTO T 277 (or ASTM C 1202). The RCPT is performed by monitoring the amount of electrical current that passes through a sample 50 mm thick by 100 mm in diameter in 6 hours (Fig 2.5). This sample is typically cut as a slice of a core or cylinder. A voltage of 60V DC is maintained across the ends of the sample throughout the test. One lead is immersed in a 3.0% salt (NaCl) solution and the other in a 0.3 M sodium hydroxide (NaOH) solution (ASTM C 1202).

Figure 2.5. AASHTO T277 (ASTM C1202) test setup

The total charge passed is determined and this is used to rate the concrete according to the criteria included as Table 2.5.

Table 2.5. RCPT Ratings (per ASTM C1202)

Charge Passed (coulombs)	Chloride Ion penetrability
> 4000	High
2000-4000	Moderate
1000-2000	Low
100-1000	Very Low
<100	Negligible

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.

2.9.2 Ponding Test

All of the steps of the ponding test will be explained in detail in Chapter 3. However a brief summary of the test and its importance and its drawbacks is discussed here.

The traditional widely used method of determining the resistance of concrete to chloride ion penetration is the American Association of State Highway and Transportation Officials' (AASHTO) T 259 - Standard Method of Test for Resistance of Concrete to Chloride Ion Penetration.

In what is commonly referred to as the ponding test, the top surface of three or more concrete slabs that are at least 3-in. (75-mm) thick and 12-in. (300-mm) square are exposed to a sodium chloride solution for a period of 90 days. This is illustrated in Figure 2.6 (Stanish et al., 1997). The slabs are then allowed to dry out and samples of concrete taken at depths from 11/416 to 11/42 in. (1.6 to 13 mm) and from 11/42 to 1

in. (13 to 25 mm). The chloride ion content of each sample is then determined in accordance with AASHTO T 260 - Standard Method of Test for Sampling and Testing for Chloride Ion in Concrete and Concrete Raw Materials. A companion specimen that was not ponded is used to determine the baseline chloride ion content in the specimens. The baseline chloride level is subtracted from the recorded chloride content of the ponded specimens to obtain the absorbed chloride ion content.

Figure 2.6. AASHTO T259 Salt Ponding Test Setup (Stanish et al., 1997).

The Ponding test has several limitations including the following:

1. It takes at least 132 days from the time that the samples are made to complete the test. This means that the concrete samples must 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 71/416- and 11/42-in. (11- and 13-mm) 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 (THE SOAKING 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 in to 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).

2.9.3 Other Existing Methods

Several other methods were developed to overcome some of the deficiency mentioned above about the Ponding and the RCPT. These are the NordTest NTBuild 443, the Electrical Migration techniques, The Rapid Migration Test, the Resistivity techniques, the pressure techniques and the Sorptivity techniques.

A summary of the test methods listed above is grouped into Table 2.3. There are divided into three main categories (long term, short term, and other). A summary of some of the advantages and disadvantages to each testing procedure is also provided.

An examination of Table 2.6 reveals that each test has strengths and weaknesses. For example, and AASHTO T259 (salt ponding test) model the actual chloride ingress well, however as long-term tests they are not suitable for use as a quality control test during construction. Other methods, like the RCPT, have a more nebulous relationship with what actually occurs in the concrete, but have the advantage of a short duration. Finally, some tests fall between these two extremes.

Table 2.6. Summary of Permeability Test Methods (Stanish et al., 1997)

Test Method		Considers Chloride Ion Movement	At a Constant Temperature	Unaffected by Conductors in the Concrete	Approximate Duration of Test Procedure
Long Term	AASHTO T259 (salt ponding)	Yes	Yes	Yes	90 Day after curing and conditioning
	Bulk Diffusion (Nordtest)	Yes	Yes	Yes	40 - 120 Days after curing and conditioning
Short Term	RCPT (T277)	No	No	No	6 hours
	Electrical Migration	Yes	Yes	No	Depends on Voltage and Concrete
	Rapid Migration (CTH)	Yes	Yes	No	8 hours
	Resistivity	No	Yes	No	30 Minutes
	Pressure Penetration	Yes	Yes	Yes	Depends on Pressure and Concrete (but potentially long)
Other	Sorptivity Lab	No	Yes	Yes	1 week incl. Conditioning
	Sorptivity-Field	No	Yes	Yes	30 minutes

2.10 Effect of Fly Ash, and Slag on Concrete Properties

By definitions, 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.

2.10.1 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 Hungry Horse Dam in 1953, utilizing 120,000 metric tons of fly ash. The oil crisis in 1970s led to the greater use of coal fire in electric power plants and fly ash containing higher levels of calcium oxide has since become available since, which for chloride resistance is not a good development.

Fly ash (0.1 μ m to 0.1 mm, with an average of 15 μ m) is generally finer than Portland cement (1 μ m-100 μ m). 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 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 2.7 (Neville, 1996) illustrates the basic comparison of ingredients of fly ash and Portland cement.

Table 2.7. Typical Chemical Compounds in Fly Ash and Portland Cement (Neville 1996)

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

The setting of Portland cement is related to the hydration of the silicate components, C₃S and C₂S as shown in Figure 2.7:

Figure 2.7. 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 it 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 can be shown as in Figure 2.8:

Figure 2.8. Hydration of Fly Ash and Silicate Components in Concrete

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

- Improved workability
- Lower heat of hydration
- Lower cost concrete
- 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 took more time to attain the required strength and thus 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. 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 (Alhozaimy et al., 1996).

2.10.2 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 μm contribute to early strength, while particles larger than 10 μm and smaller than 45 μm contribute to later strength. Since particles greater than 45 μm are difficult to hydrate, slag is mostly pulverized to particles with diameters less than 45 μm (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.

2.11 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 effects 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.

2.11.1 Specific Electrical Conductivity of Concrete Pore Solution

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

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

where $\lambda_{i,0}$ is the equivalent conductivity at infinite concentration. Table 2.8 lists the equivalent conductivity of aqueous ions commonly identified in concrete pore solution.

Table 2.8. Equivalent Conductivity of Aqueous Ions at Infinite Concentration at 25°C (Adamson, 1973)

Ion	Na ⁺	K ⁺	Ca ²⁺	SO ₄ ²⁻	OH-	Cl ⁻
Equivalent Conductivity λ_0 (m ² .mol ⁻¹ .ohm ⁻¹)	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:

ρ = specific electrical conductivity of aqueous solution (m⁻¹.ohm⁻¹)

ρ_{water} = specific electrical conductivity of water (=10⁻⁵ m⁻¹.ohm⁻¹)

C_i = equivalent electrical concentration of ion I (equiv.m⁻³)

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

Appreciable concentrations of Na^+ , K^+ , OH^- , Ca^{2+} and SO_4^{2-} from the cement components enter into the mixing water during concrete mixing. After setting and early hydration, the Ca^{2+} and 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 OH^- , Na^+ and K^+ using the above equations.

2.11.2 Effect of Supplementary Cementing Materials on Specific Electrical Conductivity of Concrete Pore Solution

The use of supplementary cementing 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 supplementary cementing 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 used as a basis 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 percent 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.

In their same study, Shi et al., 1998 has 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. They finally found 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 2.9

Table 2.9. Specific Conductivity of Pore Solutions in Different Hardened Cementing Materials (Shi et al 1998)

Cementitious materials	Specific conductivity, 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

Supplementary cementitious materials such as silica fume, fly ash and ground blast furnace slag 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 increase of 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 the above stated, it can be said 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.

2.12 Ion and Mass Transport in Concrete Mixes during Ponding Test

Ionic and molecular diffusion are the two main modes of chloride transport during the ponding or the soaking 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 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 μ 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 blocking partially 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) try to find a correlation between the charge-passed data derived from 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 a RCPT. To supplement the results, the electrical resistivity and compressive strengths of the concrete mixtures also were 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 were following 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 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.

2.13 Effect of the Interface Zone and Aggregate Type on Permeability of Concrete

In the past, concrete has been considered as 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 et al., 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. The main reason for this is that, during mixing, dry cement particles are unable to become

closely packed against the relatively large particles of aggregate. There is thus 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 μm . 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, there is the main interface zone, some 50 μm thick, containing products of hydration of cement with large crystals of calcium hydroxide but without any 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). Thus, a lower permeability of concrete results. However, this is not the case when siliceous gravel is used during mixing.

2.14 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.

Two tests are generally used to determine concrete permeability to chloride ions and other aggressive solutions: the American Association of State Highway and Transportation Officials (AASHTO) test method T-277, *Rapid Determination of the Chloride Permeability of Concrete*, and test method T-259, *Resistance of Concrete to Chloride on Penetration*. The AASHTO T259 test has long been favored, among the 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.

In the original report, “Rapid Determination of the Chloride Permeability of Concrete” by Whiting which was published in 1981 and 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 2.10 and established a correlation (Figure 2.9) 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 2.10. Charge Passed versus Total Integral Chloride (Whiting, 1981)

Charge Passed (Coulombs)	Chloride Permeability	Type of Concrete	Total Integral Chloride to 40.6 mm (1.6 in) Depth after 90 day Ponding test
> 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 2.11. 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:

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

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 2.9 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

Figure 2.9. Correlation Data of ASTM C1202 Document (Whiting, 1981)

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.

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 on 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 twenty two 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 author’s opinion, the correlation did not represent a large data base 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 2.12. Concrete Mixtures used in the by Whiting and Dziedic 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 chloride permeability test. 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 2.10, originally devised by Whiting in 1981. Results of that comparison are presented in Table 2.13 which that there is no consistency in rating the chloride penetrability of the concrete mixtures tested.

Table 2.13. 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

CHAPTER 3

TEST SETUP AND APPROACH

In a combined effort between TxDOT and Texas Tech University (TTU), researchers at TTU began a process that potentially will lead to the development of new guidelines as to when bridge decks can be open to (a) construction traffic and (b) full traffic without compromising concrete durability. To achieve this objective, various mix designs have been subjected to different curing durations to observe which, if any, will have an effect on the durability of concrete. Wet mat curing durations tested were for 2, 4, 8, 10, and 14 days from the time of pour. Also, a “no moist curing” is considered; hereafter referred to as 0 day cure.

To achieve this objective, seven concrete mix designs (four fields and 3 labs) used in different districts within Texas were being tested in laboratory facilities located at Texas Tech University. Of the seven mixture designs, four were actually tested in the field in five different TxDOT districts. At each site, a relatively small scale, though full size, bridge deck was constructed. In addition, numerous concrete specimens were cast alongside the bridge deck. By having the four bridge decks throughout the state, as opposed to simply in a laboratory setting, realistic environmental effects are inherently considered when assessing the quality of a particular concrete mixture.

Cast specimens from the field and the laboratory were subjected to the following tests to assist in determining the durability of concrete: permeability (ponding test and RCPT), compressive strength, freeze thaw resistance, petrography analysis, tensile strength, shrinkage and fracture tests. Although the combination of all

the data from the above tests helps determine the quality and durability of the concrete, this thesis is focused on the permeability of concrete and on the ponding test.

3.1 Mixture Designs

Seven mixes located across Texas were tested. These include: San Antonio, El Paso, Pharr, Fort Worth, Atlanta, Houston and Lubbock. A predominant local mixture design was used for each model bridge deck slab. Ground granulated blast furnace slag (replacing 50 % cement) was used at the El Paso test site. The site in Fort Worth, Atlanta used Class F fly ash replacing 22% and 21% respectively cement. At the San Antonio and Houston site, class C fly ash was used to replace about 20% and 27% respectively of Portland cement and Lubbock site contained no mineral admixture. After RCPT was performed on Lubbock site, permeability was found to be extremely high. For this reason, a new mix design containing mineral admixture (31% fly ash) was developed on Lubbock site (also referred as New Lubbock). The mixture design information for all the districts tested is summarized in Table 3.1.

Table 3.1. Mix designs Used in Bridge Decks in Different Districts of Texas

Parameter	Districts						
	San Antonio	El Paso	Pharr	Fort Worth	New Lubbock	Atlanta	Houston
Cement Type	I/II	I/II	I	I/II	I/II	I	I/II
Mineral Admixture	Flyash C 20%	Slag 50%	None	Flyash F 22%	Flyash F 31%	Fly ash F 21%	Flyash C 27%
Coarse Aggregate	LS	LS	Sil	LS	LS	Sil	LS
W/C	0.43	0.42	0.41	0.43	0.45	0.46	0.46
Air	6%	5%	6%	6%	6%	6%	5%

LS = Lime Stone

Sil = Siliceous gravel

3.2 Test Site Setup

Test sites were designed and cast to realistically model actual TxDOT bridge design and construction procedures as closely as possible. A TxDOT Class “S” concrete mixture design was used for each concrete deck mixture.

Square 12”×12” specimens were cast as shown in Figure 3.1. Since the primary objective of this research project involves evaluation of the effects of different curing durations on the durability of concrete, concrete specimens were removed from water according to predetermined durations. As mentioned above, the curing periods studied are 0-, 2-, 4-, 8-, 10- and 14 days. Curing periods were measured and terminated based on actual calendar days irrespective of any extreme temperature fluctuations that might have occurred.

Figure 3.1. Casting of the 12" × 12" Specimens

3.3 Test Procedure

All specimens, were tested according to AASHTO T259 and AASHTO T260. These methods cover the determination of the resistance of concrete specimens to penetration of chloride ions. These methods are intended for use in determining the effects of variations in the properties of concrete on the resistance of the concrete to chloride ion penetration. Variations in the concrete may include, but are not limited to, changes in cement type and content, water cementitious materials ratio, aggregate type and proportions, admixtures, treatments, curing and consolidation. The test process requires three steps; casting and ponding the samples, drilling the samples and testing them.

3.3.1 Ponding the Specimen

As shown in Table 3.2, for each site, 18 samples (12''×12'') have been cast. As mentioned above, the curing periods studied are 0-, 2-, 4-, 8-, 10-, and 14 days curing. Three samples for each day of curing. From these 3 samples two are ponded and one is a control (Figure 3.2). For all the laboratory specimens of the test sites, specific codes are assigned (Figure 3.3).

Figure 3.2. Fort Worth Sample

Figure 3.3. Coding System for Sample Notation

After the curing phase has ended for each specimen, the samples are stored until 28 days of age in the drying room. Immediately after the specified drying period stipulated above (i.e. the 29th day of specimen age), 3.2 ± 1.6 mm of the slab surface is abraded using grinding or sandblasting techniques if the concrete is to be subjected to wear from vehicle traffic. If the concrete or treatment is to be used on surfaces not subject to wear from vehicle traffic (which is not the case in this research project) then the abrading step may be omitted. Fig 3.4 and Fig 3.5 show two samples abraded, one with grinding and the other with a sandblasting technique. In our test, the surface of Lubbock and Fort Worth has not been abraded while for the other sites, 50% of the surface has been abraded using the sandblasting technique.

Figure 3.4. Sample Abraded using Grinding Technique

Figure 3.5. Sample Abraded using Sandblasting Technique

After that, we place approximately 19 mm high by 13 mm wide dams around the top edge of all specimens except those which will become the control specimen (Figure 3.6). All slabs are returned to the drying room as specified for an additional 13 days (i.e. until 42 days of age).

Figure 3.6. Construction of Dams for the Houston Samples

The slabs (or specimens) with dams and the 6 inch core field specimen are subjected to continuous ponding with 3 % sodium chloride solution to a depth of approximately 13 mm (0.5 in) for 90 days for Fort Worth and New Lubbock while the other sites has been ponded for 180 days (six months). The solution is prepared by diluting crystals of sodium chloride in a defined amount of distilled water. Glass plates are placed over the ponded solutions to retard evaporation of the solution (figure 3.7). Placement of the glass plates is done in such a manner that the surface of the slab is not sealed from the surrounding atmosphere. Additional solution is added if

necessary to maintain the 13 mm (0.5 in) depth. All slabs remain in the drying room for the duration of the ponding period. A summary of the information on all the sites is presented in Table 3.2.

After 90 days of exposure unless stated elsewhere, the solution is removed to dry and then the surfaces are wire brushed until all salt crystal buildup is completely removed.

Figure 3.7. Houston Samples Ponded for 180 Days

Table 3.2. Test Program Setup

Parameter	Districts						
	San Antonio	El Paso	Pharr	Fort Worth	New Lubbock	Atlanta	Houston
Casting Testing	Field	Field	Lab	Field	Lab	Lab	Field
Abraded	50%	50%	50%	No	No	50%	50%
# 12" × 12"	18	18	18	18	18	18	18
Ponding Duration	180 days	180 days	180 days	90 days	90 days	180 days	180 days
# of drill depth	4	4	4	4	4	4	4
# of drilling	2	2	2	2	2	2	2
# of tests	144	144	144	144	144	144	144
Total # of tests	1008						
Drill pattern (see p.92)	B	B	B	B	B	B	B

3.3.2 Drilling the Specimen

AASHTO T259 recommends that the samples should be obtained from each specimen at each of the following depth as seen in Pattern A in Figure 3.8. However, because of the different setup of the drilling machine that we are using and in order to get more refined information at the top surface of the specimen, Pattern B in Figure 3.8 was adopted.

Drill Pattern A

Drill Pattern B

Figure 3.8. Drill Pattern A&B

In our drilling procedure, we use the Gilson Model HM-343 (Figure 3.9). This drilling machine is designed to take precise concrete samples for chloride ion penetration evaluation. This machine has some unique features:

- 1) No cross contamination between samples. A clean sample path is created when each sample is taken.
- 2) Rapid sample collection. The collection vessel, filter and tube are a single unit. Sample container and tube are inserted into a fixed position ready to collect

the sample. The somewhat low cost used collection containers may be discarded after use.

- 3) Only two holes drill bits are needed. A 5/8" diameter bit drills a pilot/connected companion hole for the powder sample collection system.
- 4) The heavy gauge drill guide and template ensure vertical holes and correct overlap of the sample and companion powder collecting holes.
- 5) A powerful Vacuum Motor removes the sample powder produced as the core bit progresses.

Figure 3.9. Gilson Model HM-343

The sample drilling Assembly's components are:

- 1) A two wheeled self contained cart with stainless steel panels and service tray.
All system components are contained in the unit.
- 2) A heavy duty rotary impact hammer drill.

- 3) A hole drilling Template.
- 4) A drilling guide including ½” stop controls.
- 5) A vacuum motor and filter
- 6) A sampling assembly including vacuum piping, tubing guide, and sample bottle holder.
- 7) Single use- sample collection bottles, bags and tubes.
- 8) Masonry bits: A 2” core bit and a 5/8” companion hole bit.

The steps of drilling are illustrated in Figure 3.10 and are as follows:

- a) The first step is to identify/mark the location of holes to be drilled. Two holes per sample typically are performed.
- b) Attach the 5/8” drill bit to the drill motor, and position it over the mark with power switch off.
- c) Turn on the “Main/Aux” power switch. Then turn on the “Vacuum/Drill” switch and drill to the desired depth. The average maximum drilling depth is approximately 4”. The drill stop can be used to control drilling depth by moving the clevis pin on the depth stop gauge to the desired stop point.
- d) One of the advantages of model HM-343 is that it allows the bit to advance ¼” beyond the drill stop set point if the operator continues drilling after the stop point is reached. When the stop point is reached, the drill is turned off. An additional safety item is that the drill will not operate unless the vacuum switch is “On”. To reduce the time, it sometimes is more convenient to drill several companion holes before changing to the core bit.

- e) After the companion hole has been drilled, all powder and debris from the companion hole and core whole area is removed. A sample collection assembly is used to collect the powder from the companion hole.
- f) Next, the companion hole is removed and the core bit is installed.
- g) The cart's drilling template is aligned over the drilled and cleaned companion hole. A sample collection bottle with collection bag and tube is placed into vacuum holder. The collection tube is guided into the companion hole and located at the end of the tube near the top of the companion hole. After the coring bit has advanced about an inch, the tube is pushed to the middle of the companion hole.
- h) The first drill guide stop point is at $\frac{1}{4}$ " depth. All subsequent stop points are at $\frac{1}{2}$ " intervals. So, $\frac{1}{4}$ " is drilled into the concrete sample, the material is collected into the bag and the drill guide is reset to the first $\frac{1}{2}$ " collection depth set point.
- i) The new sample collection bottle is loaded using the same procedure described above. With drill stop pin is set, drilling to $\frac{1}{2}$ " depth is completed. The procedure is repeated for the next $\frac{1}{2}$ "; $\frac{3}{4}$ "- $1\frac{1}{4}$ " intervals. Thus, so for each hole, three powder samples are collected if the $\frac{1}{4}$ " is discarded or four powder samples if the $\frac{1}{4}$ " is collected.
- j) Finally, each sample collection bottle is marked with four numbers:
- Sample's number
 - Site's name
 - Hole's number
 - Depth's number

Figure 3.10. Steps of Drilling

3.3.3 Testing the Specimen

After the drilling phase is completed, the sample collection bottles are moved to a partially controlled environmental lab (e.g. temp $65^{\circ} \pm 10^{\circ}$) where the samples are tested to determine the chloride ion in the concrete. At the beginning of this research project, we followed the AASHTO T260 guidelines explicitly.

This method covers procedures for the determination of the acid soluble chloride ion content or the water soluble chloride ion content of aggregates, Portland cement, mortar and concrete. The total amount of chloride is usually equal to the acid-soluble chloride. However, organic additives or minerals that contain acid-insoluble chloride may be present in concrete and concrete raw materials. These constituents

may become acid soluble during long term exposure to the alkaline environment in concrete or mortar.

The age of concrete mortar or hydrated Portland cement at the time of sampling will have an effect on the water soluble chloride ion content.

Two procedures are presented in AASHTO T260. The first is related to the determination of acid-soluble chloride ion and the second is related to the determination of the water soluble chloride ion content. In our test, the second procedure is followed. This procedure is described as follows:

- 1) Initially, the mass to the nearest milligram of a 3 g powdered sample representative of the material under test is determined. In general the concrete powder is received in a pulverized condition. However, when samples are received in the laboratory in other than pulverized condition, the sample is crushed and ground to a powder. All crushing is done dry (i.e. without water). All material must pass a 0.300 mm ($N_0.50$) sieve. All pulverizing tools and sieve is washed with alcohol or distilled water and is dried before use with each separate sample.
- 2) The sample is transferred quantitatively to a beaker of capacity 150 – 200 mL. 60-70 mL of distilled water is added. The beaker is covered with a watch glass and brought to a boil on a hot plate magnetic stirrer using a small magnet. The sample is boiled for 5 minutes, and then left standing for 24 hours in a fume free atmosphere. (Fig 3.11)
- 3) The clear liquid is filtered in the beaker through double filter paper (Whatman $N_0.41$ over $N_0.40$ or equivalent) into a 250 mL beaker (Fig 3.12). Care must be taken to quantitatively transfer any adherent drops on the watch glass. A stirring rod

generally is used to aid in the transfer. Sufficient hot distilled H_2O is added to cover any residue left in the original beaker. The solution is stirred for one minute on a magnetic stirrer and filtered into a 250 mL beaker with a swirling action. The beaker and the stirring rod are washed once into the filter using hot distilled H_2O . The filter paper is lifted carefully from the funnel and the outside surface of the paper is washed with hot distilled H_2O . The paper is set aside and the interior of the funnel and its tip is washed with hot distilled H_2O . One to two drops of methyl orange indicator is added to the 150 mL beaker. Next concentrated HNO_3 is added one drop at a time (four to seven drops) with continuous stirring until a permanent pink to red color is obtained. If the sample contains blast furnace slag or other sulfide-bearing material, 3 mL of hydrogen pyroxide (30% solution) is added. Once all of the above is completed, the volume of the solution is brought to 125 to 150 mL using distilled H_2O .

- 4) The Cl^- electrode is filled with the solution recommended by the manufacturer (Thermo Orion 2003). The solution is read with a millivolt gauge to determine the approximate equivalence point by immersing the electrode in a beaker of distilled H_2O . The approximate millivolt reading is unsteady in H_2O as it contains no ions. Four mL of 0.01 normality NaCl is added to the cooled sample beaker using constant swirling. The beaker of distilled H_2O is removed from the electrode. The electrode is then wiped with absorbent paper and immersed in the sample solution. The entire beaker electrode assembly is placed on a magnetic stirrer and gentle stirring is begun. Using a calibrated buret, standard 0.01 normality AgNO_3 solution gradually is added to bring the millivolt reading to -40 mV of the equivalence point determined in distilled H_2O . The amount of AgNO_3 required is

recorded. Next, standard 0.01 normality AgNO_3 solution is added in 0.10 mL increments and the millivoltmeter reading is recorded after each addition.

- 5) As the equivalence point is approached, equal additions of AgNO_3 solution cause larger changes in the millivoltmeter reading. Past the equivalence point, the changes per unit volume will again decrease. The titration is continued until the millivolt reading is at least 40 mV past the approximate equivalence point. The endpoint of the titration usually is near the approximate equivalence point in distilled water and may be determined by two methods:

- a) By calculating the differences in millivoltmeter readings between successive AgNO_3 additions (Fig 3.13). The endpoint is the peak of the plot.
- b) By plotting the volume of AgNO_3 solution added versus the millivoltmeter readings. The endpoint will correspond to the point of inflection of the curve as indicator (Fig 3.14)

The endpoint will be near the midpoint which produces the largest change in millivoltmeter readings. It may be determined by plotting midpoints versus differences and defining the AgNO_3 volume which corresponds to the maximum difference on a smooth symmetrical curve drawn through the points. The percent Cl^- is calculated from the following equation (AASHTO T260):

$$\text{Cl}^- \text{ percent} = \frac{(3.5443(V_1 N_1 - V_2 N_2))}{W}, \quad (3.1)$$

Where V_1 is the Endpoint in mL of AgNO_3 , V_2 is the Normality of AgNO_3 , W is the mass of original concrete sample in grams, V_2 is the volume of NaCl solution added in mL, and N_2 is the normality of NaCl solution.

Figure 3.11. Boiling the Specimen for Five Minutes

Figure 3.12. Filtration of the Solution

Figure 3.13. Max Millivolt Difference Corresponding to the Endpoint

Figure 3.14. Point of Inflection Corresponds to the Endpoint

3.4 Difficulties in AASHTO T260 Test

Several difficulties occurred during the titration process:

- a) It was extremely difficult to determine the equivalence point in the distilled water. In fact, the millivolt reading in distilled water generally fluctuates from +20% -20 % from sample to sample. This is expected as the chloride electrode measures chloride ions in a solution and the distilled water contains no chloride ions. As a result, it was difficult to determine accurately the -40 mv and the +40 mv of the equivalence point in water as stated by the AASHTO T260 method.
- b) The current AASHTO T260 experiment is extremely time consuming as one is forced to take readings for each addition of 0.1 mL of silver nitrate. Generally 50-150 readings depending on the amount of chloride ions in the solution are required to determine the endpoint. In fact, a sample generally takes 2 hours from its preparation to testing with 1008 samples to test (excluding casting, curing, abrasion and drilling). Thus, we looked for an acceptable shortcut.

3.5 Modifications to the AASHTO T259/260

The first modification was to change the drilling pattern as mentioned in section 3.3.3. The second was to reduce the testing time. To solve this problem, a chloride ion selective electrode (ISE) was used. The ISE was calibrated it with five different solutions. These solutions were obtained by diluting a 100 ppm solution twice, five times, and 10 times to get solutions with concentration ranging from 1 ppm to 100 ppm (assuming that the concentration of chloride ions range between these two

numbers). By doing this step, the determination of the equivalence point in distilled water becomes unnecessary. Thus, the revised required steps are as follows:

- Step 1 to Step 3 in section 3.3.3 remains the same.
- Step 4 is altered as follows: The Cl^- or the Ag^+ electrode is filled with the solution recommended by the manufacturer. Four mL of 0.01 normality NaCl , is carefully added while swirling constantly to the cooled sample beaker. The beaker of distilled H_2O is removed from the electrode. The electrode is wiped with absorbent paper and immersed in the sample solution. Next, the entire beaker electrode assembly is placed on a magnetic stirrer and gentle stirring is performed. Using a calibrated burette, standard 0.01 normality AgNO_3 solution is added gradually to bring the concentration reading to 2 ppm or 3 ppm. Additional standard 0.01 normality AgNO_3 solution is added in 0.10 mL increments, recording the millivoltmeter reading after each addition. Note that using the PH meter available to us, the concentration can be recorded in ppm and/or millivolts after each addition of 0.1 mL of AgNO_3 . Thus, the modification described is focused directly on the area close to the endpoint (see the blue box in Figure 3.13).
- Step 5 no longer applies

Although the time of the experiment has been reduced from two hours per sample to approximately 40 minutes per sample, this modification to AASHTO T260 is still considered time consuming for this research project as more than 1000 samples are tested. Thus, instead of performing the remaining samples using the modification mentioned above to AASHTO T260, the chloride ion concentration is taken directly in the solution using our chloride ion selective electrode (ISE) since the electrode is

already calibrated. (Fig 3.15) To ensure that these two methods (modified AASHTO T260 and the Chloride Ion Selective Electrode) converge, all samples of San Antonio field cores (taken directly from the bridge) were tested using these two methods. The results are shown in Figure 3.16 where it is clear that the concentrations of chloride using the two methods are very close to each other. Thus, it was depicted to follow the direct measurement of all the Chloride concentration for the next seven sites using the Chloride Ion Selective Electrode.

Figure 3.15. Determination of the Concentration of the Solution Using the Chloride ISE

Figure 3.16. Comparisons between the Modified AASHTO T260 and the Chloride ISE

CHAPTER 4

TEST SETUP AND ANALYSIS OF THE PONDING

TEST RESULTS

The experiments were conducted to investigate the effect of wet mat curing duration on chloride ion permeability in the ponding test. For each sample, two holes were drilled on the unabraded finished surfaces of the specimens from Fort Worth and New Lubbock districts and on the abraded finished surfaces for Houston, San Antonio, El Paso, Pharr and Atlanta (see Table 3.2). Samples were collected from four different depths (Figure 3.8); 1/16" to 0.25", 0.25" to 0.75", 0.75" to 1.25" and 1.25" to 1.75" for a total of 144 samples per site (i.e. 2 holes $\times$ 4 depths $\times$ 18 specimen per site). The chloride content for each sample was determined using an electrode calibrated with standard solutions as described in Chapter 3.

4.1 Fort Worth Site

For the Fort Worth site, concrete was mixed at a water cementitious ratio of 0.43 and 25% of the required cement content was replaced with class F fly ash. The cement: fly ash: fine aggregate: coarse aggregate ratio was 1.00:0.33:3.15:4.66 (volumetric). The coarse aggregate used was limestone. The test results for Fort Worth are shown in Table 4.1. Included in this table are the chloride concentrations for all the samples. It should be noted that each number in the table is an average of four numbers. The first, second, third and fourth column shows the chloride concentration for the first, second, third and fourth layer respectively. It can be seen from Table 4.1, that within each column, as the curing duration increases, the chloride

concentration decreases, thus concrete becomes less permeable; e.g. the chloride concentration decreases from 57 ppm (part per million) for FA (0 day curing) to 44 ppm for FF (14 days curing) and this is due to the fact that the concrete microstructure has been changed due to the curing duration. In fact, concrete microstructure becomes more dense (i.e. less permeable) as the curing duration and sample increase.

Table 4.1. Concentrations for Fort Worth Ponding Specimens in ppm.

Non Abraded - Ponded (90 days) - Type I/II cement - 22% FA (class F) - LM				
	0 - ¼"	¼" - ¾"	¾" - 1¼"	1¼" - 1¾"
FA (0 days)	57	44.5	7.5	2.5
FB (2 days)	51	40.75	7	3
FC (4 days)	48	31.5	5.5	2.5
FD (8 days)	47	18.5	3.75	2.75
FE (10 days)	44	18	3.75	2.25
FF (14 days)	44	16	2.75	2.75

To further illustrate the effect of curing on the permeability of concrete, Figures 4.1 & 4.2 are shown. These Figures represent a set of relations between the chloride concentration and the curing duration for the four depths under study. As shown in these Figures, chloride was concentrated in the upper two layers (up to 0.75 in) whereas the chloride content was extremely small in the bottom two layers and almost negligible in the bottom layer. This extreme decline in chloride concentration through the depth of the specimen is important to observe. As the concrete samples were dried for 28 days prior to ponding, when they came in contact with the salt solution, the transport of the solution due to capillary action prevailed only in the superficial layers that present open and connected pores. As discussed in Chapter 2, even if the pores were connected into the deep interior of concrete, the capillary

transport takes place only to a certain distance (e.g., 1.25 inch in the case of Fort Worth site) as the pore walls provide resistance to the flow of liquid. In general, the degree of this resistance depends on pore dimensions, with smaller pores presenting larger resistances than larger pores.

Another important conclusion shown in Figure 4.1 is that the effect of curing on the chloride concentration after 8 days of curing is extremely small. Specifically, while the chloride concentration decreases from 44.5 ppm (0 days curing, layer 1) to 18.5 ppm (8 days curing, layer 1), it decreases just by only 2.5 ppm from 18.5 ppm (8 days curing, second layer) to 16 ppm (14 days curing, second layer). This is possibly due to the fact that during the first few days of curing, the top layer of the concrete becomes completely saturated and the capillary pores in the top layers are filled with water so that even with an interruption of the wet mat curing, the inner concrete surface will still be saturated with a relative humidity above 80%.

Figure 4.1. Chloride Concentrations versus Curing Duration for Fort Worth

Figure 4.2. Chloride Concentrations versus Layer Number for Fort Worth

Figure 4.3 shows the chloride concentration for all the control samples for Fort Worth site for all depths. It can be seen that all the numbers falls between 2 and 3 ppm for all the samples which is negligible. In fact this % of chloride may have entered the concrete during mixing, either in the water or through the cement ingredients.

Comparing the ponded and control specimens for each curing duration (Figure 4.2 versus Figure 4.3) shows conclusively that the chloride due to ponding is concentrated in the top two layers (up to 0.75 in) and partially penetrated the third layer (up to 1.25 in). However the fourth layer remains unaffected as both curves, (e.g. ponded and control samples) for all curing durations, merge together at Layer # 3 which extends from a depth between 1.25" and 1.75". Generally, the location of reinforcement is below this area since all numbers falls below the threshold value of

corrosion which is 0.9 lb/yd³ (see section 2.8), equivalent to 5 ppm of chloride in solution.

Figure 4.3. Chloride Concentrations for Fort Worth Control Specimens

4.2 New Lubbock Site

For the New Lubbock site, concrete was mixed at a water cementitious ratio of 0.45 and 31% cement was replaced with class F fly ash. The cement: fly ash: fine aggregate: coarse aggregate ratio was 1.00:0.54:3.43:5.39 (volumetric). The coarse aggregate used was limestone. Table 4.2 shows the test results for New Lubbock. It can be seen from this table that the permeability of concrete is inversely proportional to the curing duration. As the chloride concentration decreases, permeability decreases and vice versa. i.e. the chloride concentration decreases from 40 ppm (part per million) for NLA (0 day curing) to 31 ppm for NLF (14 days curing) and this may be due to the fact that the concrete pore structure has been changed.

Table 4.2. Concentrations for New Lubbock Ponding Specimens in ppm

Non abraded - ponding (90days)- Type I/II cement - 31% FA (class F) - LM				
	0 - ¼"	¼" - ¾"	¾" - 1¼"	1¼" - 1¾"
NLA (0 days)	40	25.5	4.5	3
NLB (2 days)	35	24	4.5	3.5
NLC (4 days)	31	17	4.25	3
NLD (8 days)	31	16.2	3.75	3
NLE (10 days)	30.5	16	3.75	3
NLF (14 days)	31	12.75	3.25	2.25

The importance of curing on permeability of concrete is illustrated in Figures 4.4 and 4.5. Again, chloride was concentrated in the top two layers (up to 0.75 in) whereas the chloride content was negligible in the bottom two layers. This extreme decline in chloride concentration through the depth of the specimen may due to the resistance of the pore walls to the flow of liquid. As shown in Figure 4.4, the effect of curing on layer 2 and 3 is almost negligible. This can be explained as follows:

Concrete that is remote from the surface, that is at same depth, is hardly subjected to moisture movement, which affects only the outer zone, typically the first inch (Neville, 1996). In reinforced concrete, this depth represents all or most of the clear cover. Thus, concrete in the interior of a structural member generally is unaffected by significantly long curing durations. However, the properties of concrete in the outer zone are greatly influenced by curing and this is well illustrated in Figure 4.4, layer 0. In fact, it is this zone that is subject to weathering, carbonation and abrasion, and the permeability of the outer zone concrete has a paramount influence on the protection of steel reinforcement from corrosion (Neville, 1996).

Figure 4.4. Chloride Concentrations versus Curing Duration for New Lubbock

Figure 4.5. Chloride Concentrations versus Layer Number for New Lubbock

Another important conclusion shown in Figure 4.4 is that the effect of curing on the chloride concentration after 4 days of curing is extremely small. That is, for the New Lubbock mixture, while the chloride concentration decreases from 25.5 ppm (0 days curing, layer 1) to 17 ppm (4 days curing, layer 1), it decrease just by 2.5 ppm from 17 ppm (4 days curing, layer 1) to 12.75 ppm (14 days curing, layer 1). Thus no appreciable improvement (decrease in chloride concentration) is found beyond 4 days of wet mat curing.

Figure 4.5 shows that the location of steel reinforcement seems to be safe at 1.25 in below the top surface since all values of layer 3 falls below the threshold content of 1-2 lb/yd³ (see section 2.8).

The results of control samples for New Lubbock are shown in Figure 4.6. As expected, the chloride content is almost negligible in all layers at different curing regimes. In general, chloride may be incorporated in the concrete through the use of contaminated aggregate or admixtures containing chlorides. In addition, the Figure shows that the distribution of chloride in the control specimen within the hardened cement paste is not uniform.

Figure 4.6. Chloride Concentrations for New Lubbock Control Specimens

4.3 El Paso Site

For El Paso site, concrete was mixed at a water cementitious ratio of 0.42 and 50 percent of cement replaced with ground granulated blast furnace slag (GGBS). The cement: slag: fine aggregate: coarse aggregate ratio was 1.00:1.00:4.87:6.55 (volumetric). The coarse aggregate used was limestone. The chloride permeability of concrete from this site was tested after 180 days of soaking. Table 4.3 shows the results of the El Paso site tests.

It has been found that using pozzolanic materials (e.g. GGBS), the permeability of concrete reduces to a larger extent in the first few days. I.e., in this case, the concentration of chloride decreases from 79 ppm to 60.5 ppm (92.1% decrease over 2 days), while it decreases only by 1.5 ppm over the next 12 days of curing (7.8 % decrease).

Table 4.3. Concentrations for Fort El Paso Ponding Specimens in ppm.

Abraded - 180 days ponding - Type I/II cement - 50% slag - Limestone				
	0 - ¼"	¼" - ¾"	¾" - 1¼"	1¼" - 1¾"
EPA (0 days)	78	41	8.5	5.75
EPB (2 days)	60.5	29.5	7.5	5.25
EPC (4 days)	59	28.5	7.25	6.75
EPD (8 days)	58.75	28	9.5	7.25
EPE (10 days)	59	28	9	7
EPF (14 days)	59	29.5	6.75	6

From Figure 4.7 & 4.8, it can be seen that the chloride concentration for 0 cure day concrete is much higher than any other concrete for other curing durations. This observation is explained if one concludes that the resistivity of chloride ion penetration grew more in case of longer curing durations. Also, almost horizontal current plots were observed after 2 days of curing for all depths which lead us to conclude that 2 days of curing is sufficient for the El Paso mixture, i.e. a mixture with a 50% replacement of cement with GGBS. In general, since a blend of portland cement and GGBS contains more silica and less lime than portland cement alone, hydration of the blended cement produce more C-S-H and less lime than portland cement alone (Neville, 1996). The resulting microstructure of the hydrated cement paste is dense. However, the initial hydration of GGBS is very slow as it depends on the breakdown of the glass by the hydroxyl ions released during the hydration of the Portland cement (Neville, 1996). In a manner similar to blended cement containing pozzolanas, reaction of GGBS with calcium hydroxide takes place. The progressive release of alkalis by the GGBS, together with the formation of calcium hydroxide by Portland cement, results in a continuing reaction of GGBS over a long period. In our

case, 2 days appears to be sufficient. However, prolonged moist curing (28 days and beyond) of concrete containing GGBS is particularly important because the initial low rate of hydration results in a system of capillary pores which allows the loss of water under drying conditions. If this happens, hydration can not take place and thus no improvement in concrete permeability is achieved beyond that. The resistance of the pore walls leads to the concentration of chloride in the top layers and prevents the chloride ions from penetrate deeper in the concrete

Figure 4.9 shows the chloride concentration for all depths for all of the control samples for the El Paso site tests. It can be seen that all of the values falls between 5 and 6 ppm for all the samples which is more than expected. In fact this % of chloride may have entered the concrete during mixing, either in the water or through the cement ingredients.

To determine the safest place to locate the reinforcement, a comparison has been made between the ponded and the control specimens for each curing duration (Figure 4.8 versus Figure 4.9). It can be depicted that the top two layers are not the appropriate location since all numbers for all curing duration are much higher than the threshold content (see section. 2.8) which suggests that the steel reinforcement be placed below layer 3 which extends from 1.25" to 1.75". Chloride ion values in this area fall below the threshold value of corrosion which is 1-2 lb/yd³ (equivalent to 5-10 ppm of chloride in solution. See section. 2.8).

Figure 4.7. Chloride Concentrations versus Curing Duration for El Paso

Figure 4.8. Chloride Concentrations versus Layer Number for El Paso

Figure 4.9. Chloride Concentrations for El Paso Control Specimens

4.4 Atlanta Site

For the Atlanta site, concrete was mixed at water cementitious ratio of 0.46 and 21 percent of the required cement content was replaced with Fly Ash class F. The cement: fly ash: fine aggregate: coarse aggregate ratio was 1.00:0.34:2.92:4.77 (volumetric). The coarse aggregate used was siliceous gravel. The chloride permeability of concrete from this site was tested after 180 days of ponding. The results of Atlanta site are shown in Table 4.4. It can be seen that within each column, as the curing duration increases, the chloride concentration decreases, thus concrete becomes less permeable. Specifically, the chloride concentration decreases from 100 ppm (part per million) for AA (0 day curing) to 75.5 ppm for AF (14 days curing).

Table 4.4. Concentrations for Atlanta Ponding Specimens in ppm

Abraded - 180 days ponding - Type I cement 21% FA (class F) - Sil				
	0 - ¼"	¼" - ¾"	¾" - 1¼"	1¼" - 1¾"
AA (0 days)	100	40.5	8	3
AB (2 days)	92	31	4	2.5
AC (4 days)	79	23	4	2.5
AD (8 days)	78	22.5	3.5	3
AE (10 days)	78	21	3.5	2.5
AF (14 days)	75.5	21	3.5	2.5

Figures 4.10 & 4.11 show the relation between the chloride concentration and the curing duration. As shown, most of the reduction occurs during the first four days of curing, with no appreciable improvement in concrete permeability from longer curing durations.

The chloride concentration for the top quarter is extremely high (100 ppm or 20 lb/yd³). This could be due to two reasons. The first is that in the case of fly ash, the products of reaction closely resemble C-S-H produced by hydration of Portland cement. However this reaction does not start until sometime after mixing. So the structure of the concrete is not well established and porous since the fly ash has not yet reacted (Neville, 1996). With no curing, permeability is expected to be extremely high. The second reason is related to the use of siliceous gravel in the Atlanta mixture. It is well known that the use of gravel in a concrete mixture produces a relatively weak interface zone (Asbridge et al., 2001). This is due to the roughness and to the surface texture of the siliceous gravel. A more detailed explanation of the transition zone and the effect of siliceous gravel and limestone on it are presented in a later section.

Figure 4.10. Chloride Concentrations versus Curing Duration for Atlanta

Figure 4.11. Chloride Concentrations versus Layer Number for Atlanta

The results of the control samples for Atlanta Site are presented in Figure 4.12. As expected, chloride content is negligible in all layers for all curing durations except for the 0 day curing specimen.

Figure 4.12. Chloride concentrations for Atlanta Control Specimens

4.5 San Antonio Site

For the San Antonio site, concrete was mixed at a water cement ratio of 0.43 and 20 percent of the required cement content was replaced with Fly Ash class C. The cement: fly ash: fine aggregate: coarse aggregate ratio was 1.00:0.29:2.68:4.55 (volumetric). The coarse aggregate used was limestone. The chloride permeability of concrete from this site was tested after 180 days of ponding. Table 4.5 shows the results of San Antonio.

Unlike previous sites, the curing duration for this mixture shows no effect on the permeability of concrete for layer 0. I.e. the chloride concentration for SAA is 64 ppm for 0 days curing while the concentration for SAF is 62.5 ppm for 14 days

curing. However, curing appears to have played a significant role in reducing the chloride ingress in layer 1 of concrete, as shown in Figure 4.13. While 0 day curing concrete shows high permeability, the 2-, 4-, 8-, 10-, 14 cure days concrete show much lower permeability.

Table 4.5. Concentrations for San Antonio Ponding Specimens in ppm

Abraded - 180 days ponding Type I/II cement - 20% FA (class C) - LM				
	0 - ¼"	¼" - ¾"	¾" - 1 ¼"	1 ¼" - 1 ¾"
SAA (0 days)	64	36	6	3
SAB (2 days)	61	25.5	4.5	3
SAC (4 days)	64	25	4	3
SAD (8 days)	63	25.25	4	3
SAE (10 days)	63	25	4	3
SAF (14 days)	62.5	23	5	3

From the plot of Figure 4.13, increased curing duration shows no appreciable effect on permeability for all curing durations for layer 2 and 3. This is likely due to the fact that the interior of the concrete is hardly subjected to moisture movement and thus no positive effect of curing on the interior of concrete occurs. In contrast, curing is extremely critical for the upper layers where concrete is subjected to environmental condition such as evaporation and temperature. In this later case, curing provides the satisfactory moisture required to allow the continuation of hydration.

Figure 4.14 shows a relation between the chloride content and the layer number. As expected most of the chloride is located in the upper two layers, decreasing as the depth level increases. This phenomenon could be due to the pore walls which provide resistance to the flow of liquid. In general the degree of this

resistance depends on pore dimensions, with smaller pores presenting larger resistance than larger pores, as described in Chapter 2.

Figure 4.13. Chloride Concentrations versus Curing Duration for San Antonio

For the San Antonio site, it is found that the chloride content for layer 2 falls below the threshold chloride content as shown in the shaded area in Figure 4.14, so the steel reinforcement can be put at a depth of 1.25 in below the top surface of the concrete. Typically, in bridge deck, steel, reinforcing bars are specified with a clear cover of 2 in or more.

The complete test results for the control samples of San Antonio are shown in Figure 4.15. Similar to previous sites, the amount of chloride is extremely negligible for all layers and curing durations except for the 0 day curing specimen where the concentration reaches 7 ppm in solution. This is an extremely high number for a control specimen. This high number may be due to the fact that at 0 days curing, the

top surface prematurely dries. To maintain equilibrium in the sample, water carrying chloride ions likely moves toward the top surface and evaporates leaving the chloride ions at the top surface. For longer curing durations, the concrete top surface becomes partially saturated and no movement of water toward the top surface occurs. Thus, lower chloride concentrations are found.

Figure 4.14. Chloride Concentrations versus Layer Number for San Antonio

Figure 4.15. Chloride concentrations for San Antonio Control Specimens

4.6 Pharr Site

For the Pharr site, concrete was mixed at a water cementitious ratio of 0.41 and no mineral admixture was used. The cement: fly ash: fine aggregate: coarse aggregate ratio was 1.00:0.00:1.95:3.97 (volumetric). The coarse aggregate used was siliceous gravel. The chloride permeability of concrete from this site was tested after 180 days of ponding. Results from the Pharr site tests are shown in Table 4.6.

From the plot of chloride concentration versus curing duration, it is shown that the initial concentration at 0 day curing were higher for the Pharr mixture than for any other concrete mixture tested. I.e. the chloride concentration decreases from 41 ppm (part per million) for HAA (layer 1, 0 day curing) to 28 ppm for HAF (layer 1, 14 days curing). These results indicate that curing helps the hydration of cement particles. As the curing duration increases, more calcium silicate hydrate likely is

formed. Thus, voids in the concrete structure tend to become discontinuous and smaller and the permeability of the concrete is reduced.

Table 4.6. Concentrations for Pharr Ponding Specimens in ppm

Abraded - 180 days ponding - Type I cement No mineral admixture - Sil				
	0 - ¼"	¼" - ¾"	¾" 1 ¼"	1 ¼" - 1 ¾"
HAA (0 days)	90	41	6	3
HAB (2 days)	89	36	7	3
HAC (4 days)	80	35	6	3
HAD (8 days)	75	30	5.5	3
HAЕ (10 days)	76	29	6	2
HAF (14 days)	74	28	3	2

Figure 4.16 and 4.17 indicate the same set of relations between the chloride concentration and the curing duration for the four depths under study as presented previously for the other test mixtures. It is noticed is that chlorides are concentrated in the upper two layers (up to 0.75 in). In constraint, chloride content is negligible in the lower two layers-and almost negligible in the bottom layer. Pore wall resistance likely plays a principal role of the declination of chloride concentration through the depth of the specimen (Neville, 1996).

Interesting, the curing duration does not appear to play a significant role with respect to the permeability of the Pharr mixture concrete after 8 days. As shown in Figure 4.16, while chloride concentration decrease 93% $[(90-75)/(90-74)]$ when curing increases from zero to 8 days; it just decreases by 7% $[(75-74)/(90-74)]$ after that, which led us to conclude that 8 days of curing is enough for Pharr site.

The hatched area in Figure 4.17 represents the threshold content to initiate the corrosion in concrete structures exposed to chloride in service (see section.2.8). As seen from the plot, the top two layers are not the appropriate location since all numbers for all curing duration are much higher than the threshold content. However, based on the plot, steel placed below 1.25" from the top surface would be a location relatively immune to chloride attack.

Results from the control specimens for the Pharr site are presented in Figure 4.18. Similar to previous site results, the amount of chloride appears to be distributed randomly across the specimen. As shown in Figure 4.18 also, for the control specimens curing does not appear to have a significant effect on the concrete permeability as the chloride content ranges from 1 to 3 ppm for all curing durations.

Figure 4.16. Chloride Concentrations versus Curing Duration for Pharr

Figure 4.17. Chloride Concentrations versus Layer Number for Pharr

Figure 4.18. Chloride concentrations for Pharr Control Specimens

4.7 Houston Site

For the Houston site, concrete was mixed at water cementitious ratio of 0.46 and 27% of the required cement content was replaced with Fly Ash class C. The cement: fly ash: fine aggregate: coarse aggregate ratio was 1.00:0.43:3.04:5.33 (volumetric). The coarse aggregate used was limestone. The chloride permeability of concrete from this site was tested after 180 days of ponding. The results of Houston site are shown in Table 4.7 and Figure 4.19.

For this mixture, it is evident that the length of curing duration plays a major role in reducing the concrete permeability. It can be seen from Figure 4.19 that the permeability of 0 day cure concrete is significantly higher than the permeability of any other concrete subjected to other curing duration. In addition, it is shown that after 4 days of curing, no significant improvement in concrete permeability occurs. That is, while the chloride concentration decreases from 60 ppm (part per million) for HA (level 0, 0 day curing) to 45 ppm for HC (level 0, 4 days curing), it just decreases by 3.5 ppm after that. Similar to other test mixture, no effect of curing is seen in layer 2&3 on the permeability of concrete.

Table 4.7. Concentrations for Houston Ponding Specimens in ppm

Abraded 180 days ponding - Type I/II cement - 27% Fly ash (class C) - LM				
	0 - 1/4"	1/4" - 3/4"	3/4" - 1 1/4"	1 1/4" - 1 3/4"
HA (0 days)	60	31	5.5	2.5
HB (2 days)	54	27	4.5	2.25
HC (4 days)	45	23	4	2.5
HD (8 days)	44	22	4	2
HE (10 days)	43	21.5	4.25	1.5
HF (14 days)	41.5	21	3	1.5

Figure 4.19. Chloride Concentrations versus Curing Duration for Houston

The relation between the chloride content vs. the layer number with respect to the threshold level (see section 2.8) is shown in Figure 4.20. The huge decrease in chloride concentration shown is likely due to the resistance of the pore walls as they prevent further chloride to penetrate through the concrete. In general, small pores provide higher resistance than larger ones. The hatched area represents the threshold chloride content to initiate the corrosion (see section 2.8). It can be seen that all chloride concentrations for the top two layers are much higher than the values of the threshold, leading one to assume that the placement level of reinforcement should be greater than 1.25 inch from the top surface of the concrete.

Control specimen results for the Houston are shown in Figure 4.21. Similar to all previous sites, negligible amount of chlorides are found inherently in the concrete. These small amounts are likely due to a certain amount of chlorides found in the mixing water and/or aggregates.

Figure 4.20. Chloride Concentrations versus Layer Number for Houston

Figure 4.21. Chloride Concentrations for Houston Control Specimens

4.8 Discussion

Analyzing all the test results from the seven sites, it has been found that pozzolanic materials impose a great effect on the concrete permeability (Figure 4.1 versus Figure 4.4). Without any pozzolanic materials (in the Pharr site mixture), permeability values were found to be the highest (after 4 days of curing), which generally signifies a poor quality concrete.

Using 50% Granulated Blast furnace slag as a cement replacement material (in the El Paso site mixture, see Figure 4.7), it has been found that concrete permeability somewhat surprisingly is relatively high, compared to the other sites subjected to 180 days of ponding. Whereas, the use of fly ash (Fort Worth (Figure 5.1) versus New Lubbock (Figure 4.4) and San Antonio (Figure (4.13) versus Houston (Figure 4.19)), lower values of permeability were obtained. It has been also observed that as the initial wet mat curing period increases, fly ash concrete becomes considerably more impermeable than less cured fly ash concrete.

In general, the duration of wet mat curing has been found to be an important criterion in reducing the permeability of concrete. From the results of the seven sites, it has been found that 2 days of curing (for El Paso and San Antonio) 4 days of curing (New Lubbock, Atlanta and Houston) and 8 days of curing (Pharr and Fort Worth) provided the effective reduction in permeability of concrete.

Sites that show the highest permeability were Pharr and Atlanta. And this may be due to the fact that siliceous gravel and Type I cement were used for these two mixtures. Siliceous gravel, when used in concrete mixes, leads to a formation to a weak interface zone. A detailed on the effect of the siliceous gravel on the interface zone was presented in Chapter 2.

4.8.1 90- Day Ponding Comparison: Fort Worth versus New Lubbock

A comparison is made between Fort Worth and New Lubbock mixtures. A summary of this comparison is shown in Figures 4.22 through 4.25. Both sites were ponded for 90 days and contain 22% and 31% Fly Ash Class F respectively (Table 3.1). As shown, as the % of fly ash increases from 22% to 31%, concrete permeability decreases by almost 40% for layers 0 and 1 up to 4 days of curing. This likely is due to the fact that more fly ash has reacted with the calcium hydroxide produced during cement hydration to form additional calcium silicate hydrate, which fills large capillary voids and disrupts their continuity (Alhozaimy et al., 1996). The blocking of capillary voids reduces the permeability of concrete. Another reason of this reduction is that fly ash had possibly influenced the microcracking process at the aggregate paste interface by altering the volume and shrinkage characteristics of the paste, and also by changing the bleeding properties of cement paste and the microstructure at the interface zone (Neville, 1996).

This comparison also leads us to conclude that curing duration plays an important role in determining the permeability of concrete. After 8 days of curing, permeability of New Lubbock is slightly lower than that of Fort Worth (i.e. 22.5%, layer 0, Figure 4.22)

Figure 4.22. Comparison of Fort Worth versus New Lubbock (layer 0)

Figure 4.23. Comparison of Fort Worth versus New Lubbock (layer 1)

Figure 4.24. Comparison of Fort Worth versus New Lubbock (layer 2)

Figure 4.25. Comparison of Fort Worth versus New Lubbock (layer 3)

4.8.2 180- Day Ponding Comparison: San Antonio versus Houston

An additional direct comparison between Houston and San Antonio site is shown in Figure 4.26 through Figure 4.29. Both site of these test specimen have been ponded for 180 days and contain 27% and 20% Class C fly ash respectively. Similar to the New Lubbock on the previous two site mixtures, the permeability test results for the Houston mixture are lower than those of the San Antonio site for layer 0 and 1. Again, this likely is due to the fact that the higher percentage of fly ash in the Houston mixture results in a finer pore structure in both the cement paste matrix and along the paste aggregate interface in the concrete.

4.8.3 Discussion of Direct Comparisons

The duration of ponding and the nature of the top surface of the concrete (whether it is abraded or not) appears to play a major in determining the permeability of the concrete. It can be seen that the Houston and San Antonio mixtures have higher permeabilities than the Fort Worth and New Lubbock mixture. This could be due to two reasons. The first is that the Fort Worth and New Lubbock mixtures were ponded for only 90 days each whereas the Houston and San Antonio mixtures were ponded for 180 days. Thus more time was allowed for the chloride ions to diffuse through the concrete and overcome the resistance of the pore walls, and higher permeabilities for the San Antonio and Houston mixtures. The second reason for the higher Houston and San Antonio mixture permeabilities is that the top surface of Fort Worth and New Lubbock site specimens were not abraded, while the Houston and San Antonio site specimens were abraded. It is highly probable that this thin layer at the top surface of the concrete (when it is not abraded) plays the role of a protector for the concrete. In

fact, the non-abraded surface appears to provide a shielding effect for the top surface, avoiding the direct contact between the chloride ions in the solution and the interface zone at the top surface of the concrete.

Figure 4.26. Comparison of San Antonio versus Houston (layer 0)

Figure 4.27. Comparison of San Antonio versus Houston (layer 1)

Figure 4.28. Comparison of San Antonio versus Houston (layer 2)

Figure 4.29. Comparison of San Antonio versus Houston (layer 4)

4.8.4 180- Day Ponding Comparison: Pharr versus Atlanta

As discussed in Chapter 2, siliceous gravel is well known by its smooth surface texture to lead to the formation of a weak bond between the aggregate and the cement paste. This weaker bond leads to the formation of a weak interface zone, which increases the permeability of concrete by providing channels for the chloride ions to pass. This fact may be the primary reason why sites such as Pharr and Atlanta with siliceous gravel are showing higher permeability results than sites with fly ash such as Fort Worth, New Lubbock, San Antonio, Houston and El Paso.

A comparison made between the Pharr and Atlanta site mixtures is shown in Figures 4.30 & 4.31. Both sites have siliceous gravel and were ponded for 180 days. The main difference between them is that Pharr has no mineral admixtures added while the Atlanta site mixture had 21% of the cement replaced with Class F fly ash.

An interesting point was observed from Figure 4.31. Initially, the values permeability values are the same shown for Atlanta for 0 days of curing. However, as the length of curing duration increases, the permeability of the Pharr mixture becomes greater than that of the Atlanta mixture.

This phenomenon could be due to the following reason as discussed in Chapter 2. In the presence of fly ash, the chemical reaction becomes very slow. A consequence of this delay in the reaction of fly ash is the beneficial pattern of heat evolution. However, this delayed heat generation can lead to a higher permeability in the first couple of days in comparison with a mix that does not have fly ash, since most hydration products had not been formed in this short amount of time. This explains why we are getting higher permeability number for Atlanta in the first few days. At a later stage, with the presence of fly ash, more hydration products diffuse away and precipitate within the capillary pore system; this results in a reduction in the capillary porosity and consequently, a finer pore structure and lower permeability number (Asbridge et al., 2001). This could explain the lower permeability values for Atlanta after 2 days of curing (Figure 4.31).

Figure 4.30. Comparison of Pharr versus Atlanta (layer 0)

Figure 4.31. Comparison of Pharr versus Atlanta (layer 1)

CHAPTER 5
CORRELATION BETWEEN AASHTO T277
AND AASHTO T259/260

5.1 Discussion of the Comparison between AASHTO T277 and AASHTO T259/260

As discussed in Chapter 2, Whiting (1981) introduced the total integral chloride *I*. this values was calculated using the acid soluble chloride content at 0.2 in (5.1 mm) intervals from the surface of the ponded specimen to a depth of 1.6 in (41 mm). This allowed chloride penetration data from the 90 day Ponding test to be presented as a single value. However, in this research project, only the water soluble chloride was determined as the focus was to determine the free chloride ions responsible for the corrosion. Thus, the comparison was made between the Ponding test (water soluble chloride) and the Rapid Chloride Permeability Tests.

The results of the Rapid Chloride Permeability Tests for the seven sites are presented in Table 5.1. Using the permeability definitions presented and discussed in the FHWA report (Table 2.9), the mixtures were classified based upon their water soluble integral chloride and this is illustrated in Table 5.2. Figure 5.1, 5.2 and 5.3 show the classification of the seven sites for 4, 8 and 10 days of curing. To make comparison with Whiting's original research, all mixture with 14 days of curing are classified based on their water soluble integral chloride and their coulombs values as shown in Table 5.3. Three sites (Pharr, Atlanta and Fort Worth) exhibit identical water soluble integral chloride and coulomb classifications while the other four sites showed some discrepancies. For example, the El Paso and San Antonio mixtures exhibit moderate water soluble integral chloride while exhibiting very low coulomb

values. The New Lubbock mixture exhibits very low water soluble integral chloride values, while exhibiting low coulomb values. The Houston mixture exhibits low integral chloride values, while exhibiting very low coulomb values. As a result, it is concluded that the two tests are not always consistent in predicting the permeability levels defined in the original test development report of AASHTO T277 and this is due to the reasons mentioned in section 2.9.1. However, it is important to note that in the case of this study, almost all of the AASHTO T277 results ended in a lower classification than the ponded test results and this is for sites ponded for 90 and 180 days. Most discrepancies arose from the fact that the total integral chloride resulted in a higher classification.

Table 5.1. AASHTO T 277 Test Results (Afroze, 2002)

Curing Duration	El Paso	Fort Worth	San Antonio	New Lubbock	Houston	Atlanta	Pharr
0	3170.4	2411.3	1266.2	933.4	644.2	3572.5	3189.6
2	769.9	1624.5	1232.2	1024.8	716.6	3257.2	2364.6
4	617.0	1734.2	831.4	1222.0	784.0	2612.4	3088.8
8	567.4	1470.2	773.7	1176.3	820.6	2713.5	2502.5
10	595.9	1303.6	861.9	1057.0	750.9	3091.4	2999.1
14	400.5	1672.7	696.4	1126.5	969.9	2412.6	2607.7

Table 5.2. Classification of Sites Based on Water Soluble Integral Chloride

Curing Duration	El Paso	Fort Worth	San Antonio	New Lubbock	Houston	Atlanta	Pharr
0	1.18	1.04	0.96	0.66	0.86	1.27	1.19
2	0.91	0.95	0.79	0.62	0.76	1.04	1.13
4	0.90	0.79	0.80	0.50	0.65	0.86	1.05
8	0.93	0.61	0.80	0.48	0.63	0.85	0.95
10	0.92	0.58	0.79	0.48	0.61	0.83	0.94
14	0.90	0.54	0.78	0.42	0.58	0.81	0.88

Table 5.3. Classification of Sites Based on Water Soluble Integral Chloride and Coulombs values

	El Paso	Fort Worth	San Antonio	New Lubbock	Houston	Atlanta	Pharr
Water Soluble Integral Chloride	0.9	0.54	0.77	0.42	0.57	0.81	0.87
	Moderate	Low	Moderate	Very Low	Low	Moderate	Moderate
Coulombs value	400.5	1672	696	1126	969	2412	2607
	Very Low	Low	Very Low	Low	Very Low	Moderate	Moderate

Figure 5.1. Classifications of Concrete Mixtures for 4 Days of Curing

Figure 5.2. Classifications of Concrete Mixtures for 8 Days of Curing

Figure 5.3. Classification of Concrete Mixtures for 10 days of Curing

5.2 Linear Regression Analysis

The correlation between AASHTO T277 and AASHTO T259 for this experimental program is investigated further by performing a linear regression analysis on three sets of data. Three cases are considered: 1) the water soluble integral chloride values, *I* values, were coupled with their corresponding coulomb values for the sites subjected to 180 days of ponding for 14 days of curing, 2) the 180 day chloride results in % weight of concrete for the top ¼ in were coupled with their corresponding coulomb values for 14 days of curing. We should note here that El Paso results were not included in the correlation for both methods because of the inconsistent classification shown in Table 5.3 and 3) the water soluble integral chloride values, *I* values, were coupled with their corresponding coulomb values for all sites and for all curing durations. Results of these three regression results are shown in Figure 5.4, 5.5 and 5.6. As shown, the uppermost ¼ in resulted in an R^2 correlation coefficient of 0.625 (Figure 5.5) and exhibit a better correlation to the T277 results than the water soluble integral chloride which displayed an R^2 coefficient of 0.478 (Figure 5.4). In the original FHWA report, the authors used the total integral chloride and reported an R^2 correlation coefficient of 0.70 (Whiting, 1981). However, the correlation is slightly lower in this case and, possibly due to the fact that our mix includes mineral admixtures while all the mixes tested in Whiting's research do not contain mineral admixtures.

It can be seen from Figure 5.3 that the correlation of AASHTO T277 and AASHTO T260 for Atlanta, Fort Worth and San Antonio are relatively good ($R^2 = 0.73, 0.56$ and 0.45 respectively). However, bad correlation is shown for New Lubbock and Houston mixtures. This is due to the inconsistent results obtained for the

RCPT in these two sites. I.e., the 0 day coulombs for both sites are higher than the coulombs values for the 14 days curing concrete (Table 5.1) which can be translated that non cured concrete has better permeability than a well cured concrete and this is unrealistic. The inconsistent results for Houston mixture is due to the fact that two different concrete mixes with two different compressive strength, were used during the mixing. The New Lubbock discrepancy results were due to construction problem (bad compaction) in addition to environmental issues (very dry and windy conditions). The following remarks can be depicted from Figure 5.4 through 5.6.

- a) From the regression analysis of these three sets of data, it can be seen that a poor correlation exists in the 700-1300 coulombs range. This point seems to agree well with Whiting's original research (Figure 5.4).
- b) The original correlation between AASHTO T259 and T277 in the FHWA-81 report could not be used to accurately predict the permeability of concrete with a water cementitious ratio of 0.4 and 0.5 (Figure 5.5 & 5.6). However, the RCPT can serve as a general tool to compare the relative permeability of similar mixtures design with similar constituents and admixtures.

Figure 5.4. Water Soluble Chloride Ion Content by Integral – Correlation Data

Figure 5.5. Water Soluble Chloride Content by % Weight – Correlation Data

Figure 5.6. Correlation of AASHTO T277 & AASHTO T259/260 for all Curing Durations

CHAPATER 6

SUMMARY OF RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary of Results

To summarize the results of this research project, a comparison of permeability test results from all the seven sites is shown in Figure 6.1. It can be seen that these sites can be divided into three groups based on the chloride penetrability on the Ponding test: those with the lowest permeability (Fort Worth and New Lubbock), moderate permeability (El Paso, San Antonio and Houston) and those with high permeability (Atlanta and Pharr). The first group includes Fort Worth and New Lubbock. They had the lowest permeability results. This could be due to three reasons. First of all, Fort Worth and New Lubbock are the only sites that were ponded for only 90 days, while the others sites were ponded for 180 days. The second cause is that Fort Worth and New Lubbock were tested almost two years after casting, while the other five sites were tested after 8 months of casting. As a result, most hydration had occurred in Fort Worth and New Lubbock leading to the formation of more hydration products and thus a denser pore structure and low permeability. The third reason is that the top surface was not abraded, thus providing extra protection to the concrete from the chloride ion penetration.

The second group includes El Paso, San Antonio and Houston and. As shown in Figure 6.1, permeability test results from these three sites lies between the results of the first and third groups. This can be intuitively expected since they were ponded for

180 days and had limestone coarse aggregate that display better aggregate-cement paste bond.

The third group includes Pharr and Atlanta where siliceous gravel is used as coarse aggregate. Permeability test results were shown to be the highest. This may be due to the smooth surface texture of the siliceous gravel, which leads to the formation of a weak interface transition zone and to higher permeabilities.

Figure 6.1. Comparison of Permeability Results among The Seven Sites (layer 0).

Based on Ponding test results, the effect of curing on chloride permeability is negligible after 2 days of curing for El Paso and San Antonio mixtures, 4 days of curing for New Lubbock, Atlanta, Houston and 8 days of curing for Pharr and Fort Worth mixtures. These finding are summarized in Table 6.1.

Table 6.1. Summary of the Effect of Curing on Ponding and RCPT

Site	Compressive Strength (psi),	No significant effect of curing after	
		RCPT	Ponding
El Paso	6117- 10 days of curing	2 days	2 days
San Antonio	8156- 10 days of curing	4 days	2 days
New Lubbock	6835- 10 days of curing	No clear trend	4 days
Atlanta	6315- 10 days of curing	4 days	4 days
Houston	5762- 10 days of curing	No clear trend	4 days
Pharr	5250- 8 days of curing	No clear trend	8 days
Fort Worth	6464- 10 days of curing	8 days	8 days

6.2 Conclusions

A six-year research project was conducted to investigate the effects on concrete bridge deck durability from mixture design parameters, curing duration and the age at which loads are applied. This thesis focuses on the effects of wet mat curing duration and mix design parameters on chloride permeability of bridge deck concrete using AASHTO T259/260 ponding tests.

As discussed in Chapter 2, permeability of concrete plays a major role in determining the service life of the bridge deck. For reinforced concrete bridge decks, a key form of deterioration is steel corrosion due to chloride ingress into concrete. This leads to subsequent deterioration in strength, serviceability, aesthetics and overall durability of the bridge deck. Chloride ingress is primarily the result of de-icing chemicals used on bridge decks. This thesis discusses the mechanisms of corrosion and the factors that affect chloride ion permeability test methods (see Chapter 2).

To investigate the effect of curing on chloride ion permeability of concrete, the ponding (AASHTO T259) test was chosen. Seven concrete mix designs used in different districts within Texas were tested in laboratory facilities located at Texas

Tech University. At the beginning of the project, the AASHTO T260 test method was followed to determine the chloride content. However, several modifications were adopted. The first modification has the aim to reduce the time of testing. For this reason a modified form of the AASHTO T260 test was developed. In a later phase of this research, a third method was adopted in which direct concentration inside solution specimens was measured using a chloride ion selective electrode. The second modification involved a change in the pattern of drilling. Because of the setup of the drilling machine used and to refine the result at the top surface of the sample, Pattern B was adopted (Figure 3.8).

From the ponding results of the mixtures (Figure 4.1, Figure 4.4, Figure 4.7, Figure 4.10, Figure 4.13, Figure 4.16 and Figure 4.19) it was observed that chloride permeability decreased with increase curing duration. This is attributed to the fact that curing improves the hydration process resulting in dense pore structures that lead to a decrease in concrete permeability.

Experimental results show that 2 days of curing is beneficial to the reduction of chloride permeability results for El Paso and San Antonio mixtures. New Lubbock, Atlanta and Houston results shows that 4 days of curing is necessary to the reduction of chloride permeability except for Fort Worth and Pharr site where 8 days of curing can be recommended (see Table 6.1).

Results from El Paso site shows that concrete permeability is relatively high, compared to the other sites subjected to 180 days of ponding. And this leads to conclude that a different % of cement (has to be replaced by slag to receive satisfactory permeability results. In fact, TxDOT specification currently recommends 30 to 35% of cement replacement when slag is used in concrete mixture.

Fort Worth and New Lubbock site, which contained 22% and 31% class F fly ash respectively, showed a low permeability (low and very low total integral chloride) and this is due to the fact that the two sites were ponded for 90 days, the top surfaces were not abraded and the samples were tested nearly two years after they were cast.

The Pharr and Atlanta sites, which contained siliceous gravel as coarse aggregate, show the highest permeability among all the sites. This is maybe due to the development of a weak aggregate-cement interface transition zone in concrete mixes containing siliceous gravel. This conclusion is asserted by getting moderate water soluble integral chloride and coulombs values (Table 5.3).

It was also found that permeability of concrete decreases as percentage of fly ash (either class F or class C) increases from around 20% to around 30%, and this is well shown in the comparison made between Fort Worth and New Lubbock mixtures (Figure 4.22) and the comparison made between San Antonio and Houston mixtures (Figure 4.26).

From the seven sites under study, it was shown that steel reinforcement can be put at a distance of 1.25 in below the top surface as chloride concentration there falls below the threshold chloride content (see section 2.8). However, in reinforced concrete bridges where huge amounts of concrete is used, thermal cracking in addition to plastic shrinkage is expected and thus, a higher cover thickness is recommended.

A comparison has been made between the ponding test (AASHTO T259/260) and the rapid chloride permeability tests (AASHTO T277) based on the water soluble integral chloride content for all curing durations and on the % weight of concrete. From this comparison, it can be concluded that there exists a correlation between

AASHTO T259 and AASHTO T277 although the correlation is not perfect. And this discrepancy arose from the fact that the integral chloride content resulted in a higher classification (Table 5.3). It is also shown that that the correlation using the % weight of concrete ($R^2 = 0.62$) is higher than the correlation using the water soluble integral chloride ($R^2 = 0.48$).

From the comparison of results of these two tests, it was found that the classification of El Paso, New Lubbock, San Antonio and Houston mixtures based on these two tests showed different trends, while trends were the same for Pharr, Atlanta and Fort Worth mixes, which leads to the conclusion that RCPT may not represent the true long term chloride penetration. This conclusion is asserted by a recent study by Walsh et al. 1998 in which they show that only 1% of chloride ions pass through concrete during the RCPT. Also, the electrical conductivity from RCPT is mainly due to hydroxyl ion conductivity. Therefore, it may be better to consider an alternative test method, which can provide a direct measurement of the chloride ion concentration rather than an indirect process where concrete conductivity is used. This is the main reason why the ponding is always recommended, although it has practical limitations such as length of test.

6.3 Recommendations for Future Research

The focus of this research project is to determine the concrete permeability using the ponding test (AASHTO T259/260) and Minimum amount of effort is done to study the correlation between the ponding test and the RCPT. the test results carried out in this research project were from only seven mix design located across Texas. In future research, effort should be made to:

- Verify the results obtained in this research project by developing new concrete mixes with much less variables (type of cement, aggregate type, % voids air, % cementitious materials and materials sources).
- Determine the appropriate percentage of slag in concrete mixture to obtain low permeability result and to avoid the discrepancy in classification between the ponding test and the RCPT shown in this research.
- Determine a well verified correlation between AASHTO T259/260 and AASHTO T277 and this requires 50-80 design mixes with different cementitious materials (fly ash, silica fume and slag).

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