Effect of Chemical Admixtures on Conductivity of Mortars

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Abstract

Effect of Chemical Admixtures on Conductivity of Mortars

Xiaorong Wu

The effect of available commercial chemical admixtures namely ASTM Types A, C, D, E, F and AEAs on the electrical conductivity of mortars was investigated using modified electrical technique. Interpretation of the electrical conductivity (reciprocal of resistivity) of mortars was combined with results from calculating Na^+ and K^+ ion concentrations in the pore solution of mortars, measuring non-evaporable water content, gravimetric water porosity as well as conductivity of chemical admixtures. The water to cement ratios used were 0.485 and 0.35 with a sand to cement ratio fixed to 2.75. The dosage of chemical admixtures varied from low, medium and high in accordance with the indication by manufacturers.

The results showed that the different types of chemical admixtures exhibited different effects on the electrical conductivity of mortars. In the high water to cement ratio condition, the conductivity values of mortars with added Types A, D and F chemical admixtures were raised due to alteration of the pore solution chemistry, severe set retardation and increase in porosity. The high conductivity of mortars with Type C chemical admixtures was due to the introduction of a large amount of strong electrolyte $Ca(NO_2)_2$ to the pore solution which overwhelmed its accelerating hydration rate. On the contrary, the high degree of hydration of mortars with added Type E chemical admixtures offset their high alkali concentration in the pore solution. In the low water to cement ratio condition, the presence of types A, D, E and F chemical admixtures decreased the conductivity of mortars which was attributed to deflocculation, improving the microstructure and reducing porosity. Appropriate addition of AEAs reduced the conductivity of mortars in low and high water to cement ratios owing to the entrained micro-air bubbles in mortars separating the paths of conductivity.

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Lastly, I am gratefully to my husband, he taught me the value of hard work by his own example, which I will benefit a lot in my life.

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A	cross sectional area of specimen
A	oven-dry mass
AEAs	Air-entraining admixtures/agents
BI	bleeding index
C	saturated surface-dried mass
C3S	tricalcium silicate
C-S-H	calcium silicate hydrate
CH	calcium hydroxide
C_4ASH_{18}	monosulfoaluminate
$C_6AS_3H_{32}$	ettringite
c_i	ionic concentration
D	immersed apparent mass
e	unit of electron charge
f	moisture factor
G_i	conductivity coefficient of each ionic species
K	cell constant, 0.1/cm.
k	observed conductance of solution, *m***S.**
I	current (micro amps)
I_M	ionic strength (molar basis).
I_0	current (amperes) immediately after voltage is applied
I_t	current (amperes) at t min after voltage is applied.
I_S	segregation index
ITZ	interfacial transition zone
L	thickness of sample (cm)
Na2Oe	sodium equivalent (Na2O + 0.658 K2O) (%)
N_A	Avogadro's number
PEO	Polyethylene oxides
PNS	poly-b-naphthalene sulfonates
PPO	polypropylene oxide
Q	total charge passed (Coulombs)

SNF	sulfonated naphthalene formaldehyde condensate
u_i	mobility of ion
V	applied voltage (volts)
Vf	volume fraction of sand
w/c	water to cementing materials ratio
w105	mass after drying at 105°C (g)
w1050	mass after drying at 1050°C (g)
z_i	ionic valence
β_i	connectivity or structure factor of each constituting component
β	pore connectivity factor
σ_0	conductivity of pore solution
σ_0	conductivity of ionic solution
$(\sigma_0\,\varphi\,\beta)_{ref}$	concrete conductivity at the reference moisture condition.
σ_1	conductivity of the pore solution
σ_c	electrical conductivity of cement composite
σ_i	conductivity of each component in composite
σ_m	electrical conductivity of mortar
σ_P	electrical conductivity of cement paste
σ_t	total composite conductivity
Ψ_i	area of fraction in the cross section of each component
Ψ_p	area fraction of pores
Ψ_s	area fraction of solids
φ_i	volume fraction of each constituting component
φ	volume of porosity
λ_i	equivalent conductivity of each ionic species
λ^0_i	equivalent conductivity of an ionic species at infinite dilution
ρ	specific electrical conductivity of aqueous solution $m^{-1}\Omega^{-1}$
ρ_{water}	specific electrical conductivity of water, which is 10^{-5} $m^{-1}\Omega^{-1}$
λ_i	equivalent electrical conductivity of ion I, m^2 equiv.$^{-1}\Omega^{-1}$
$\lambda_{i\,0}$	equivalent electrical conductivity of ion I at infinite concentration, (m^2 equiv.$^{-1}\Omega^{-1}$)

$\sigma\Lambda$	standard deviation of the conductivity values
$\sigma\Lambda_{av}$	average conductivity.

1.0 Introduction

Concrete is the most commonly used structural material. Concrete hydration is a complex process, it includes several phases (solid, liquid and gel) developing at the same time, and interacting with each other during the hydration process. Researchers have given a lot of effort to try to fully understand the cementitious system, from the microscopic level to the macro scale. For the macro scale, standard methods including strength and slump are used to judge properties of concrete; and for the microscopic level, sophisticated techniques, such as scanning electron microscopy (SEM), X-ray diffraction, and mercury intrusion porosimetry are used to study and analyze the microstructure of concrete (McCarter, 2002). Recently, the application of electrical techniques to monitor concrete conductivity has been receiving more attention. The conductivity of concrete can assist in assessing the performance of concrete in its service life, due to it providing useful information related to microstructure and pore solution chemistry composition (Chrisp et al, 2002; and Gu et al, 1995). Regarding concrete durability, McCarter (2002) addressed "it is the 'holy grail' of the engineer to develop a parameter which will qualify durability, and perhaps, electrical methods have a role to play in this respect." The conductivity of concrete is related to concrete permeability which is an important indicator of durability. Permeability is directly related to resistance to freeze-thaw, chemical attack, alkali-aggregate reaction and ability to ionic diffusion (Liu. et al, 2000). The advantage of electrical techniques is that they measure conductivity of pastes, mortars or concrete with time without disturbing the structure (Nokken, 2004).

Many electrical techniques have been standardized or developed in the last two decades, the aims of these techniques are trying to reveal the microstructural development of concrete under a specific condition, or to predict the durability of concrete in its service life. These methods include the rapid chloride permeability test (RCPT) which is standardized as ASTM C1202; the rapid migration test (RMT) standardized as AASHTO TP 64-03; AC impedance spectroscopy used to detect microstructure development of samples (Coverdale et al, 1994; Gu et al, 1995); time domain reflectometry (TDR) to control quality of concrete on site (Yu et al., 2004), and electrokinetic probes to assess segregation and bleeding of concrete mixed with chemical admixtures (Jolicouer et al., 2000). Among these techniques, the most popular and widespread is the rapid chloride permeability test (RCPT), which measures the amount of electrical current caused by migration of ions passing through the specimen. It was developed by Whiting in 1981, and was standardized as the AASHTO Standard T277 in 1983 and then as the ASTM Standard C1202 in 1991.

The rapid chloride permeability test has been subject to considerable debate by many scientists since it has been in use. The test measures the electrical conduction for all ionic migration in pore solution instead of only chloride ion due to the high voltage potential (60 V / DC) applied (Liu et al, 2000). Furthermore, the high applied voltage may cause a temperature increase during the test, resulting in higher measured coulomb values, the Joule effect (Julio-Betancourt and Hooton, 2004). McGrath and Hooton (1999) suggested using the coulombs of the first 30 min to estimate the total coulombs of 6 hours. Lane

(2005) modified this standard method by conducting the test for 1 minute to 10 minutes, and using conductivity as indicator to express chloride ion permeability in concrete. He found the good relationship between conductivity and total Coulombs, and the conductivity measurement was more precise than the RCPT. Some authors proposed to use a lower voltage instead (McGrath and Hooton, 1999; Zhang et al, 1994).

Because the rapid chloride permeability test measures electrical migration of all ions carrying charge in the pore solution, the concentration of ionic species influences the test value. Mineral and chemical admixtures change the concentration of ions in the pore solution. When using the rapid chloride permeability test to measure the specimens mixed with these materials, the results do not correlate to the real chloride ion penetrability of these specimens (Liu and Beaudoin, 2000; Shi, 2003). Liu and Beaudoin (2000) suggested setting two criteria to assess the ionic permeability of concrete for any permeability testing method based on the measurement of concrete electrical properties: one for plain concrete and another for concrete containing mineral additives.

In this study, a modified method is used to investigate the electrical conductivity of mortars. The method overcomes the above shortcomings, and is expected to be applicable for prequalification and quality control.

Interestingly, there are numerous papers to criticize the scientific accuracy of the rapid chloride permeability test for the concrete mixed with mineral and chemical admixtures. However, seldom can one find quantitative measurement or comparison the effects of chemical admixtures on ion permeability (diffusion) of concrete. Xu et al (2000) investigate the effects of PNS based superplasticizers on the interfacial transition zone (ITZ) through AC impedance; however, they did not give the quantitative measurement of the pore chemistry in superplasticized concrete/mortars. Therefore, there is a lot of work to do in order to either set the new criteria or for the accurate assessment of permeability of concrete mixed with admixtures.

Concrete chemical admixtures have shown noticeable growth worldwide, and the role of chemical admixtures in concrete has therefore become increasingly important each year. The use of chemical admixtures contributes in a remarkable way to the production of high performance concrete. "They enable the design of concrete with specified characteristics, from self-leveling flowing concrete in common building construction up to the enormous challenges in regards to high strength, high durability and high performance concrete for outstanding and breathtaking civil engineering projects." (Kern et al, 1994). Hanehara and Yamada (1999) concluded that "the contribution of the development and improvement of organic admixtures to advanced ultra-high-strength concrete is remarkably larger than that of cement".

Generally, chemical admixtures are classified based on functions such as air entraining admixtures/agents (AEA), accelerating admixtures, water reducing (WR) and set-controlling admixtures, and miscellaneous other admixtures (e.g. gas-forming, expansion-producing, permeability-reducing; corrosion-inhibiting; decreasing alkali-aggregate reaction, etc.).

Each group is on-going innovation, for instance, the development of water reducers from simple organic chemicals to polymer with graft branches. These innovations brought significant improvements for performance of concrete. However, understanding and quantifying effects of chemical admixtures in concrete are the complex task (Flatt et al., 2001). Many chemical admixtures alter the hydration of cement paste through mechanisms that are not generally understood (Juenger et al., 2002). Modern cementitious materials rely on admixtures, in most cases organic compounds to improve their performance. Questions remain to be answered, such as: how do they work and perturb the cement hydration process and what effects of their ionic concentration have on the pore solution of concrete? Jolicouer et al (1998) pointed out "to understand the consequences of admixture-cement interaction, and to optimize the functional properties of admixtures, appropriate descriptions of their mode of action must be developed." Therefore, fully understanding mechanisms of the interactions of cement and admixtures and effects of admixtures on concrete service life is necessary for material engineers.

The main objective of this study is to investigate the effects of chemical admixtures on electrical conductivity, hydration and microstructure of mortars, and their inter-relationship.

Specific objectives are:

- To quantify the effect of chemical admixtures on conductivity of mortars:
    - Investigate several types of commercially available chemical admixtures
    - Vary dosage rates and water to cement ratio of mortars
- To determine the roles of cement hydration, porosity, admixture conductivity and

composition on the changes in bulk conductivity of mortars.

2.0 Literature review

2.1 Cement science

The raw materials of cement—lime, silica, alumina and iron oxide interact with one another in the kiln around 1200-1400°C to form clinker. The composition of the clinker is usually expressed by its oxide contents and by the proportions of four main compounds (also called Bouge compounds), $3CaOSiO_2$ (C_3S), $2CaOSiO_2$ (C_2S), $2CaOAl_2O_3$ (C_3A) and $4CaOAl_2O_3Fe_2O_3$ (C_4AF). The clinker mixed along with a certain proportion of gypsum to control set is milled together to certain fineness to form cement. ASTM C150 defines the chemical compositions and physical properties of different types of cement.

When cement mixes with water, a chemical reaction results in hardened paste, this reaction process is called hydration. Cement hydration is very complicated physical-chemical reaction. The main hydration products are calcium silica gel (C-S-H gel), calcium hydroxide (CH), monosulfoaluminate (C_4ASH_{18}), and ettringite ($C_6AS_3H_{32}$). In the mature cement matrix, C-S-H gel occupies 50-60% of paste volume, and calcium hydroxide makes up 20-25% of the solid, 10-15% for monosulfoaluminate (Mindess et al, 1981; Lea. 1998). The rate of hydration for the main four phases during the first few days is in the order as $C_3A > C_3S > C_4AF > C_2S$ (Ramachandran et al, 1998). When added to cement chemical admixtures, most of admixtures affect the hydration of C_3A and C_3S.

2.1.1 Hydration development

When cement mixes with water, the hydration process begins. Typically, hydration process is divided into 5 stages by the evolution of the reaction with time (Lea, 1998).

These 5 stages are expressed as: I-initial hydration process (0-15 min); II-induction period (15min-4hr); III-acceleration and setting (4-8 hr); IV- deceleration and hardening (8-24 hr); V-curing (1-28 days) (Lea, 1998; Mindess et al, 1981; Taylor, 1990). First solubilization of compounds produces ionic species (e.g. Na^+, K^+, Ca^{2+}, $SO^{2-}{}_4$, OH^- and Al^{3+}); then the layer around cement particle becomes thicker and thicker, leading to the induction period. When the Ca^{2+} concentration becomes high enough to break up the thick layer, a large number of hydration products form and the reaction enters to acceleration and setting period. Afterward, the hydration process slows down.

As hydration proceeds, the hydration products, such as C-S-H gel and calcium hydroxide crystals, fill in the capillary pores resulting in the reduction of capillary pores and the increase of gel pores (Spiratos et al 2006). Cement paste becomes denser and total porosity decreases. Hydration also decreases the connectivity of the capillary pore system. As cement hydration processes, a strongly ionic solution is created in the capillary pore system.

There are many methods to determine cement hydration, such as conduction calorimetry, thermogravimetric techniques and continuous X-ray diffraction scanning of wet pastes undergoing hydration (Spiratos et al 2006).

2.1.2 Pore structure

Cement-based materials are porous. In the cement paste matrix, there are two main types of pores, gel pores and capillary pores. The C-S-H gel is main component of cement paste, and governs the microstructure of cement paste. The C-S-H gel is an amorphous gel, which contains 28% porosity (Aligizaki, 2006). The diameter of pores in the C-S-H gel is approximately several nanometers, called gel pores. Because of their small size, which is only one order of magnitude larger than that of the water molecules, the gel pores have very low permeability. (Aligizaki, 2006; Spiratos et al, 2006)

Capillary pores are formed by the initially water-filled spaces existing in the hardened cement paste as interconnected channels or interconnected cavities (Spiratos et al 2006). Capillary pores are highly irregular in shape and have wide range of sizes, from 2 nm to 10 μm. Capillary pores mainly have effects on transport properties of cement paste, but have little contribution to the hydration rate, which is opposed to the gel pores (Aligizaki, 2006).

Mehta (1986) and Mindess et al (2002) gave the distinct classification of gel pores and capillary pores. In Mehta's classification, the size of gel pores and capillary pores is 1nm to 3 nm and 10nm to 5 μm, respectively. Mindess et al (2002) defined the size of gel pores as 0.5nm to 10nm, and the size of capillary pores as 2.5 nm to 10 μm. There is a section between 2.5 nm to 10 nm which is overlapped by gel pores and capillary pores. Mindess et al (2002) indicated that the size of 10nm to 10μm affect permeability of paste. Table 2.1 lists the definition the size of gel pores and capillary pores by different authors. The discontinuous capillary pores significantly reduce concrete permeability. The total porosity, pore size distribution, pore shape and pore connectivity determine the diffusivity and permeability of concrete.

Table 2.1 Pore diameter of gel and capillary pores

Reference	Gel pore diameter (nm)	Capillary pore diameter (nm)
(Powers and Brownyard, 1948) (in Young, 1988)	<10	10 – 1000
(Verbeck, 1966)	1 - 8	8 – 13,000
(Mindess and Young, 1981)	2.5 – 10 (gel) 0.5 – 2.5 (micropores)	10 – 50
(Mehta and Monteiro, 1993)	1 – 3	10 – 1000
(Hearn et al., 1994)	1.5 – 2	-

Techniques used to characterize the pore structure include mercury intrusion porosimetry (MIP), gas adsorption, nuclear magnetic resonance and small-angle scattering. Mercury intrusion porosimetry has proven over several decades to be a useful technique in characterizing cement-based porous materials. Diamond (2000) argued that mercury intrusion porosimetry is an inappropriate method to measure pore size distribution in cement paste, but the threshold diameters and intrudable pore space information are still valid.

2.1.3 Interfacial transition zone

The aggregate - cement paste interfacial transition zone (ITZ) is known to be the weakest region in concrete, influencing both mechanical properties and durability performance (Tasong, 1998). The ITZ refers to the cement paste around the edge of aggregate particles, which is different from the matrix in other locations, in this region large pores and preferentially oriented calcium hydroxide crystals exist. The ITZ results from the water to cement (w/c) ratio gradient developed at the near-aggregate surface region (Tasong, 1998). The ITZ thickness is usually reported as 30 and 50 μm, and the maximum porosity of ITZ is about three times higher than the matrix paste (Xu et al, 2000). The results of migration testing showed that the approximate chloride migration coefficient of ITZ is 2.83 times greater than that of the matrix for the ITZ thickness is to be 20 μm (Yang, et al 2002). Shah (2000) and Delagrave et al (1997) pointed out that the ITZ and percolation effects increase permeability of concrete.

2.2 Chemical admixtures

2.2.1 Concrete admixtures

“An admixture can be defined as a material added in small quantities, during the mixing process, to modify the properties of concrete, mortar or grout in the fresh and/or hardened state” (Buekett, 1998). This definition usually refers to chemical admixtures. The supplementary cementitious materials (SCM) including fly ash, granulated blast furnace slag and silica fume are often called mineral admixtures and are used in greater quantity. Additive is a term to describe materials incorporated into cement during grinding of clinkers (Buekett, 1998).

The benefits from the use of admixtures are becoming increasingly obvious. Concrete is no longer just a mixture of cement, sand and stone, it becomes a mixture of admixtures (Mailvaganam, 1998). Mailvaganam (1998) pointed out, in the guest editorial of a special issue of Cement & Concrete Composites devoted to cement chemical admixtures, that “admixtures chemically alter the rate of cement hydration, and /or the nature of hydration products, they can be used to control the type of products formed so that many properties can be designed into concrete."

2.2.2 Admixture categories

ASTM has issued a classification scheme for chemical admixtures, which provides practical definitions of various admixtures in terms of their functional properties and performances (Ramachandran et al, 1984). In ASTM C494M-05 and ASTM C260-94, the classification of chemical admixtures is

Type A	Water reducers, normal setting,
Type B	Retarding admixtures,
Type C	Accelerating admixtures (including corrosion inhibitors),
Type D	Water-reducing and retarding admixtures,
Type E	Water-reducing and accelerating admixtures,
Type F	Water-reducing, high range admixtures (HRWR),
Type G	Water-reducing, high range, and retarding admixtures.

Air-entraining admixtures/agents (AEAs).

The American Concrete Institute also provides classification of chemical admixtures, including air entraining admixtures (AEA), accelerating admixtures, water reducing (WR) and set-controlling admixtures, admixtures for flowing concretes and miscellaneous other admixtures (e.g. gas-forming, expansion-producing, permeability-reducing; corrosion-inhibiting; reducing alkali-aggregate reaction, etc.) (Jolicoeur et al, 1998).

ASTM also gives the specifications ASTM C1017M-03 for use of superplasticizers to make flowing (high-slump) concrete:

Type I Plasticizing, and

Type II Plasticizing and retarding

The water reduction of type I is 5% or more, and type II is 12% or more. Type I is corresponding to ASTM C494M-05 Type A, type II equals to ASTM C494M-05 Type F (Jolicoeur et al, 1998).

There is another functional sub-classification of water reducers, like "first", "second", and "third" generation referring to lignosulfonate, naphthalene sulfate formaldehyde condensate (NSFC) and melamine sulfonate formaldehyde condensate (MSFC), and polycarboxylate based superplasticizers (e.g., PCA, PCE, CAE) (Spiratos et al, 2006 ; Coppola, 2003). This classification is not very scientific, as it reflects neither the chemical properties of the admixtures, nor their performance in field application (Jolicoeur et al, 1998; Spiratos et al, 2006).

2.2.3 Chemical composition and characterization

Water reducer

"Water reducers are the group of products which possess as their primary function the ability to produce concrete of a given workability, as measured by slump, at a lower water cement ratio than that of a control concrete containing no admixture"(Rixom et al, 1986). Water reducers can work in practice in three ways (Rixom et al, 1986):

"1. By the addition of the admixture, concrete possesses the same workability as that of the control concrete, with increased compressive strengths in comparison to the control concrete at all ages. (reducing W/C).

2. The added admixture as a part of mixing water to a concrete without changing mix proportions, a concrete possess similar strengths, but has a greater workability than the control concrete. (Increasing workability).
3. By adding admixture, concrete obtains similar workability and strength development with that of a control concrete, but contains lower cement than a control concrete without adversely effects on durability or properties." (Lowing cement content and cost).

There are numerous chemicals can be used as water reducers. Water reducers can be classified by reduction of water, as normal water reducers, mid-range water reducers (plasticizers) and high range water reducers (superplasticizers). The main difference between plasticizers and superplasticizers can be expressed as either slump increase or water reduction. The slump increase at a given mix composition is about 150-200 mm for the superplasticizers and about 50-70 mm for the plasticizers. On the other hand, the superplasticizers are capable of reducing water requirements at a given slump by about 20-30%, whereas plasticizers can reduce water contents by only about 5-12% (Collepardi, 1998).

Water reducers also can be sorted by chemical composition. Rixom et al (1986) and Ramachandran (1984) sorted water reducers and retarders in the one group. The following classification combines ideas of these two authors.

a. <u>hydroxycarboxylic acids</u>

This group of chemicals possesses both hydroxyl and carboxyl groups in their molecules.

The typical water reducers of this group are citric acid and tartaric acid. Usually, the commercial products are the sodium or calcium salts, like sodium gluconate and glucoheptonate. Their water retardation is about 5-10%. They have considerable retarding effect on cement setting (Rixom et al, 1986) and can promote bleeding. Some literature lists them in the group of retarders.

b. hydroxylated polymers

The hydroxylated polymers are derived from naturally occurring polysaccharides, such as cornstarch by partial hydrolysis. They are stable under the alkaline conditions of a cement system, and behave as efficient water-reducing agents (Rixom et al, 1986). The water retardation is 3-6% (CIV 1299, 2006).

c. lignosulphonates

Lignosulphonates are by-products of paper-making-pulp subsequently neutralizing, precipitating and fermenting (Rixom et al, 1986). Its molecular structure is shown in Figure 2.1. Commercial lignosulphonates are usually calcium or sodium based with sugar content of 1-30 % (Rixom et al, 1986). Many lignosulphonates are of less purity; they can entrain a small proportion of air into the concrete, which is undesirable for concrete quality. The sugars present in the lignosulphonates do have a retarding influence on the setting of the cement. Therefore, lignosulphonates can be added with a small quality of an air-detraining agent to offset entrapped air, and addition of accelerating agents to compensate for the retarding influence (Rixom et al, 1986; Ramachandran, 1984). Lignosulphonates can be modified (MLS) as de-sugarized product with reduced retarding effects, and used as superplasticizers (Collepardi, 1998). They possess 10-15 % water reduction (CIV 1299). They are called the first generation superplasticizers.

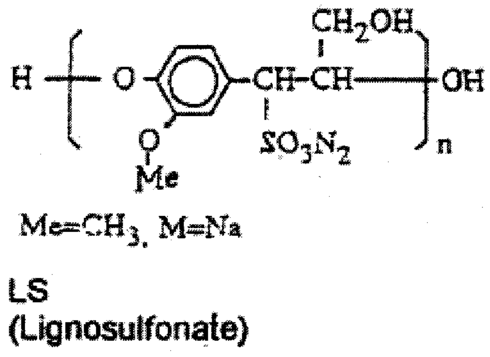


Figure 2.1 Molecular structure of lignosulphonates (Collepardi, 1998)

d. Salts of naphthalene formaldehyde sulphonic acids

The first and most widely accepted compounds of this group are the poly-b-naphthalene sulfonates (PNS), also named as sulfonated naphthalene formaldehyde condensate (SNF) (Rixom et al, 1986). The molecular structure is illustrated in Figure 2.2. "It is produced from naphthalene by sulphur trioxide sulphonation, and then reaction with formaldehyde leads to polymerization. The sulphonic acid is normally neutralized with sodium hydroxide" (Rixom et al, 1986). PNS is used as a superplasticizer, or high range water reducer. The low polymerization commercially PNS can lead to air entrapment in the concrete due to its tendency to reduce the surface tension of the aqueous phase. The higher molecular weights are more effective and they don't affect the surface tension, and don't cause air entrapment (Spiratos et al, 2006).

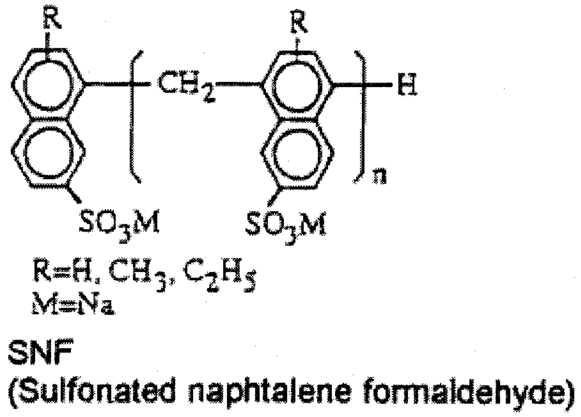


Figure 2.2 Molecular structure of sulfonated naphthalene formaldehyde (Collepardi, 1998)

e. <u>Salts of melamine formaldehyde sulphonates</u>

It is another broadly used superplastizer, also called as polymelamine sulfonates (PMS). Its molecular structure is illustrated in Figure 2.3.

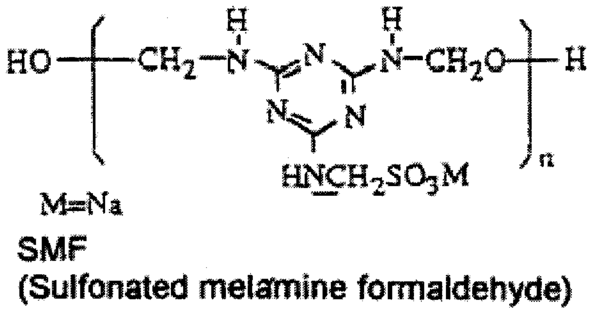


Figure 2.3 Molecular structure of sulfonated melamine formaldehyde (Collepardi, 1998)

f. <u>carboxylated polymers</u>

Polyacrylate and polycarboxylate belong to this group, they are all bearing carboxylic acid group (COOH) and are very high effective dispersants (Spiratos et al, 2006). They emerged in the early 80's, and are a fairly new superplasticizer. Numerous families of such polymers have been proposed, most of them share a common polyacrylate, or polymethacrylate main chain, with a wide variety of side chains (Spiratos et al, 2006). Polyethylene oxides (PEO), polypropylene oxide (PPO), or mixed PEO-PPO (EO-PO) are present as chains (Collepardi, 1998). Because of their large variety of monomer compositions and structures which can take part in addition polymerization reaction, this group of polymers offer a great range of possibilities to form functionality superplasticizers. (Spiratos et al, 2006). The molecular structure of polycarboxylate ester is showed in Figure 2.4.

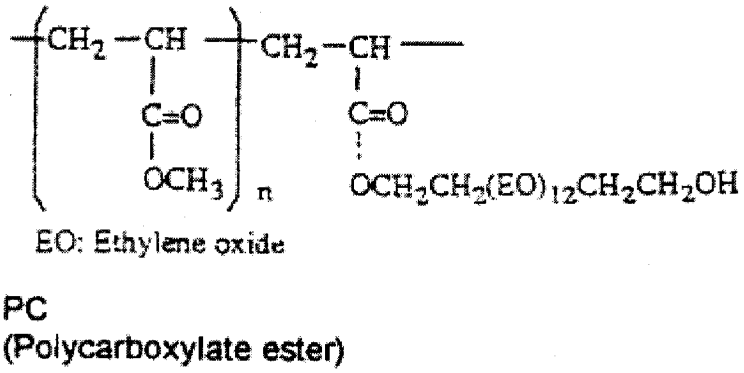


Figure 2.4 Molecular structure of polycarboxylate ester (Collepardi, 1998)

Accelerators

Many substances are known to act as accelerators for concrete. They include calcium chloride, calcium formate, calcium nitrate, calcium nitrite, triethanolamine (TEA) earth metal carbonate salts, etc (Rixom et al, 1986). Among these materials, calcium chloride was most popularly used. Because the chloride ion can cause corrosion of reinforced concrete, the use of calcium chloride has been restricted. The chloride free accelerators and organic chemicals have emerged in the market.

Corrosion inhibitors

Protection of reinforced concrete from attack by chloride ions in the service life has gained remarkable consideration. The development of corrosion inhibitors serves that purpose. Calcium nitrite, calcium nitrate and cathodic inhibitors, like aminoalcohols are widely used in the real world (Rixom et al, 1986). In general, the effects of an inhibitor are "(1) to raise the level of chloride ion necessary to initiate corrosion and (2) to decrease the rate of corrosion even if it starts" (Gaidis et al, 2004).

Air entraining admixtures/agents

Air entraining agents belong to a class of chemicals called surfactants (Rixom et al, 1986). Usually, these kind of chemicals have two different portions arranged at opposite ends of its molecule, one is polar, and another is non-polar. The polar head is hydrophilic, and the non-polar tail is excluded from water. At the air-water interface, this special molecular structure makes this chemical have strong capacity of adsorption at the interface and surface activity (Rixom et al, 1986).

2.2.4 Interactions of cement and chemical admixtures

Water reducers

The key interpretation that water reducers can improve workability of concrete or decrease water cement ratio without adversely affecting workability is adsorption and dispersion (Rixom et al, 1986). Figure 2.5 shows the dispersion of cement particles by a water reducer. Water reducers, especially superplasticizers, are viewed as powerful dispersants, which can break-up the agglomerates of cement particles, and liberate the water trapped in these agglomerates. Numerous papers discuss this phenomenon. The water reducer molecules are adsorbed onto the surface of the hydrating cement particles;

they convey a negative electrical charge to these surfaces. The surface potential generates an electrostatic/ steric repulsion between particles, and promotes deflocculation and dispersion, which improves the cement particle contacting with water and hydration (Spiratos et al, 2006). Jolicoeur et al (1998) concluded 7 types of physico-chemical effects which may occur upon interaction of chemical admixtures with cement particles at the interface (interphase) with the pore solution. These authors indicated that admixtures bearing charged groups (e.g. SO_3^-, COO^-) could interact with the particle surface by electrostatic forces. "Polar functional groups (e.g. OH^-) of chemicals, like sugars can also interact strongly with the highly polar hydrated phases, through electrostatic forces and hydrogen-bonding interactions" (Jolicoeur et al, 1998). Recently, many researchers found

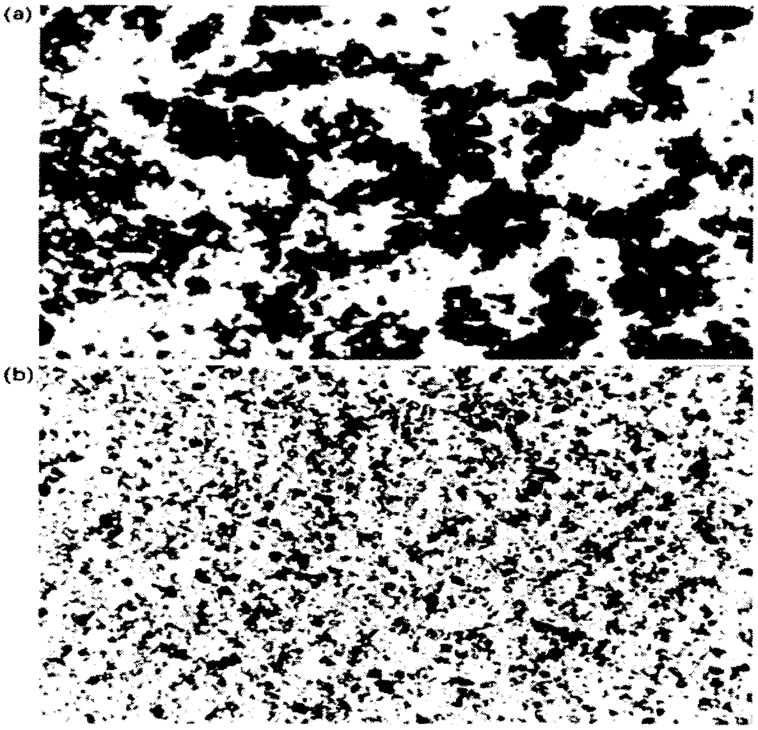


Figure 2.5 Dispersion of cement particles by a water-reducing admixture.
(a). Before addition (b). After addition (Ramachandran, 1984)

there are two types of repulsion for superplasticiziers. For PNS and PMS, eletrostatic effects are most important; for polycarboxylate superplasticizers, the steric repulsion between polymer layers is dominant (Blask et al, 2003). Jolicoeur et al (1998) elucidated for high molecular weight polymers, physical interference (steric) will lead to additional short-range repulsive forces. It can be said that the steric effects play an important role in improving workability, since low molecular weight dispersants usually exhibit weak water reduction and low paste fluidification properties (Spiratos et al, 2006). In general, the relative importance of electrostatic and steric effects in particle-particle repulsion will depend on both the chemical nature of the polymer (composition, structure) and its molecular weight (Jolicoeur et al; 1998). Bonen and Sarkar (1995) found by experiments that the adsorption capacity of the cement particles of PNS superplasticer is mainly determined by PNS molecular weight, cement fineness, and C_3A content.

Retarders

Typical setting retarders include lignosulfonate, gluconic acid, and glucose. They retard the setting time and early hydration by delaying hydration of C_3A as well as other cement compounds (Ramachandran, 1984). Although C_3A is present only as a small percentage in cement, it affects setting and early hydration of cement significantly. The main reactions between these organic chemicals and cement are adsorption and precipitation (Ramachandran, 1984). They react with cement system by binding calcium ions to prevent nuclei forming, or strengthening the surface barriers (CIV 1229, 2006). Suzuki and Nishi (1959) proposed that the precipitation of insoluble hydration products which produced by organic retarders reacting with calcium ions was responsible for retardation of C_3A hydration rate as well as that of other compounds by forming a barrier to access by water.

Accelerators

$CaCl_2$ was the most widely used accelerator. There is a lot of literature about the reaction mechanism of cement and $CaCl_2$. They are studied from appearance of a hydration heat peak, microstructure, hydrates and hydrate surface area (Ramachandran, 1984; Rixom et al, 1986). The simple conclusion of the published work is that common accelerators, such as calcium chloride, calcium nitrite and calcium formate accelerate setting time of cement by directly providing sufficient calcium ions to reach saturation earlier and breaking down barriers earlier (CIV 1229, 2006). Amine based accelerator (e.g. triethanolamine (TEA)) can interfere with iron in barrier, to make barrier soluble (CIV 1229, 2006).

Corrosion inhibitors

Corrosion inhibitors are used for the protection of reinforced steel from chloride corrosion. Calcium nitrite is most widely used, and it has been preferred over other corrosion inhibitors (sodium nitrite, sodium benzoate), because of its compatibility with concrete properties (Gaidis, 2004). The mechanism of calcium nitrite protecting reinforced steel is associated with the role of nitrite ions in reacting with ferrous ions on the surface of steel to form an oxide, which protects the steel from corrosion (Gaidis, 2004). Cement is thought to have the ability to bind some chloride ions, as Friedel's salt ($Ca_2Al(OH)_6Cl \cdot 2H_2O$, or $C_3A \cdot CaCl_2 \cdot 10H$), rendering it ineffective (or at least, less effective) as a catalyst for corrosion (Yauri and Glasser; 1998). There is a concept of a threshold value for chloride, which is in the range of 1–1.6 pounds of chloride per cubic yard of concrete (0.6–1 kg/m^3) (Gaidis, 2004). Below this level of chloride, the alkalinity of concrete is enough to minimize corrosion. In cement pore solution, both nitrite and chloride ions (anions) tend to react with ferrous ions (cations), hence the amount of nitrite ions is a key factor in being effective in inhibiting corrosion. The concept of the ratio of $[NO_2^-] : [Cl^-]$is used for expressing the appropriate dosage of corrosion inhibitor and showing an increase in the chloride threshold level (Gaidis, 2004).

When ASTM C1202 is used for testing the concrete contained calcium nitrite, the final result (total columbs) would be higher than that of a control sample. It was also observed that the temperature in chambers of each cell increased proportionally with the total charge. This is primarily because a direct current (DC) of 60 V induced heat, which in turn accelerates the flowing speed of ions (Ann et al, 2006). The temperature strongly affects the mobility of ions (Ann et al, 2006).

Air entraining admixtures/agents (AEAs)

Air entraining agents/admixtures are chemicals called surfactants which usually have hydrophilic (polar) head and hydrophobic tails. The important role of AEAs playing in fresh concrete includes two parts, one is to make air bubbles uniformly dispersed, and another is to stabilize the generated microscopic air bubbles (Rixom et al, 1986).

When AEAs are mixed with cement and water, the hydrophilic heads absorb onto cement particles and new hydration products which are surrounded by liquid phase, whereas the hydrophobic tails stick onto air bubbles which introduced by mixing and stirring process (Ramachandran, 1984). The mechanism of AEAs in pastes or concrete can be simply described by Figure 2.6 At the appropriate dosage, AEAs generate microscopic bubbles, and in the appropriate water condition, the hydrophobic tails and hydrophilic heads connect cement particles and bubbles to form like bridge (Lea, 1998; Rixom et al, 1986; Ramachandran, 1984).

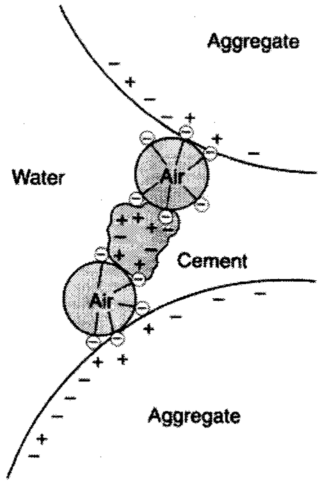


Figure 2.6 Mechanism by which entrained air bubbles remains stable within concrete (Lea, 1998).

The foaming capacity of AEAs depends on their effectiveness to reduce the surface tension of the solution, their diffusion ability. (Ramachandran, 1984). Their hydrophobic tails stick out of the solution to reduce the distortion of water molecules and thus lower the overall free energy of the system (Ramachandran, 1984). The shearing action tends to break up larger bubbles into smaller ones when the surface energy requirement for new surface is smaller (Ramachandran, 1984).

The stabilization of microscopic bubbles from coalescing into large ones can be achieved by the orientation of surfactant adhering to the cement particles (Rixom et al, 1986). The electric repulsion between the hydrophilic head molecules reduces the attraction of the bulk liquid phase and less surface tension as well (Du et al, 2005). The surface tension of bubble adsorbed by agents is thermodynamically stable; the free energy is lowered on coalescence which causes surface destruction (Ramachandran, 1984). Typically, the bubbles in air-entrained pastes are between 0.25 mm to 10μm (Rixom et al, 1986). They are different from the "entrapped air "existing in non-air-entrained pastes. The latter is larger, irregular and easy to credit to consolidation failure (Ramachandran, 1984).

At very low dosages, surfactants do not reduce the surface tension of the solution. However, for high dosages, there is a phenomenon called micelle formation that "above a certain surfactant concentration [critical micelle concentration (cmc)] the monomer concentration is almost constant and do not contribute to the reduction of surface tension" and there is no more increase in entrained air (Du et al, 2005). This is why a minimum dosage of AEA is required in concrete.

The nature and concentrations of the surfactants determine the physical and chemical properties of the interface at the air bubble surfaces, including surface tension and stability (Du et al, 2005).

2.3 Electrical conductivity of concrete

Electrical conductivity of concrete is used as a parameter to express the capacity of ionic diffusion in concrete. Because it is very sensitive to cement composition and application environment of concrete, it can be used to reflect concrete properties from setting behavior, development of microstructure to durability in various conditions.

2.3.1 Mechanisms of electrical conduction of concrete

There are two types of electrical conduction, one is electronic, and another is ionic (Gu et al, 1995). Electronic conductivity is by electron motion in solid phases; and ionic conductivity is ionic motion in liquids (Gu et al, 1995). Concrete system includes two components, pore solution and solids, including hydrates, aggregates and unhydrated cement. Concrete is porous and permeable to fluids. Changes in electrical properties can be related with the formation of discontinuous pore structure (Nokken, 2004).

There are several electrical conductivity models of the cement system, these will be briefly described.

Whittington et al.'s Model

Whittington et al (in Gu et al, 1995) assumed there were three electrical paths in concrete system: (a). through the aggregate and paste, (b). through the aggregate particles in contact with each other, (c). through the paste. The model is shown in Figure 2.7. Three parameters x, y and z represent the cross section of (a), (b), and (c), respectively. Current through path (b) is given by x, through path (c) is given by z. The portion that travels through aggregate in path (a) is represented by w. The resistance of each element and the total resistance of the model can be determined by parameters x, y, z, and w (Gu et al,1995)

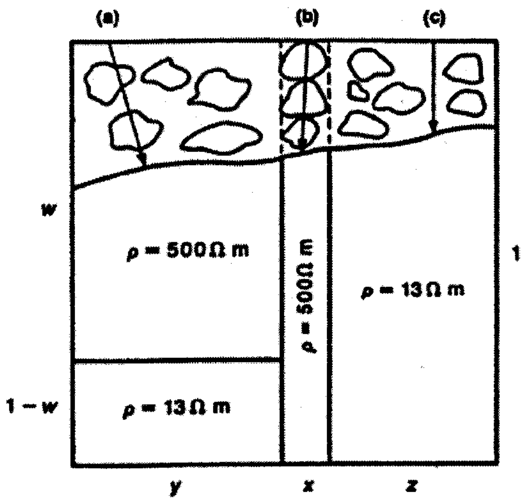


Figure 2.7 Schematic of Whittington et al.'s Model (Gu et al, 1995).

Bruggeman's asymmetrical effective medium theory

Bruggeman's asymmetrical effective medium theory has been used for predicting conductance of heterogeneous systems which low conductivity grains are embedded in a highly conductive matrix (Xu and Beaudon; 2000). For Portland cement mortars, it can be expressed as

$$\sigma_m = \sigma_P (1-V_{f,\,sand})^{3/2} \qquad \text{Eq. 2.1}$$

where

σ_m is the electrical conductivity of mortar

σ_P is the electrical conductivity of cement paste

$V_{f,\,sand}$ is the volume fraction of sand in the mortar.

The assumptions of this theory include that sand grains are spherical and nonconductive; sand is introduced into a continuous background of conductive cement; the conductivity of the cement matrix does not change with increasing volume fraction of sand; and there is no interfacial effect (Xu and Beaudon; 2000). Xu and Beaudon applied this model to detect the effect of superplasticizers on interfacial transition zone of mortars.

Xie et al.'s MODEL

Xie et al (in Gu et al, 1995) developed a conductivity model based on the assumption that each component of hydrating cement contributes to the conductivity of cement composite at the macroscopic level and the size of each component was small compared with the specimen size. This model is expressed by:

$$\sigma_c = \sum_{I=1}^{N} \Psi_i \times \sigma_i \qquad \text{Eq.2.2}$$

where:

σ_c is the electrical conductivity of cement composite

σ_i is the electrical conductivity of its component

Ψ_i is the area of fraction in the cross section of each component

When the conductivity of the solids is negligible comparing with that of the pore solution, then the model can be expressed as

$$\sigma_c = \Psi_p \times \sigma_1 = (1-\Psi_s) \times \sigma_1 \qquad \text{Eq. 2.3}$$

where

Ψ_p is the area fraction of pores

σ_1 is the conductivity of the pore solution

Ψ_s is the area fraction of solids

This model is based on the concept that the electrical conductivity of the hydration cement system depends on two parts: 1). micro structural characteristics, including parameters of aggregate and interface, porosity, pore-size distribution, and pore connectivity etc. 2). The conductivity of pore solution (Gu et al; 1995).

Rajabipour et al.'s life cycle modeling

Rajabipour et al. (2004) built up a model for prediction of concrete life cycle performance. In their study, the conductivity of concrete was used to express the durability of concrete as it is strongly related with the transport properties of aggressive ionic species, water, gases in concrete for its long term performance. In the composite (Torquato, 2002)

$$\sigma_t = \sum \quad (\sigma_i \varphi_i \beta_i) \qquad \text{Eq.2.4}$$

where

σ_t is the total composite conductivity

σ_i is conductivity of each component

φ_i is volume fraction of each constituting component

β_i is connectivity or structure factor of each constituting component

In the cement-based system, the conductivity of saturated porosity is several orders of magnitude higher than that of other components; hence its conductivity can be expressed as (Garboczi, 1990)

$$\sigma_t = \sigma_0 \varphi \beta \qquad \text{Eq.2.5}$$

where

σ_t is the total concrete conductivity

σ_0 is the conductivity of pore solution

φ is the volume of porosity

β is the pore connectivity factor

but when concrete is cured at the different moisture conditions, Rajabipour et al.(2004) introduced a moisture factor f in above equation.

$$\sigma_t = (\sigma_0 \varphi \beta)_{ref} f \qquad \text{Eq.2.6}$$

where

f is moisture factor, when concrete is in the reference moisture condition, $f=1$

$(\sigma_0 \varphi \beta)_{ref}$ is concrete conductivity at the reference moisture condition.

2.3.2 Conductivity of pore solution

When cement mixes with water, the soluble ions release to water, including Ca^+, Na^+, K^+, SO_4^{2-} and OH^-. The concentration of these ions is constantly altering as the hydration develops, particularly at early hydration times. In general, the conductivity increases sharply in the first instants of mixing cement and water due to the rapid dissolution of alkali sulfates (Jolicoeur et al 1998). This results in an increase of Na^+, K^+, and SO_4^{2-} ions, and the first hydration products form surrounding the surface of cement particles, increasing Ca^{2+} and OH^- ions in solution (Jolicoeur et al 1998). Following this period, the conductivity increases slowly as the hydration reaction proceeds. When numerous calcium hydroxide crystals begin to precipitate, the conductivity decreases sharply, combined with decrease of the concentration of Ca^{2+} in solution until reaching a negligible level (Khayat et al; 2003). These ionic species exist in pores of cement paste as a strong electrolyte. Different ionic species possess different conductivity. Table 2.2 lists the conductivity of some common ions existing in concrete pore solution. Pore solution conductivity can be either measured by a conductivity cell or calculated. The electrical conductivity of pore solution is typically 4-2.86 $\Omega^{-1}m^{-1}$(Gu et al, 1995; Liu et al, 2000).

Table 2.2 Equivalent conductivity at infinite dilutionλ^0 and conductivity coefficient G at 25°C (Snyder et al, 2003)

species	$Z\lambda^0$ (cm^2 S/mol)	G $(mol/l)^{-1/2}$
OH^-	198.0	0.353
K^+	73.5	0.548
Na^+	50.1	0.733
Ca^{2+}	59.0	0.771
SO^{2-}_4	79.0	0.877

Christensen et al (1992) found that during the hydration process, the increase of the conductivity of pore solution was a factor of 3 to 4. Pore solution can be expressed from cement pastes by special device (Barneyback and Diamond, 1981).

The conductivity of an ionic solution is a function of the valence, concentration and mobility of the dissolved ions (Bockris, 1970). It can be expressed as (Bockris, 1970)

$$\sigma_0 = e N_A \sum z_i c_i u_i \qquad \text{Eq.2.7}$$

where

σ_0 conductivity of ionic solution

e unit of electron charge

N_A Avogadro's number

z_i ionic valence

c_i ionic concentration

u_i mobility of ion

Snyder et al (2003) proposed a single parameter model to estimate the electrical conductivity of cement pore solution, which is

$$\sigma_{calc} = \sum z_i c_i \lambda_i \qquad \text{Eq.2.8}$$

$$\lambda_i = \lambda^0_i / (1 + G_i I^{1/2}_M) \qquad \text{Eq.2.9}$$

$$I_M = 1/2 \sum z^2_i c_i \qquad \text{Eq.2.10}$$

where

z_i each ionic valence,

c_i each ionic molar concentration.

λ_i the equivalent conductivity of each ionic species

λ^0_i the equivalent conductivity of an ionic species at infinite dilution

G_i conductivity coefficient of each ionic species

I_M the ionic strength (molar basis).

They used this model to compare the experimental results with calculated results; the accuracy is within 8% for K: Na ratios ranging from 4:1 to 1:1 (Snyder et al, 2003).

Shi (2003) used other equations to calculate the conductivity of pore solution. At a given temperature, the specific conductivity of a solution is

$$\rho=\rho_{water} + \sum c_i \lambda_i /1000 \qquad \text{Eq.2.11}$$

$$\lambda_i =\lambda_{i\,0} -(0.2289\lambda_{i\,0} +60.19)\, c_I{}^{\wedge} \qquad \text{Eq.2.12}$$

where

ρ specific electrical conductivity of aqueous solution $m^{-1}\Omega^{-1}$

ρ_{water} specific electrical conductivity of water, which is 10^{-5} $m^{-1}\Omega^{-1}$

c_i equivalent electrical concentration of ion I, equiv m^{-3}

λ_i equivalent electrical conductivity of ion I, m^2 equiv.$^{-1}\Omega^{-1}$

$\lambda_{i\,0}$ equivalent electrical conductivity of ion I at infinite concentration, m^2 equiv.$^{-1}\Omega^{-1}$

Snyder et al (2003) mentioned that Equation 2.8 was used in the condition of a concentration of around 0.1 M aqueous univalent ions. The concentration of alkali hydroxides in the concrete pore solution is less than 1M in most cases.

The composition of concrete can alter the pore solution. Supplementary cementitious materials, such as fly ash and silica fume reduce the conductivity of concrete due to the active silica components reacting with calcium hydroxyl, and reducing pH value of pore solution (Christensen et al, 1992).

2.3.3 Factors affecting the conductivity of concrete

There are many factors that can influence concrete conductivity. From the previous models, it can be seen that conductivity of concrete is governed by the liquid phase of concrete--pore solution chemistry, porosity, pore-size distribution, pore connectivity, and moisture content of concrete (Liu et al, 2000; Rajabipour et al,2004). As mentioned previously, hydrating concrete consists of two components, solids and pore liquid. Usually, dry concrete has low conductivity; its value is around 0.09 E-3 to 0.15 E-3 $\Omega^{-1}m^{-1}$ (Gu et al, 1995). Its conductivity increases sharply with increasing moisture content. The conductivity value of moist concrete is 0.04-0.02 $\Omega^{-1}m^{-1}$, moist cement paste has the value of 0.1-0.08 $\Omega^{-1}m^{-1}$ (Gu et al, 1995). Most of models mentioned above neglect the conductivity of solid components. Hence, electrical conduction of concrete can be considered to be ionic conduction, which is the result of the ionic migration of species in liquid in concrete.

A lot of research work has shown that mineral admixtures, such as silica fume and fly ash reduce the pH value and alkali concentration (after 1 day) of the pore solution due to the active silica components in these materials reacting with hydroxyl ions of pore solution (Page, 1983; Diamond, 1983; Christensen et al, 1992). Liu and Beaudoin (2000) pointed out that the pH level of the pore solution in the cement paste containing 30% silica fume by weight is about 12.4, and the pH level of normal Portland cement paste is 13.8-13.9.

Mineral admixtures also influence the conductivity of concrete by improving the microstructure of cement paste (Liu and Beaudoin, 2000) and interfacial transition zone. Xie and Beaudoin (1992) applied silica fume coated aggregate to densify the interfacial transition zone. The effect of mineral admixtures was not studied in this thesis; it will not be discussed further.

Chemical admixtures can also alter the chemical composition of pore solution in cement paste and microstructure. Some chemical admixtures, such as lingnosulfonate, sulfonated naphthalene formaldehyde raise the concentration of Na^+ or K^+ or Ca^{2+} in the pore solution of cement paste depending on the metal species contend in their formulas (Rixom et al, 1986; Ramachandran et al, 1984; Spiratos, et al, 2006). Calcium nitrite inhibitor significantly increases conductivity of concrete as seen during performance of the rapid chloride permeability test (ASTM C1202-97). High range water reducing agents achieve a densified paste structure due to their high efficiency of water reduction (Xu and Beaudoin, 2000). These authors also indicated that the improvement of the interfacial zone by addition of superplasticizer in low W/C ratio mortars does not occur in high W/C ratio mortars because of possible bleeding, segregation and increased water layer thickness around the aggregate.

2.4 Techniques of measuring electrical conductivity of concrete

The application of electrical techniques for monitoring durability of concrete has received more attention recently (Chrisp et al, 2002). The most widespread methods include the rapid chloride permeability test (referring to ASTM C1202/AASHTO T277), and AC impedance method. Khayat et al (2003) developed a method using embedded sacrificial electrodes in specimens to assess segregation and bleeding of cement mixed with chemical admixtures.

2.4.1 The rapid chloride permeability test (RCPT)

The ability to resist penetration of chloride is an important parameter for concrete durability and protecting reinforced concrete from deterioration. One standard method, AASHTO T259-80 "Resistance of Concrete to chloride penetration" (also named the ponding test) has been used to measure the chloride permeability. The period of this test typically takes 90 days or longer. Because of the long time, Federal Highway Administration (FHWA) developed standard FHWA/RD-81/119, "Rapid Determination of the Chloride Permeability of Concrete." Since that time this method has been standardized as AASHTO T277 (American Association of State Highway & Transportation Officials) in 1983 and ASTM standard C1202 in 1991 (Lane, 2005; Grace technical bulletin TB-0100, 2006).

The test measures the amount of electrical current (in Coulombs) passing through a specimen with a given thickness when the ends of the specimen is exposed to 3% NaCl solution and 0.3N NaOH solution, respectively. The potential applied is 60V DC for 6 hours, and the readings of current are taken in every 30 minutes. Coulombs passed through the specimen is calculated by (ASTM C1202-97)

$$Q = 900\,(I_0 + 2I_{30} + 2I_{60} + \ldots + 2I_{300} + 2I_{330} + I_{360}) \qquad \text{Eq.2.13}$$

where :

Q = total charge passed (Coulombs)

I_0 = current (amperes) immediately after voltage is applied

I_t = current (amperes) at t min after voltage is applied.

Table 2.3 is using to as qualitative determination of chloride ion penetrability of the concrete. ASTM C1202 discourages presenting results in Coulombs but rather in classifications.

Table 2.3 Chloride ion penetrability based on charge passed (ASTM C 1202)

Charge passed (Coulombs)	Chloride ion penetrability
>4,000	High
2,000–4,000	Moderate
1,000–2,000	Low
100–1,000	Very Low
<100	Negligible

2.4.2 Rapid migration test (RMT) method

The rapid migration test originally developed by Tang and Nilson (1992) (standardized by Nordtest as NT Build 492) has been now standardized as AASHTO TP 64-03 (HPC Bridge Views, 2005). The apparatus of RMT is similar to the RCPT. The test specimen is sealed except for two cured faces, which are exposed to NaCl solution and NaOH solution. A voltage is applied to accelerate the migration of chloride ions through the specimen. After test, the specimen is fractured and sprayed with $AgNO_3$ solution to detect the penetration depth of chloride. The RMT results were evaluated by University of Toronto; they showed that the results are not affected by the conductive ions in pore solution of samples (Shi, 2003). RMT has been recommended to FHWA as a possible replacement for the AASHTO T 277 rapid chloride test (Hooton et al, 2002).

2.4.3 AC Impedance Spectroscopy

"The AC impedance spectroscopy (IS) technique involves application of a small amplitude sinusoidal voltage or current signal to a system; a response current or potential signal is generated and recorded" (Gu et al., 1995). It is powerful method to investigate electrical properties and interfaces of materials. McCarter was one of the first researchers to introduce this method to study cement-based materials.

The impedance of the system evaluates results through analysis of the ratio of the amplitudes and the phase shift between the voltage and the current, or the real and imaginary parts. Impedance data is plotted in the complex plane by real versus imaginary impedance (Gu et al., 1995). For the cement-based materials, the high-frequency arc (HFA) (original arc) is related with the bulk impedance behavior, and the second arc is attributed to the capacitance paste or concrete –electrode interface. The low-frequency intercept on the real impedance axis R1+R2, is equivalent to the DC bulk resistance, it changes with materials and their proportion, such as cement paste, aggregates, admixtures, pore solution, and provides information about microstructure, including porosity, pore size distribution, solid-liquid interface (Liu and Beaudoin, 2000). Typically, the high-frequency arc (HFA) does not appear at the very early hydration period. Xu and Beaudoin (2000) explained it as the number of available interfaces was too small to be detected at this stage, the capillary pores were not filled by hydrates yet, and a rigid network structure was not formed. Christensen et al (1992) appraised this method as "the only technique available where bulk and electrode effects can be separated and analyzed to reveal the true properties of the material under investigation". Xu and Beaudoin (2000) used ACIS to detect the effect of the varying dosages of a polynaphthalene sulfonate superplasticizer and polycarboxylate superplasticizer on the electrical resistivity and the interfacial transition zone (ITZ) characteristics of mortars with different water to cement ratio.

2.4.4 In situ monitoring of conductivity of cover-zone concrete.

Chrisp et al (2002) proposed a method to quantitatively determine the near-surface characteristics of concrete that suffered the ingress of gases or liquids containing dissolved contaminants. The electrical conductance was measured by embedding electrodes in the cover zone of concrete samples which were subjected to wet (water and NaCl solution) and dry cycling curing. The aim of this method is to assist in making realistic prediction about deterioration rates for a particular exposure condition.

Khayat et al (2003) used electrokinetic probes embedded at different depths in cement mortar to assess of stability of cement-based materials by monitoring mortar's conductivity. They introduced parameters, like bleeding indexes (BI), segregation indexes (I_S) to evaluate the stability of mortar.

The bleeding index BI = Top conductivity at peak/Mean conductivity at peak –

Top initial conductivity/Mean initial conductivity

The segregation index $I_S = 1 - (\sigma\Lambda / \sigma\Lambda_{av})$

Where $\sigma\Lambda$ is standard deviation of the conductivity values, $\sigma\Lambda_{av}$ average conductivity.

2.4.5 Time Domain Reflectometry (TDR)

Yu et al (2004a, b) proposed Time Domain Reflectometry as a method to measure water cement ratio in concrete and predict strength development of concrete. TDR provides the dielectric constant which refers to water content, and electrical conductivity which relates to cement content. Authors found there was a linear relationship between the electrical conductivity and strength of concrete. The authors suggested this method can be used for in situ concrete quality control

Rajabipour et al (2004) used the similar technique to develop the model for predicting life-cycle performance of insitu concrete.

3.0 Experimental program

In this project, cement mortar was the subject of investigation, the experimental program included two phases based on water to cement ratio. The phase one experiment used 0.485 water to cement ratio; the phase two experiment used 0.35 water to cement ratio, (named as Phase I and Phase II). The sand to cement ratio was kept at 2.75:1 in order to avoid the influence of the volume of sand, particularly that of the interfacial transition zone, and to better understand the mechanisms of conductivity of mortar added by chemical admixtures.

3.1 Phase I

0.485 water to cement ratio cement mortars, chemical admixtures were added at different dosages

Properties measured were:

- Consistency (flow)
- Conductivity
- Degree of hydration
- Gravimetric water porosity (samples with Type F chemical admixture)

3.2 Phase II

0.35 water to cement ratio cement mortars, chemical admixtures were added at different dosages

Properties measured were:

- Consistency (flow)
- Conductivity
- Degree of Hydration
- Gravimetric water porosity (samples with Type F chemical admixtures)

3.3 Materials

3.3.1 Cement

In this project, cement was type GU Portland cement provided by Lafarge North America. The chemical composition is listed in Table 3.1. The Blaine surface area of this cement was 3924 cm^2/g.

Table 3.1 Chemical and mineral composition of cement

Chemical composition (%)														Bogue Compounds (%)			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Mn_2O_3	TiO_2	P_2O_5	SrO	SO_3	LOI	Total	C_3S	C_2S	C_3A	C_4AF
19.64	4.96	2.18	61.42	2.51	0.23	0.84	0.06	0.24	0.27	0.24	3.95	3.23	99.71	54	16	9	7

3.3.2 Chemical admixtures

Various commercially available concrete chemical admixtures used in this project were provided by BASF Construction Chemicals (Master Builders) and Euclid Chemical Company. They were classified according to ASTM C494 and ASTM C260 for air entraining admixtures/agents. The information of these chemical admixtures is listed in

Table 3.2. ASTM C494 classification is as follows:

Type A	Water reducer, normal setting,
Type C	accelerating admixtures (including corrosion inhibitors)
Type D	water-reducing and retarding admixtures
Type E	water-reducing and accelerating admixtures
Type F	water-reducing, high range admixtures
Type G	water-reducing, high range, and retarding admixtures

Air entraining admixtures/agents

Table 3.2 Characteristics of chemical admixtures

Specifications	Commercial name	Genetic name (or main ingredients)	Company	Name of mixtures
ASTM Type A water-reducing admixtures	EUCON 75	Modified organic polymer of sodium glucoheptonate	Euclid Canada	WR(E75)
	Pozzolith 210	Glucose based carbohydrate	Master Builders	WR(MP210)
ASTM Type C corrosion inhibitors	EUCON CIA	30% calcium nitrite solution	Euclid Canada	CIA
	RHEOCRETE CNI	> 30% calcium nitrite solution	Master Builders	CNI
ASTM Type D water-reducing and retarding admixtures	EUCON 727	Double metallo-organic salt(derived from hydroxycarboxylic acids)	Euclid Canada	WR(E727)
	POZZOLITH 100XR	Glucose based carbohydrate type	Master Builders	WR(MP100)

Table 3.2 characteristics of chemical admixtures (continued)

Specifications	Commercial name	Genetic name (or main ingredients)	Company	Name of mixtures
ASTM Type E water-reducing and accelerating admixtures	EUCON 90	calcium nitrite	Euclid Canada	WR(E90)
	POZZUTEC 20+	Non Chloride based Accelerator containing nitrates and thiocyanates	Master Builders	WR(MP20)
ASTM Type F high range water-reducing admixtures (HRWR)	EUCON 37	Sulfonated naphthalene formaldehyde condensates(SNF)	Euclid Canada	SP 37
	RHEOBUILD 1000	Sulfonated naphthalene formaldehyde condensates(SNF)	Master Builders	HRWR
ASTM C 260 Air entraining admixtures /agents	AIREXRA	Sulfonated fatty acids	Euclid Canada	AE(E)
	MICRO AIR	Multi component Synthetic based surfactant	Master Builders	AE(M)

3.3.3 Mixtures

All of these admixtures were added to the cement mortars at the middle of the dosage range indicated by the manufacturers. Some of them were selected to be investigated at lower and /or higher dosages in order to detect the influence of addition amount on mortar's conductivity. The mixture characteristics are listed in Table 3.3. The phase (I or II) and dosage low (L), medium (M) or high (H) are indicated.

Table 3.3 Mixture characteristics

Name of mix		Chemical admixture		W/C
		Name	Dosage	
Blank	I	--	0	0.485
	II	--	0	0.35
WR(E75)	I-M	EUCON 75	352ml/100 kg cement	0.485
	I-H		480ml/100 kg cement	
	II-M		352ml/100 kg cement	0.35
	II-H		480ml/100 kg cement	0.35
WR(MP210)	I-M	Pozzolith 210	260ml/100 kg cement	0.485
	II-M			0.35
CIA	I-M	EUCON CIA	5720ml/100 kg cement	0.485
	I-L		2880ml/100 kg cement	0.485
CNI	I-M	RHEOCRETE CNI	6440ml/100 kg cement	0.485
WR(E727)	I-L	EUCON 727	76ml/100 kg cement	0.485
	I-M		124ml/100 kg cement	
	I-H		216ml/100 kg cement	
	II-L		76ml/100 kg cement	0.35
	II-M		124ml/100 kg cement	
	II-H		216ml/100 kg cement	
WR(MP100)	I-M	POZZOLITH 100XR	196ml/100 kg cement	0.485
	II-M			0.35
WR(E90)	I-M	EUCON 90	3252ml/100 kg cement	0.485
	II-M			0.35
WR(MP20)	I-M	POZZUTEC 20+	3096ml/100 kg cement	0.485
	II-M			0.35
SP 37	I-M	EUCON 37	2200ml/100 kg cement	0.485
	I-L		1120ml/100 kg cement	
	II-M		2200ml/100 kg cement	0.35
	II-L		1120ml/100 kg cement	
HRWR	I-M	RHEOBUILD 1000	1140ml/100 kg cement	0.485
	I-H		1600ml/100 kg cement	
	II-M		1140ml/100 kg cement	0.35
	II-H		1600ml/100 kg cement	
AE(M)	I-M	MICRO AIR	64ml/100 kg cement	0.485
	I-H		120ml/100 kg cement	
	II-M		64ml/10 kg cement	0.35
	II-H		120ml/100 kg cement	
AE(E)	I-M	AIREXTRA	64ml/100 kg cement	0.485

3.4 Procedures

3.4.1 Consistency

The mortar's consistency is expressed as flowability, which was conducted in accordance with ASTM C 1437 (ASTM, 2001). The blank (control) cement mortar was prepared according to ASTM C 305 (ASTM, 1999). First all mixing water was placed in the mixing bowl, the cement then was added to the water, and mixed at the slow speed for 30s. Sand was then added to the bowl slowly within 30s, changing the mixing speed to medium and mixed for 30s, then the mixer was stopped and let to stand for 1 1/2 min. Finished mixing was for 1 min at medium speed. When adding chemical admixtures, the chemical admixture was added into the mixing water and let to dissolve in the water completely before adding the cement, then followed the same procedure. The mortar was placed into the flow mold in two layers, each time the mortar filled half of the mold, and then tamped 20 times. The mold was lifted away from mortar vertically and the table was dropped 25 times in 15s letting the mortar spread, then the diameter of the mortar was measured at four equispaced intervals. The average increase was expressed as a percentage of the original base diameter, which was 100mm.

3.4.2 Electrical conductivity

3.4.2.1 Mortar's electrical conductivity

The equipment of monitoring the electrical conductivity of mortar was provided by Germann Instruments, which is also used in ASTM C1202 (ASTM, 1997a) (Figure 3.1). The equipment allows users to choose voltages from 10v to 60v, with flexible monitoring time. The maximum current allowed to pass the specimen is 500mA, and the maximum temperature is 90°C, beyond this temperature the program will shut down automatically. In this thesis, the voltage for the samples of 0.485 water to cement ratio was 20V, and for the most of 0.35 water to cement ratio samples the voltage was 10V because of the high porosity of samples caused excessive current if 20 V was selected. The electrolyte solution in the both chambers was 0.3N NaOH instead of solutions of ASTM C1202 (ASTM, 1997a) 3% NaCl and 0.3 N NaOH in each chamber. The solution was selected to approximate the pore solution as well as to minimize leaching. The use of sodium chloride would change conductivity over time due to the difference in conductivity of chloride and hydroxyl ions (Nokken, 2004).

The mortar was cast in a mold with diameter 10cm±0.5 and depth 5cm±0.5. The specimens were cured in an environment with 22°C±1 and RH ≥95% for 24 hours, then demolded, and measured for the dimensions. The specimens were wrapped with vinyl electrician's tape other than the two flat surfaces, and were vacuumed saturated under tap water in a vacuum desiccators for 3 hours. After vacuum, the specimens were put into the chambers which were filled with the electrolyte solution. After plugging in electrodes, the program developed by Zsaki and Nokken (2003) was run. The current was measured after passing the potential (20V/10V) through the specimen for 5 minutes every 3 hours in the first 6 days after demolding (7 days after casting). The specimens were then put into saturated limewater for curing until the subsequent measurement. During the 14th day, the 21st day, the 28th day and /or the 90th day after casting, the specimens were brought out of the limewater to measure the current of the specimens for 5 minutes, and then put back into the limewater again for next test.

The electrical conductivity of the specimens was calculated by the following equation:

$$\text{Conductivity} = I * L \;\; / \;\; V * A \qquad \text{Eq.3.1}$$

Where:

I = current measured at 5 minutes (micro-amps)

L = thickness of specimen (cm)

V= applied voltage (volts)

A = cross sectional area of specimen (cm^2)

Conductivity is $\mu S/cm^2$

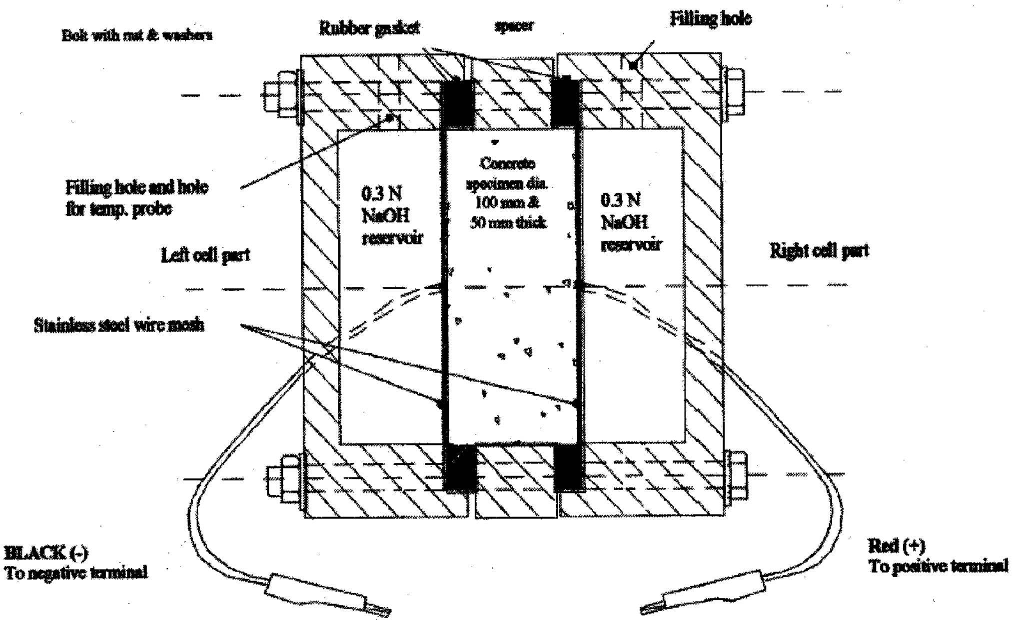


Fig. 3.1 The assembled PR-1000 PROOVE'it cell (Germann, 2002)

The conductivity of samples with 0.485 water to cement ratio was calculated by the average of 3 specimens. Only one specimen of each mixture with 0.35 water to cement ratio was tested because the variations among the three specimens of 0.485 water to cement ratio were not very significant (less than 10%) and also for saving time.

This method directly uses conductivity as parameter to express all ions' migration in the hardened samples instead of total Coulombs. The testing time is 5 minutes in every 3 hours to avoid the Joule effect and allow monitoring of long term performance of the samples.

3.4.2.2 Chemical admixture's conductivity

The electrical conductivity of chemical admixtures was measured by a YSI 3100 Conductivity instrument (Figure 3.2), the cell was 3252 for which K (cell constant) was 0.1/cm, the temperature of the solution was 25.2 °C.

The ability of a solution to conduct electric current depends upon ions: their concentration, size, mobility, valence, viscosity and the temperature of the solution. Inorganic solutions are relatively good conductors. Organic solutions are poor conductors. The electrical conductivity of chemical admixtures was calculated by equation 3.2

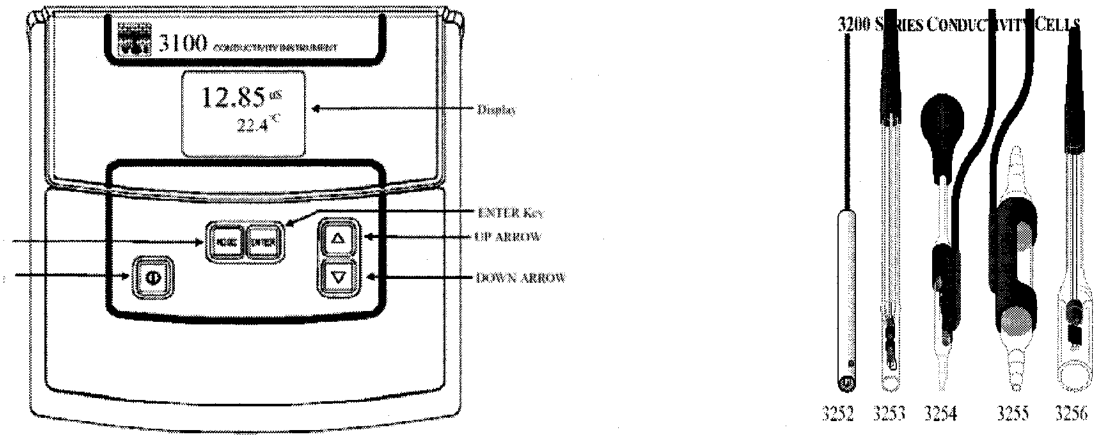
$$\text{Conductivity} = k * K \qquad \text{Eq.3.2}$$

where:

k is observed conductance of solution, *m*S.

K is cell constant. In this test, 3525 conductivity cell was selected; its cell constant is 0.1/cm.

Conductivity is expressed in *m*S/cm.



The instrument of YSI 3100

The cells

Figure 3.2 Conductivity instrument (YSI, 2006)

3.5 Degree of hydration

Non-evaporable water content between 105°C and 1050°C was used to determine the degree of hydration. The mortar was cast into the mold with dimensions, length × wide × depth of 250×2.5×2.5 cm and cured in the 22°C±1 and RH ≥95% environment for 24 hours, then demolded and cut into several pieces weighing around 30-50 g, then put into lime water until testing at the selected hydration time (1 day, 3 days, 7 days and 28 days). When the specimen was tested, it was placed in the oven to dry at 105°C for at least 24 hours, measuring the weight as W_{105}, then moved to the furnace at 1050°C for 3 hours, then let to cool to the room temperature in the desiccators, measured the weight as $W_{1050.}$ The ignition loss was non-evaporable water content. The hydration degree was calculated by equation 3.3

$$\alpha = (W_{105} - W_{1050}/W_{1050})/0.252*3.75 \qquad \text{Eq. 3.3}$$

where :

α is degree of hydration (%)

W_{105} is weight of specimen after oven dry in 105°C (g)

W_{1050} is weight of specimen after furnace dry in 1050°C (g)

0.252 is the factor of non-evaporable water at full hydration, which was determined by Hooton (Nokken, 2004).

3.75 is the coefficient of mortar converted to paste. (Sand to cement ratio was 2.75).

3.6 Gravimetric water porosity

Gravimetric water porosity was a modification of ASTM C 642, Standard test method for density, absorption, and voids in hardened concrete (ASTM, 1997b). In this study, vacuum saturation was used to replace the boiling-water saturation because vacuum saturation is the most effective saturation technique among cold-water saturation, boiling-water saturation and vacuum saturation (Safiuddin and Hearn, 2005). Also the oven drying was conducted at the final stage of testing in order to avoid micro structural damage (Safiuddin and Hearn, 2005). The measured gravimetric water porosity was the volume of permeable pore space of specimens in this standard. Prepared samples as described in 3.4.1, which were cast in the mold as that used in conductivity test. The weight of the specimens was 800g±100, and cured them in an environment with 22°C±1 and RH ≥95% condition for 24 hours, then put in the limewater for curing. At the selected age of hydration time (1 day, 3 days, 7 days and 28 days), the samples were moved to the vacuum desiccators placed under tap water for 3-hour vacuum saturation. The samples were then taken out of the desiccator, removing surface water, weighed at room temperature and expressed as C (saturated surface-dried mass), and weighed suspended in the tap water with room temperature as D (immersed apparent mass), then put in the oven for drying at 105°C for at least 24 hours, weighed as A (oven-dry mass). The gravimetric water porosity was calculated by equation 3.4

Gravimetric water porosity (volume of permeable pore space)

$$= (C-A) / (C-D) * 100\% \qquad \text{Eq.3.4}$$

where:

A = oven-dry mass (g)

C = saturated surface-dried mass (g)

D = immersed apparent mass (g)

3.7 Ionic concentration of chemical admixtures

Sodium and potassium concentrations of the chemical admixtures used in this thesis were tested by flame photometry; hydroxyl ions were determined by automatic potentiometric titration against sulphuric acid. PH was measured by PH meter.

4.0 Results

In this chapter, consistency, conductivity, non-evaporable water content and gravimetric water porosity results are given. They will be presented by phase and amount of admixture.

4.1 Phase one experiment - 0.485 water to cement ratio

4.1.1 Medium addition of chemical admixtures

4.1.1.1 Consistency

In this study, the consistency of mortar was measured by ASTM C 230. Flowability is one of terms used to describe concrete workability. In this section, all chemical admixtures were added at the medium dosage in accordance with the guidelines of each product bottle. The water to cement ratio was 0.485, which was required for standard mortar without adding chemical admixtures (ASTM C109M-01). Generally, Portland cement requires around 30% water by weight of cement to complete hydration; the additional water more than that will cause a corresponding increase of capillary porosity in solid samples (Spiratos et al, 2006).

Figure 4.1 shows the effects of chemical admixtures on consistency of the mixtures. Compared to the control sample (blank I), the flow table readings increased when various chemical admixtures were added. One point has to be mentioned, as these chemical admixtures came from different companies, even though the same type of admixtures, they may have different solid concentration, different generic groups and different optimum dosages. Thus it is hard to make detailed comparison. However, it still showed something from their behavior. The consistency of all mixtures including chemical admixtures was higher than that of the control sample. Types A, D, E and Type F are all in the family of water reducers; they just possess different setting efficiency on cement. Among them, Type F (high range water reducers) and Type E (accelerating water reducer) produced relatively high consistency, Type A (normal setting water reducer), Type D (setting retarding water reducer) and air-entraining agents gave relatively low consistency.

High range water reducing admixtures, also called superplasticizers, can exhibit much higher water reduction at relatively high additions without producing adverse side effects, such as excessive retardation (Rixom et al, 1986). In this project, the Type F admixtures EUCON 37 and RHEOBUILD 1000 are all PNS superplasticizers. SP 37 I-M exhibited the largest flow reading among all mixtures. Nevertheless, it was found that SP 37 I-M was bleeding during casting, although the recommended dosage on the bottle was 400-4000 ml/100 kg cement and the adding was 2200ml/100 kg cement (the medium dosage based on that recommendation). When checking with the product brochure, it was said: “Flowable concrete, initial slump 102mm – 38mm, the dosage is 500—1125 ml/100 kg cementitious materials”. It was obvious that the dosage of recommendation of the bottle was an over dosage. On the other hand, it showed that the much greater addition produced extreme workability (consistency) and bleeding. Another PNS based superplasticizer RHEOBUILD 1000 did not generate such high consistency. Perhaps, this dosage is not the optimum dosage for RHEOBUILD 1000. The effect of different dosages on the consistency will be shown in the latter section.

As mentioned in Chapter 2, water reducers can be added to concrete without changing mixture proportions, and produce proper workability of concrete. Generally speaking, water reducers work as dispersants to adsorb onto the surface of hydrating cement grains and generate an electrostatic repulsion among cement particles which break the agglomerates of cement particles into smaller particles, release the trapped water and lubricate cement particles as much as possible. Hence, improving the workability or flowability of concrete. Their dispersing efficiency depends on their natural species. Typically, high range water reducer (PNS) can reduce water up to 30%, and the water reduction of normal water reducer like sodium gluconate is 16% (Rixom et al, 1986; Spiratos, 2006). The high dispersing ability of chemical admixtures, and the relative high dosage, can produce high flowability of concrete, mortar and paste.

CIA-M and CNI-M are mixtures of Type C chemical admixture, corrosion inhibitors, which also can be used as accelerators. They exhibited high consistency if neglecting the contribution of amount of fluid they introduced to mortars. (5720ml and 6440ml for per 100Kg cement, respectively).

The two kinds of air entraining agents also improved consistency of mortar.

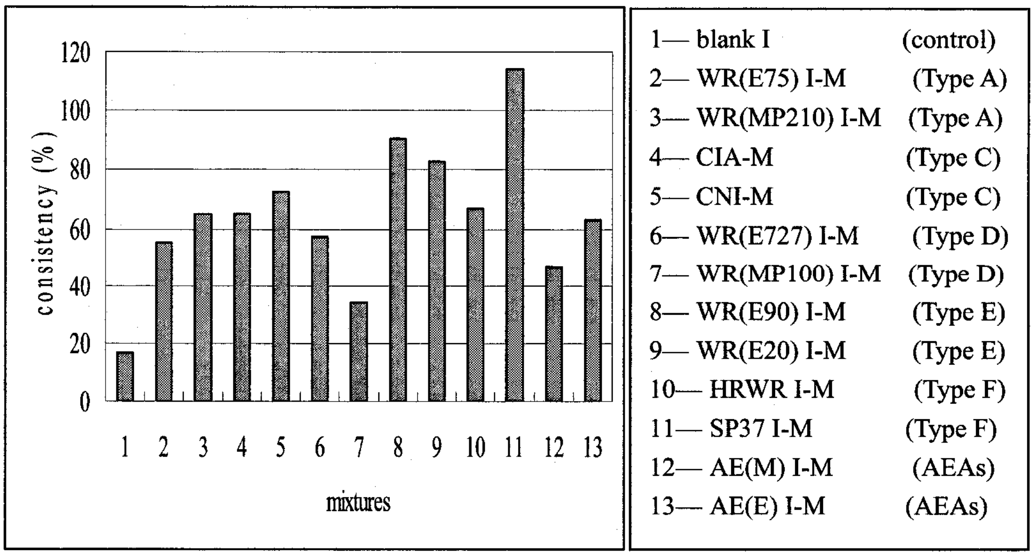


Figure 4.1 Consistency of mixtures

4.1.1.2 Conductivity

The conductivity of specimens was calculated by equation 3.1. The results shown in Table 4.1 and Figure 4.2 are the average of three specimens. The Figure 4.2 illustrates that the conductivity values of all mixtures was sharply reduced during the early hydration process (1-3 days), afterward it decreased gradually until the end of tests.

Type A

In Table 4.1, the conductivity values of mixtures WR (E75) I-M and WR (MP210) I-M were a little higher than that of control sample since the beginning of test. At 90 days, the conductivity of WR (MP210) I-M reached to the same level as that of the control sample, and the one of WR (E75) I-M was slightly higher than that of the control sample.

Type C

From Table 4.1 and Figure 4.2, it can be obviously seen that the conductivity of the samples CNI and CIA were higher than that of others since the beginning of the test. The samples CIA and CNI were EUCON CIA and RHEOCRETE CNI, respectively. They are calcium nitrite based corrosion inhibitors. It is well know that calcium nitrite based corrosion inhibitor results in high conductivity as it has been observed in RCPT tests (ASTM C1202-97). It is because that calcium nitrite solution causes high ionic concentration of the cement pore solution, which will be discussed later.

Table 4.1 The conductivity of mixtures W/C 0.485 (Phase I)

ASTM specification	Mix.	Conductivity (μS/cm)						
		1d	3d	7d	14d	21d	28d	90d
Control	Blank I	669	336	254	227	206	203	160
Type A	WR(E75) I-M	777	398	296	252	ND	195	180
	WR(MP210) I-M	863	358	263	263	228	216	160
Type C	CIA-M	925	494	371	311	320	296	243
	CNI-M	1136	669	504	451	411	379	293
Type D	WR(E727) I-M	876	333	326	320	282	266	228
	WR(MP100) I-M	1052	365	268	241	218	204	160
Type E	WR(E90) I-M	658	355	252	249	233	204	ND
	WR(MP20) I-M	685	335	268	264	235	233	183
Type F	SP 37 I-M	1000	423	322	281	258	235	166
	HRWR I-M	845	368	292	267	247	ND	ND
ASTM C 260 AEAs	AE(E) I-M	788	432	280	246	213	198	157
	AE(M) I-M	803	413	263	235	220	208	161

ND – no data

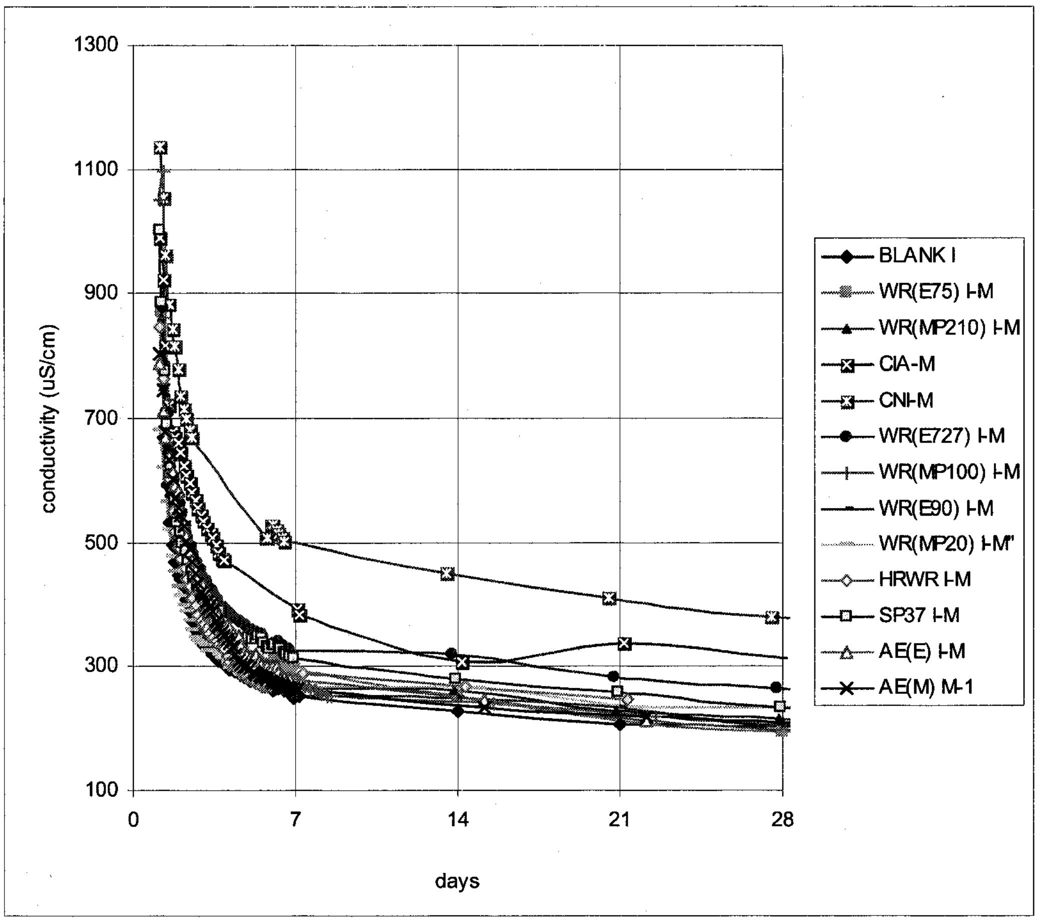


Figure 4.2 Conductivity versus casting time

Type D

WR (MP100) I-M, one of the mixtures containing Type D set retarding water reducer, had very high conductivity at the early age (1 and 2 days), the highest point of the conductivity curve was 1052 μS/cm at 1 days, which was 1.6 times of that of the control sample at the same age. However, the conductivity decreased quickly, reducing to 365 μS/cm at 3 days, almost the same value as that of the control sample and then it kept the same level with that of the control sample over time.

The other Type D mixture WR (E727) I-M exhibited high conductivity at early age, and it kept a relatively high value until the end of testing. It can be said that the setting retardation of this kind of admixture increases the conductivity of samples during the early hydration process.

Type E

The samples WR (E90) I-M and WR (MP20) I-M contained Type E accelerating water reducer. The conductivity values of these two samples were approximately the same or even a little lower than that of control sample. The main function of an accelerator is to accelerate the initial and final setting time as well as to increase the early and ultimate strength. The lower conductivity of these two samples was attributed to the rapid development of strength, especially at early ages, which is contrary to Type D samples.

Type F

The conductivity values of mixture SP37 I-M and mixture HRWR I-M were all higher than that of the control sample. As mentioned before, SP37 I-M was probably an over-dosage of EUCON 37. Therefore, the over dosage of EUCON 37 resulted in high conductivity.

Air entraining admixtures/agents

The conductivity of mixtures AE (M) I-M and AE (E) I-M were all higher than that of the control sample for the entire test period.

4.1.1.3 Degree of hydration

Degree of hydration was measured by non-evaporable water content (measured by the loss of water between 105°C and 1050°C). The results were calculated by equation 3.3. Figure 4.3 displays the degree of hydration of mixtures at 1 day, 3 days, 7 days and 28 days. As noted in the chapter 3, all mixtures are mortar, sand to cement ratio 2.75 to 1, and calculation of hydration was converted to represent cement paste.

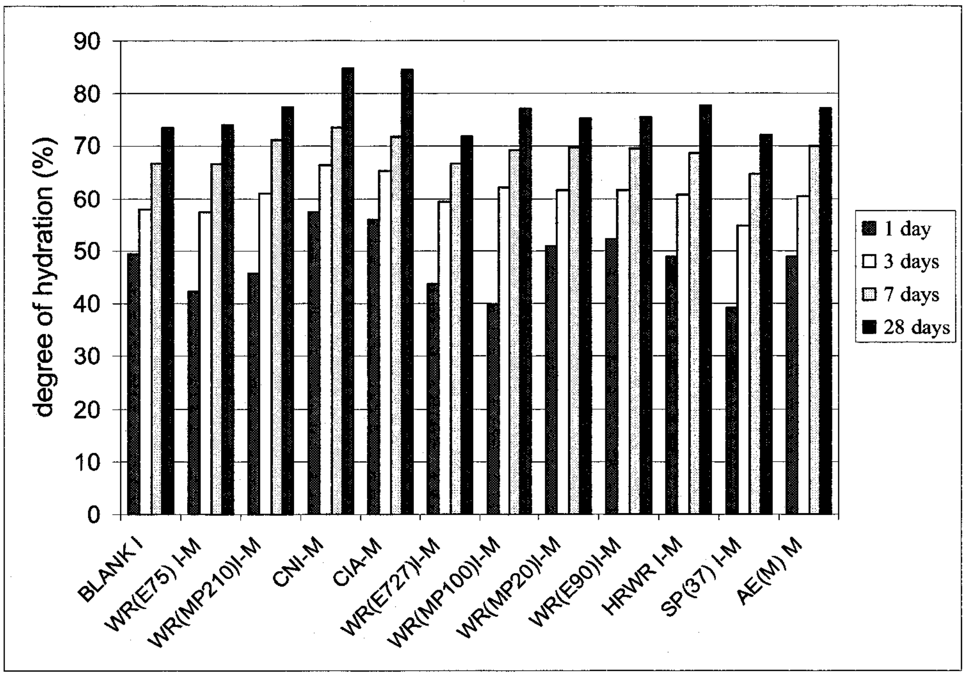


Figure 4.3 Degree of hydration

The degree of hydration of all mixtures gradually increased with time. The ultimate hydration predicted by Mills (Nokken, 2004) for Portland cement paste was 0.649 in W/C 0.40, and 0.762 in 0.50 W/C. In this section, the water to cement ratio of all mixtures is 0.485, the measuring result of the control sample at 28 days was 73%, matching Mill's prediction.

Type A

The hydration of WR (E75)I-M is considerably lower than that of the control sample at 1 day, however it caught up to the control sample at 3 days and then kept at the same level as that of the control sample for the rest of the test time. WR (MP210) I-M exhibited a lower hydration value than that of the control sample at 1 day as well. At 3 days, its hydration developed slightly faster than that of the control sample. Although EUCON 75 and Pozzolith 210 are normal setting water reducers, it seems that they delay hydration development at early age (1 day), but not significantly for the rest of time.

Type C

Mixtures CNI and CIA had the highest degree of hydration among all mixtures, not only at the earlier age, but also at the later age. The values of degree of hydration of these two mixtures of 1 day equaled to that of the control sample of 3 days, and their degree of hydration for 28 days were around 85%, much higher than that of the control sample's 73%. American Society for Testing and Materials published the research paper in 1977 to reveal that calcium nitrite can increase 28-day strength by over 6% for each per cent of calcium nitrite added (by weight of cement), starting with a large increase at the 24 h test (in Gaidis, 2004). The author pointed out that calcium nitrite was not primarily to protect steel from chloride, but simply to accelerate concrete without introducing the threat of chloride-induced corrosion, and also increasing 28-day strength, not decreasing strength as with calcium chloride.

Type D

The degree of hydration of mixtures WR (MP100) I-M and WR (E727) I-M were lower than that of the control sample at 1 day. But afterward, they increased quickly; the 3 days' value of mixture WR (MP100) I-M was over 60%, which was in the same level with that of Type E. The hydration of WR (E727) I-M developed slower than that of the control sample. The setting retarding water reducer EUCON 727 did affect the degree of hydration at early age. However, the POZZOLITH 100XR accelerated the degree of hydration after 3 days.

Type E

The degree of hydration of WR (MP200) I-M and WR (E90) I-M increased with time, but not as much as those of Type C. The interesting point is EUCO 90 is also calcium nitrite based accelerator. It is indicated that the concentration of calcium nitrite and the dosage of chemical admixture play the important role in effecting the conductivity and hydration development of sample. As corrosion inhibitor, the high concentration of calcium nitrite is necessary in order to increase the threshold of NO_2^- : Cl^- (Yang et al, 2002).

Type F

The mixture HRWR I-M possessed the same degree of hydration with the control sample at 1 day; afterward it increased slightly more than that of the control sample. Whereas, the degree of hydration of SP(37) I-M developed very slowly, its hydration values of 1 day and 3 days were considerably lower than that of the control sample for the same age, and its ultimate hydration (28 days) was still lower than that of the control sample, it was even lower than those of Type D. It was clearly shown that the over dosage of EUCON 37 severely affected the hydration development, even through superplasticizers are known as possess less retardation side effects compared with other types of water reducers.

Air Entraining Admixtures/Agents

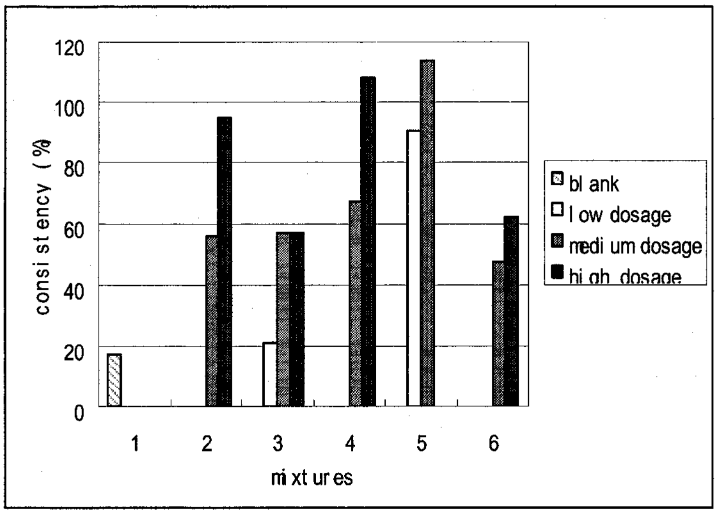
The degree of hydration of AE (M) I-M was a little lower than that of the control sample at 1 day, afterward it was slightly higher than that of the control sample.

4.1.2 Different addition of chemical admixtures

Based on the results of medium addition, 5 chemical admixtures were selected to be tested at different dosages. The selecting principle was that at least one admixture came from each type of classification. Among them, 3 were tested at their high dosages, (EUCON 75, RHEOBUILD 1000 and MICRO AIR); EUCON 37 was tested at its low dosage, and EUCON 727 was tested at both high and low dosages.

4.1.2.1 Consistency

Figure 4.3 displays the consistency of mixtures with different dosages of chemical admixtures. As expected, when the dosage is increased, the consistency of mixture WR(E75) I-H, HRWR I-H and AE (M) I-H increased; when the dosage of EUCON 37 was reduced, the consistency decreased. For the admixture of EUCON 727, when the addition was decreased, the consistency decreased. However, when increasing the addition, the consistency of WR (E727) I-H didn't change significantly comparing to the one of medium addition WR (E727) I-M. It can be said that EUCON 727 has limited ability to improve consistency by increasing dosage.



1—Blank I
2—WR(E75)I-M (type A)
WR(E75)I-H
3—WR(E727) I-L (Type D)
WR(E727) I-M
WR(E727) I-H
4—HRWR I-M (Type F)
HRWR I-H
5—SP(37) I-L
SP(37) I-M
6—AE(M) I-M (AEA)
AE(M) I-H

Figure 4.4 Consistencies of mixtures with different dosage of chemical admixtures

4.1.2.2 Conductivity

Type A (EUCON 75)

Table 4.2 lists the values of the conductivity results and the Figure 4.5 shows the behaviors of conductivity of the samples. It can be seen that conductivity values of both of two additions were higher than that of the control sample during the early hydration process. The increased dosage resulted in slightly higher conductivity during the early hydration process. For example, the high-range addition mixture WR(E75) I-H, the conductivity value of 1 day was 819 μS/cm, which was slightly higher than that of the middle-range addition mixture WR(E75) I-M at the same age. After 7 days, both of them gradually reached down to the same level with the one of control sample until the end of testing.

Table 4.2 Conductivity of mixture WR (E75) I at different dosages (W/C=0.485)

ASTM Specification	Mix	EUCON 75 Dosage (ml/ 100kg cement)	Conductivity (μS/cm) /Relative to Blank I						
			1d	3d	7d	14d	21d	28d	90d
control	Blank I	0	669	336	254	227	206	203	160
Type A	WR(E75) I-M	352	777/ 1.2	398/ 1.2	296/ 1.2	252/ 1.1	nd	195/ 1.0	180/ 1.1
	WR(E75) I-H	480	819/ 1.2	427/ 1.3	322/ 1.3	253/ 1.1	208/ 1.0	188/ 0.9	nd

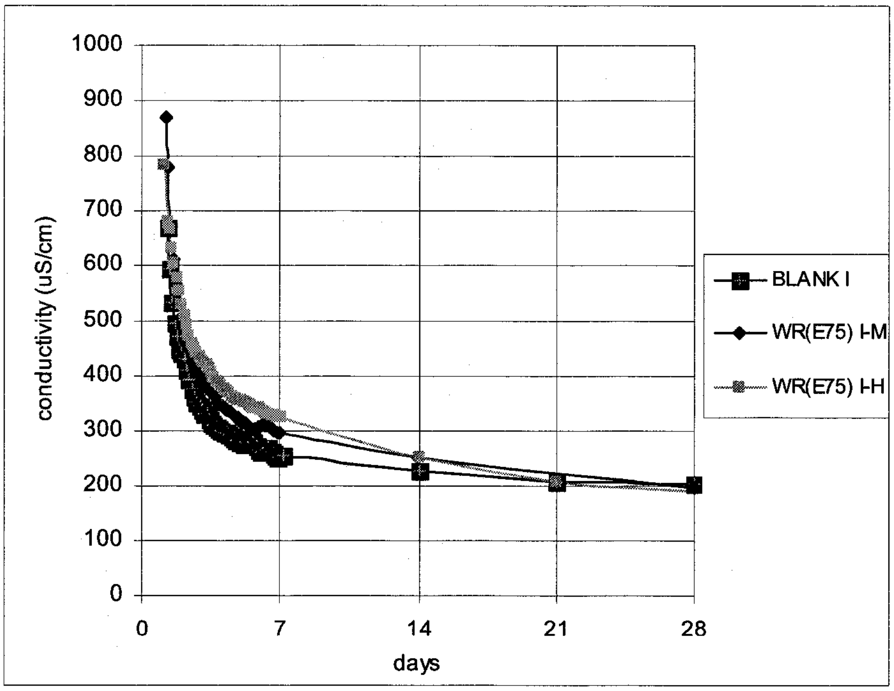


Figure 4.5 Conductivity of WR (E75) I mixed at different dosages of EUCON 75

Type C (EUCON CIA)

EUCON CIA is a calcium nitrite based corrosion inhibitor. The conductivity of mortars with middle and low range of EUCON CIA are shown in Table 4.3 and Figure 4.6. When decreasing the addition, the conductivity of CIA-L was approximately the same level with that of the control sample at all times. The conductivity increase can be attributed to the change of pore solution composition. The higher the addition of EUCON CIA, resulted in higher bulk conductivity.

Table 4.3 Conductivity of mixture CIA I at different dosages (W/C=0.485)

ASTM Specification	Mix	EUCON CIA dosage (ml/ 100 kg cement)	Conductivity (uS/cm) / Relative to Blank I						
			1d	3d	7d	14d	21d	28d	90d
Control	Blank I	0	669	336	254	227	206	203	160
Type C	CIA(E) I-M	5720	925/ 1.4	494/ 1.5	371/ 1.5	311/ 1.4	320/ 1.6	296/ 1.5	/
	CIA(E) I-L	2880	636/ 1.0	398/ 12	277/ 1.1	243/ 1.1	224/ 1.1	224/ 1.1	

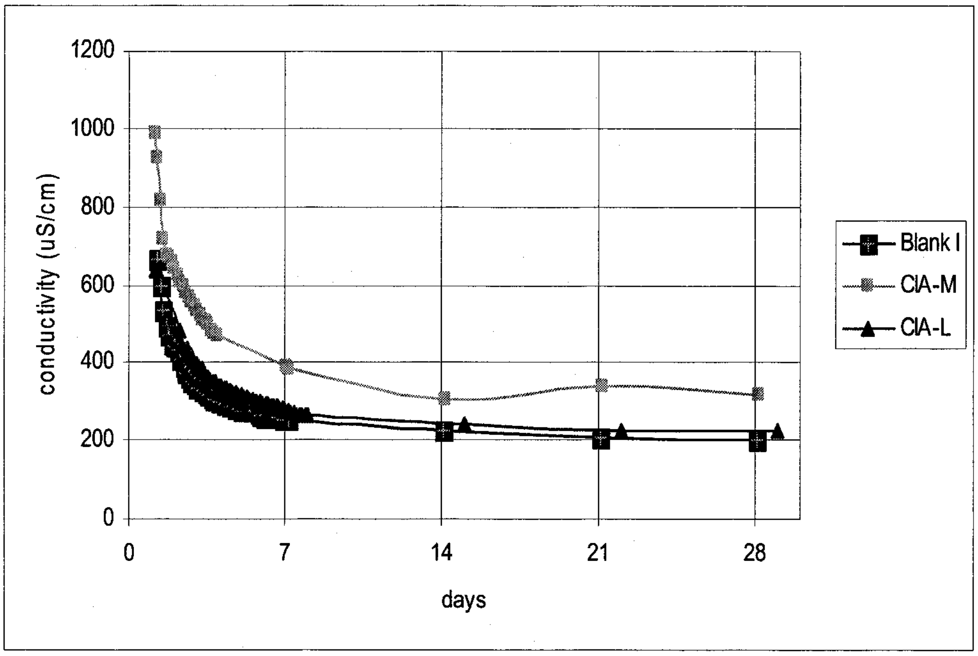


Figure 4.6 Conductivity of CIA (E) mixed at different dosages of EUCON CIA

Type D (EUCON 727)

EUCON 727 is set retarding water reducer, belonging to Type D. It contains a double metallo-organic salt derived from hydroxycarboxylic acids as the company's brochure describes. As noted in chapter 2, hydroxycarboxylic acids are organic chemicals, containing both hydroxyl and carboxyl groups in their molecules. Generally, the sodium salts are used. They have strong retarding function at the high dosages (Rixom et al, 1986). Figure 4.7 shows the conductivity curves of samples with three dosages of EUCON 727. Table 4.6 lists their conductivity values and relation to the control sample. Addition of EUCON 727 raised the conductivity of mortars, and the greater dosage of EUCON 727, the higher the bulk conductivity. WR (E727) I-L was added at low dosage, its conductivity curve almost overlapped with that of the control sample except a couple of the first testing points. It indicated that low dosage of EUCON 727 didn't change the sample's conductivity significantly. For the sample WR (E727) I-M added at mid-range dosage, the conductivity of 1 day was 1.3 times of that of the control sample, and then reduced gradually, but still kept this relation until the end of the test. WR(E727) I-H, the high addition sample, the conductivity was distinctly higher than those of other samples at the early age, the conductivity was 1627µS/cm at 1 days, it was 2.4 times of that of the control sample at the same age, 2.1 times of that of WR(E727) I-L, 2.0 times of that of WR(E727) I-M. At 7 days, the conductivity of WR (E727) I-H reduced to 1.4 times of that of the control sample and kept this level to the end of the test. The conductivity increase was probably caused by the retardation of EUCON 727. As mentioned earlier, hydroxycarboxylic acids have strong retarding function at the high dosages.

Table 4.4 Conductivity of mixtures WR (E727) I at different dosages (W/C=0.485)

ASTM Specification	Mix	EUCON 727 dosage (ml/ 100 kg cement)	Conductivity (µS/cm) / Relative to Blank I						
			1d	3d	7d	14d	21d	28d	90d
control	Blank I	0	669	336	254	227	206	203	160
Type D	WR(E727) I-M	124	876/ 1.3	445/ 1.3	326/ 1.3	320/ 1.4	282/ 1.4	266/ 1.3	228 1.4
	WR(E727) I-L	76	871/ 1.3	350/ 1.1	270/ 1.1	237/ 1.0	214/ 1.0	209/ 1.0/	nd
	WR(E727) I-H	228	1627/ 2.4	583/ 1.7	367/ 1.4	305/ 1.3	290/ 1.4	266/ 1.3	nd

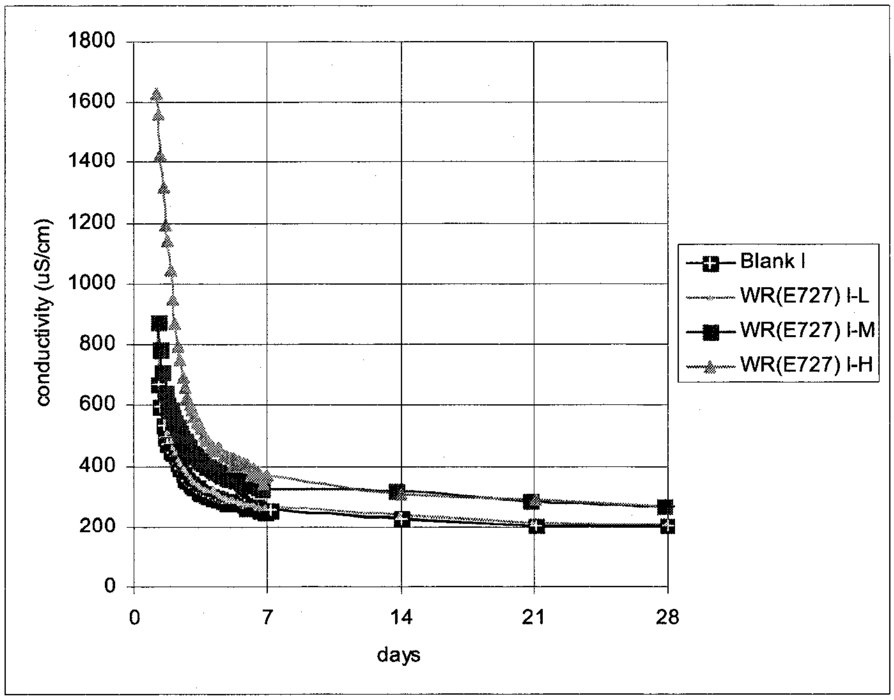


Figure 4.7 Conductivity of WR (E727) I mixed at different dosages of EUCON 727

Type F

RHEOBUILD 1000

Table 4.5 and Figure 4.8 show the mortar conductivity results of two dosages of RHEOBUILD 1000. It was easier to find that the characteristic of conductivity was that the greater the addition, the higher conductivity, especially in the early age. At 1 day, the conductivity of the high dosage sample HRWR I-H is 1.7 times of that of the control sample, and the conductivity of the mid-range dosage sample HRWR I-M was 1.3 times of that of the control sample. Since 3 days, the conductivity of HRWR I-H reduced to around 1.3 times of that of the control sample, and then it kept this level until the end of the test. Both of these two additions the conductivity values were all higher than that of the control sample for the whole test.

Table 4.5 Conductivity of mixture HRWR I at different dosages (W/C=0.485)

ASTM Specification	Mix	RHEOBUILD 1000 Dosage (ml/ 100Kg cement)	Conductivity (μS/cm) / Relative to Blank I						
			1d	3d	7d	14d	21d	28d	90d
Control	Blank I	0	669	336	254	227	206	203	160
Type F	HRWR I-M	1140	845/ 1.3	369/ 1.1	291/ 1.1	267/ 1.2	247/ 1.2	nd	nd
	HRWR I-H	1600	1155/ 1.7	418/ 1.2	322/ 1.3	285/ 1.3	258/ 1.3	248/ 1.2	nd

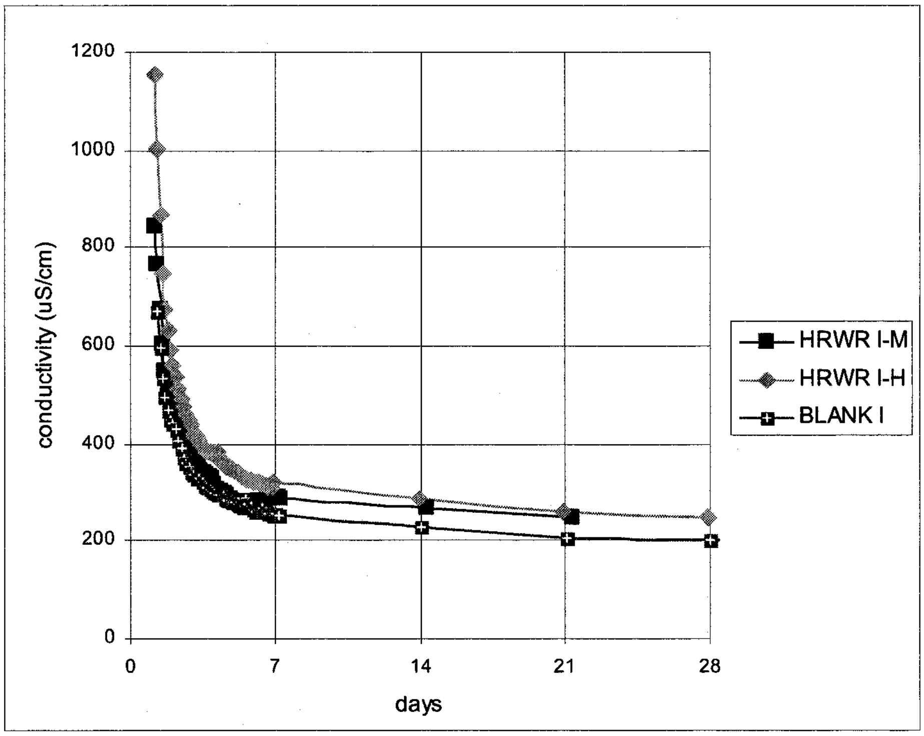


Figure 4.8 Conductivity of HRWR I mixed at

different dosages of RHEOBUILD 1000

EUCON 37

EUCON 37 is also sulfonated naphthalene formaldehyde condensates superlasticizer. The conductivity behaviors of two additions of this type of species are displayed in the Table 4.6 and Figure 4.9. As mentioned in the previous experiments, the middle range addition of EUCON 37 was probably an over-dosage. The conductivity of SP (37) I-M was higher than that of the control sample as expected. When decreasing the addition, the mixture of the low dosage SP(37) I-L, the conductivity of 1 day was 1.2 times of the one of the control sample, and it reduced to slightly lower than that of the control sample around 3 days, and then kept roughly same with the control sample until the end of the test.

Table 4.6 Conductivity of mixture SP (37) I at different dosages (W/C=0.485)

ASTM Specification	Mix	EUCON 37 dosage (ml/ 100Kg cement)	Conductivity (µS/cm) / Relative to Blank I						
			1d	3d	7d	14d	21d	28d	90d
control	Blank I	0	669	336	254	227	206	203	160
Type F	SP(37) I-M	2200	1001/ 1.5	423/ 1.3	322/ 1.3	281/ 1.2	258/ 1.3	235/ 1.2	167 1.0
	SP(37) I-L	1120	821/ 1.2	295/ 0.9	228/ 0.9	219/ 1.0	215/ 1.0	204/ 1.0/	nd

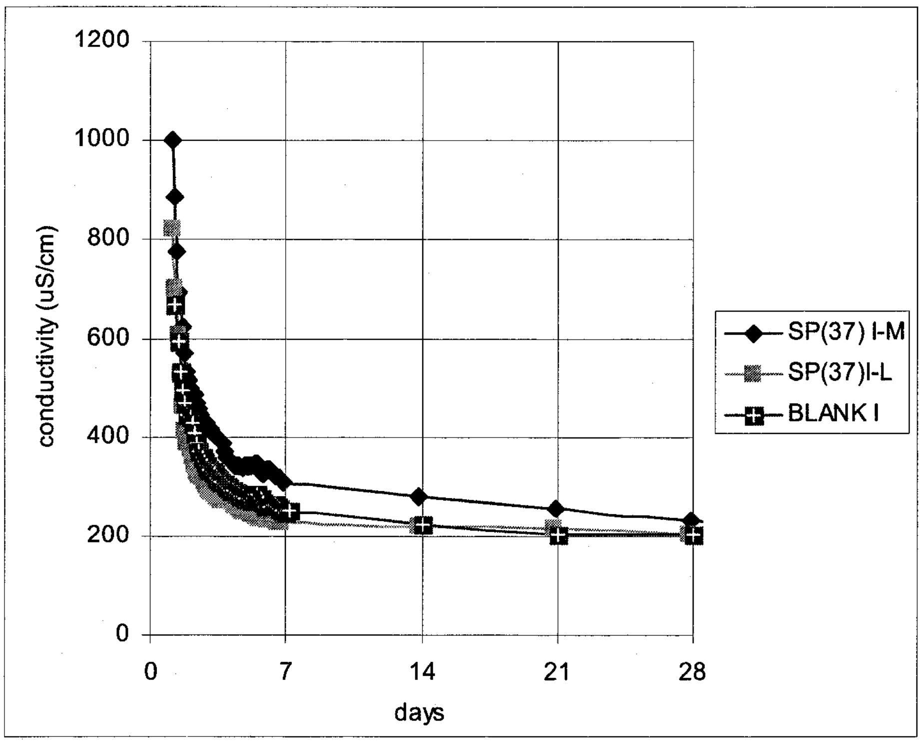


Figure 4.9 Conductivity of SP 37 I mixed at different dosages of EUCON 37

RHEOBUILD 1000 and EUCON 37 are sulfonated naphthalene formaldehyde condensates superlasticizer (SNF), also designated as PNS (polynaphthalene sulphonate). As mentioned in chapter 2, this kind of chemical admixture contains sodium which is used to neutralize the sulphonic acid during polymerization (Rixom et al, 1986). Rixom (1986) found that some of sodium ions which were not absorbed by hydrate particles or hydration products stayed in the pore solution, and also some sodium ions absorbed by hydration products at the early hydration period, leached into the pore solution gradually with time. Early work indicated that PNS was less strongly adsorbed onto the hydrating products than normal water reducers, and later work further showed that the higher molecular weight PNS was strongly adsorbed and lower molecular weight species remained in solution (Rixom et al, 1986). Whether high or low molecular weight of PNS, sodium ions and/or potassium ions gradually leach to the pore solution. Both of these ions present in the pore solution contribute to increase the bulk conductivity by raising the ionic concentration of the pore solution, especially at the addition of high dosages. On the other hand, the commercially lower polymerization PNS tends to reduce the surface tension of the aqueous phase in the concrete and can lead to air entrapment (Rixom et al, 1986). Furthermore, the retardation affection of this type of admixture, especially at high additions results in early hydration developing slowly. All these factors can contribute to raise the conductivity of mortars.

Based on the results of EUCON 37 and RHEOBUILD 1000, it can be concluded that the greater addition of sulfonated naphthalene formaldehyde condensate superlasticizer, the higher the bulk conductivity of mixtures. Although EUCON 37 and RHEOBUILD 1000 are the same species admixture, they came from different companies, they probably possess different solid concentration, purity, molecular weight, etc. All these factors will affect their behaviors. Therefore, it is unnecessary to make a detailed comparison of their mortar's conductivity between these two commercial products.

AEAs (MICRO AIR)

AIR MICRO is multi component synthetic based surfactant. AE (M) I-M was the medium dosage, AE(M) I-H was the high dosage. Table 4.7 and Figure 4.10 display the results of this admixture.

In the Figure 4.10, the medium dosage of AIR MICRO showed high bulk conductivity at the early hydration age. It is probably caused by AEAs retarding hydration development at the early age (Rixom et al, 1986). For the high dosage, the lower bulk conductivity was probably due to the larger volume of entrained air in the sample (Rixom et al, 1986), and as mentioned before, these bubbles are disconnected, which can cut the conductivity path.

Table 4.7 Conductivity of mixture AE (M) I at different dosages (W/C=0.485)

ASTM Specification	Mix	AIR MICRO Dosage (ml/ 100Kg cement)	Conductivity (µS/cm) / Relative to Blank I						
			1d	3d	7d	14d	21d	28d	90d
control	Blank I	0	669	336	254	227	206	203	160
Type A&F	A(M) I-M	64	803/ 1.2	413/ 1.2	263/ 1.0	235/ 1.0	220/ 1.0	208/ 1.0	161 1.0
	AE(M) I-H	120	393/ 1.2	213/ 0.9	160/ 0.9	175/ 1.0	134/ 1.0	128/ 1.0/	nd

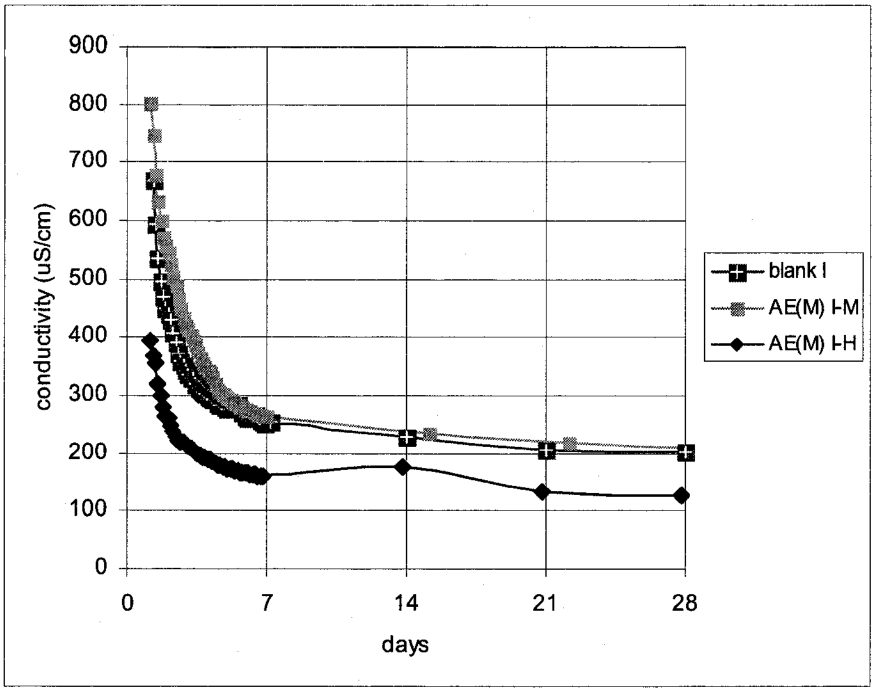


Figure 4.10 Conductivity of AE (M) I mixed at different dosages of MICRO AIR

4.1.3 Degree of hydration

The results are shown in the Figure 4.11.

Type A (EUCON 75)

The degree of hydration for mixtures WR (E75) I-M and WR (E75) I-H were similar at 1 day, and both were lower than that of the control sample. After 3 days, the hydration degree of WR (75) I-M kept the same level with the one of the control sample until the end of the test, whereas the hydration of WR (E75) I-H developed faster than that of WR (E75) I-L and the control sample. It can be said that the greater addition of EUCON 75 delayed the hydration development at the early age, but slightly affected on the late age hydration.

Type D (EUCON 727)

As expected, the degree of hydration of the mixtures with EUCON 727 exhibited lower degree of hydration with increasing addition, especially in the early hydration process. The hydration of WR (E727) I-H was only 18% at 1 day, which was much lower than that of the control sample. However, at later ages of all three mixtures did not show lowered degree of hydration.

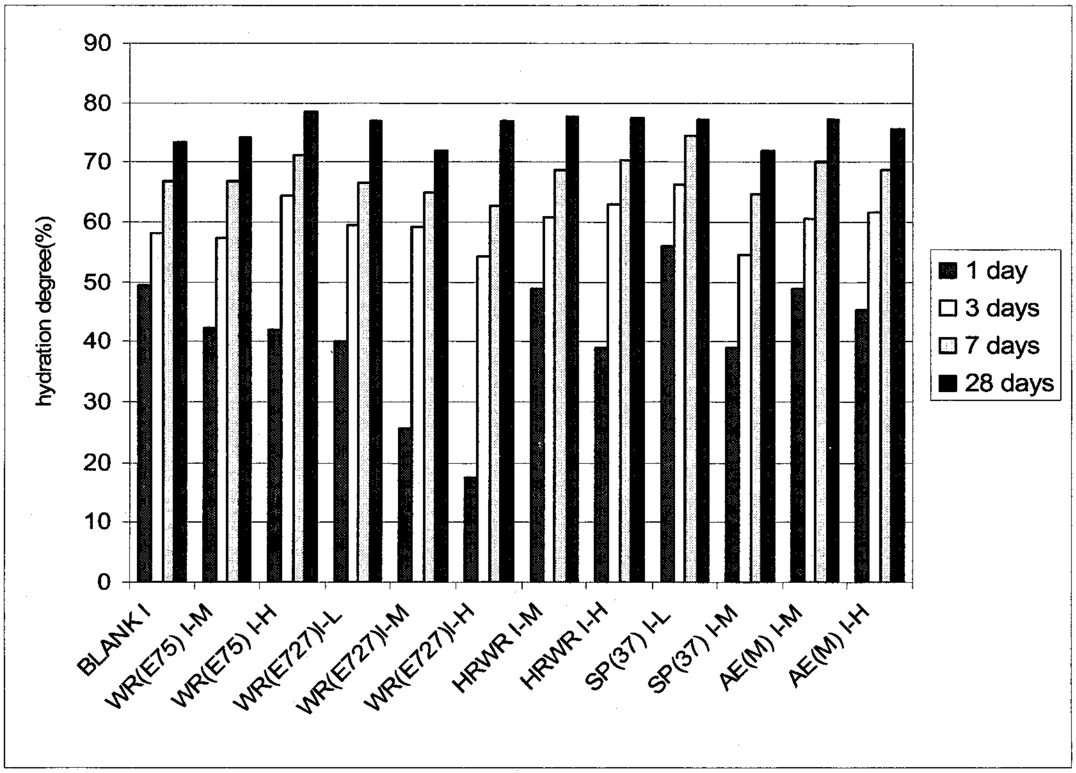


Figure 4.11 Degree of hydration

Type F

RHEOBUILD 1000

For the increased dosage of RHEOBUILD 1000, the hydration of mixture HRWR I-H was noticeably delayed at 1 day, however, it recovered by 3 days, its hydration degree climbed up a little higher than the one of HRWR I-M, and then it developed at the same speed with that of HRWR I-M at the rest of the test period.

EUCON 37

In the case of EUCON 37, the over dosage sample SP37 I-M had obviously lower hydration degree at all test periods compared to the control sample. When reducing the dosage, the degree of hydration of SP37 I-L was remarkably higher than those of SP37 I-M and the control sample. Its hydration of degree for 1 day, 3 days, and 7 days almost equaled to the one of SP37 I-L for 3day, 7 days and 28 days, respectively.

Combining of the results of RHEOBUILD 1000 and EUCON 37, mixture SP37 I-L had high degree of hydration and low conductivity. It seems that proper additions of high range water reducing agents can increase degree of hydration at either early age or late age. Increasing additions to a certain point, early hydration can be retarded; over dosage has severe effect on degree of hydration.

AEAs (MICRO AIR)

Increasing the addition of air entraining agent MICRO AIR slightly reduces the hydration degree. It is well known that air entrained pastes have lower strength than that of non-air entrained pastes. Rixom et al (1986) pointed out that some anionic air-entraining agents, such as neutralized wood resins and sulphates, their high dosage can retard C_3S peak, and sodium oleate based air-entraining agents retard ettringite and monosulphate reaction.

4.2 Phase II experiment - 0.35 water to cement ratio

4.2.1 Medium dosage addition of chemical admixtures

4.2.1.1 Consistency

In this part, the water to cement ratio reduced from 0.485 to 0.35, the sand to cement ratio was kept at 2.75. When preparing the samples, some were found to be very dry; for example, blank II, AE (M) II-M, AE (E) II-M, WR (MP210) II-M and WR (MP100) II-M were very sandy, when doing flow table reading, these materials collapsed rather than spreading. WR (MP20) II-M, WR (MP90) II-M, WR (MP75) II-M, SP (37) II-M and HRWR II-M were better, they were a little plastic, but could not read the flow, either. The reduction of water to cement ratio markedly reduces consistency of mixtures.

4.2.1.2 Conductivity

The phase II experiments exhibited significantly different conductivity results compared with those of phase I. Table 4.8 and Figure 4.12 illustrates their behavior.

Control sample

In Table 4.8, the sample of blank II exhibited pronouncedly higher conductivity than the one of blank I at all testing ages. In the Figure 4.12, the conductivity curve of blank II did not show the sharp downward slope in the early hydration period as did blank I. Its highest conductivity value was 1522 μS/cm at 1 day, 2.2 times of that of blank I. Its conductivity at 7 days was 1072 μS/cm, still above 1000 μS/cm, 4.2 times of that of blank I, and 3.1 times of that of the blank I at the age of 14 days. After 21 days, its conductivity value kept constant, but still higher than 500 μS/cm. The appearance of the sample was very porous; the high conductivity probably resulted from its high porosity which will be discussed in the next chapter.

Table 4.8 The conductivity of mixtures W/C =0.35 (Phase II)

ASTM specification	Mixture		Conductivity(uS/cm) /Relative to Blank II				
		1d	3d	7d	14d	21d	28d
control	Blank I	669	336	254	227	206	203
	Blank II	1445/2.2*	1247/3.7*	1072/4.2*	711/3.1*	578/2.8*	561/2.8*
Type A	WR(E75) II-M	1027/0.71	891/0.71	683/0.64	389/0.55	340/0.59	317/0.57
	WR(MP210) II-M	1434/1.0	1109/0.89	930/0.87	584/0.82	378/0.65	232/0.41
Type D	WR(E727) II-M	1743/1.2	700/0.56	527/0.49	542/0.76	572/0.99	503/0.9
	WR(MP100) II-M	1947/1.3	1260/1.0	1242/1.2	591/0.83	487/0.84	484/0.86
Type E	WR(E90) II-M	763/0.53	547/0.44	481/0.45	409/0.58	314/0.54	288/0.51
	WR(MP20) II-M	831/0.58	594/0.48	481/0.45	409/0.58	314/0.54	288/0.51
Type F	SP 37 II-M	494/0.34	280/0.22	219/0.2	163/0.23	145/0.25	139/0.25
	HRWR II-M	474/0.33	222 /0.18	204 /0.19	172 /0.24	153/0.26	156/0.28
ASTMC260 AEAs	AE(M) II-M	794/0.5	785/0.6	669/0.6	499/0.7	429/0.7	389/0.7

* rate of blank I.

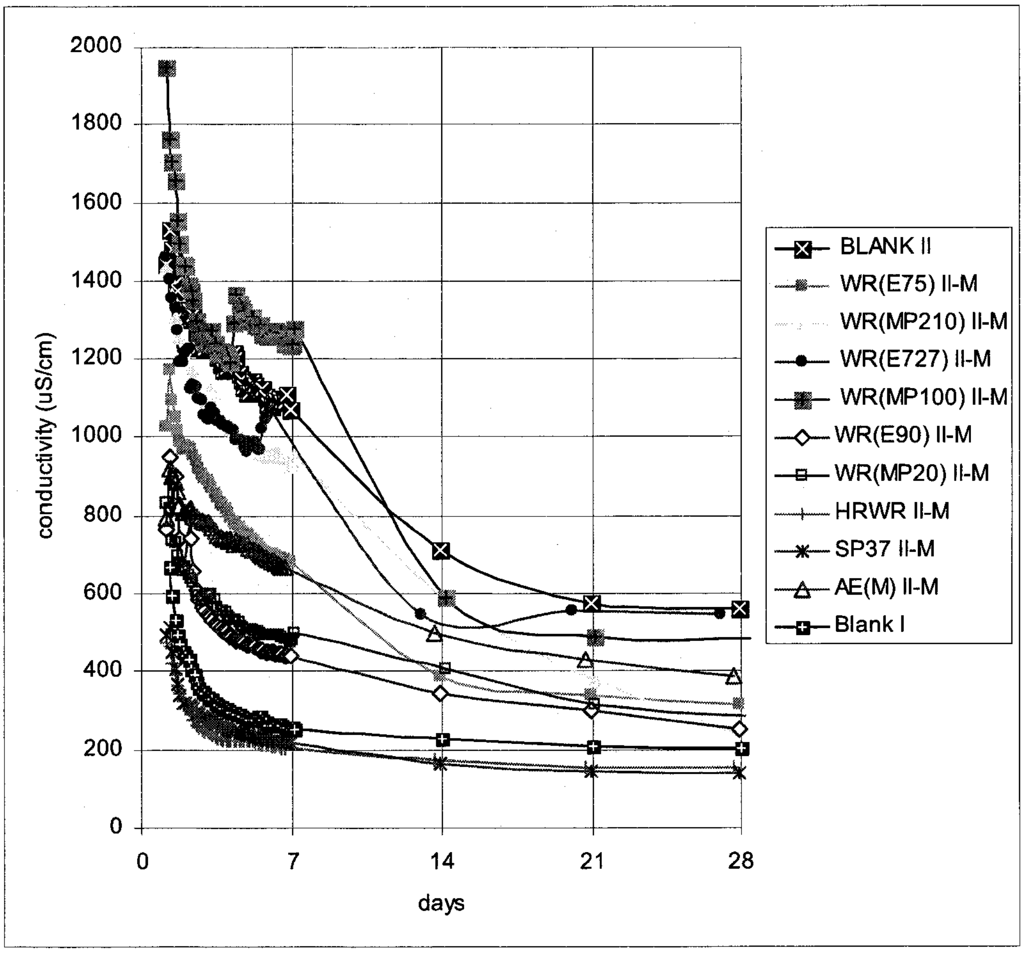


Figure 4.12 Conductivity of phase II versus time

Type A

The conductivity of mixture WR (E75) II-M was lower than that of the control sample (blank II). Its conductivity at 1 day was 0.71 times of the one of the control sample, and at 28 days, it reduced to 0.57 times of the one of the control sample. WR (MP210) II-M showed slightly lower conductivity than that of the control sample at early ages. After 14 days, it decreased rapidly. At 28 days, it was only 0.41 times of that of the control sample.

The conductivity behaviors of Type A mixtures in the phase II experiment were different from those of phase I experiment. In phase I experiment the conductivity values of the mid-range addition were all higher than that of the control sample, whereas in phase II they mostly showed the lower values than that of the control sample.

Type D

The conductivity values of WR (E727) II-M and WR (MP100) II-M were high in the early age, especially WR (MP100) II-M, its first test point almost reached to 2000 uS/cm, even higher than that of the control sample, but it reduced quickly. EUCON 727 and POZZOLITH 100XR are set retarding water reducers, their conductivity performance was similar with those of mixtures with high water to cement ratio. The high conductivity of early age was partially caused by their set retardation.

Type E

The conductivity values of WR (E90) II-M and WR (MP20) II-M were approximately half of the control sample for the whole testing time. Both of the mixtures showed the similar or lower conductivity than the control sample, which was the same behavior with what they did in the phase I. The difference was that the conductivity values are much lower than that of the control sample in this phase. Their accelerating function propelled development of micro-structure, reducing the connective path of the solid mortars.

Type F

As expected, both of the HRWR II-M and SP 37 II-M showed extremely low conductivity in the whole test. For SP 37 II-M, its first test point was only 0.34 times of the one of the control sample, then kept around 0.25 times of the one of the control sample; the mixture HRWR II-M, its first test point was just 0.33 times of the one of the control sample. As it was mentioned in phase I experiments, the mid-range dosage of EUCON 37 was an over-dosage in fact, and it caused bleeding for SP37 I-M and high conductivity value. However, in the low water to cement ratio, mixture SP 37 II-M did not induce bleeding and possessed very low conductivity.

Air entraining admixtures/agents

The conductivity curve of AE (M) II-M was lower than that of the control sample. As noted before, air entraining agents can introduce micro-bubbles into the mortars hence separate the connective conductivity path.

Conductivity Summary

From above conductivity results, it can be seen that in the low water to cement ratio mixtures, addition of water reducers can reduce bulk conductivity of samples, except for set retarding species. Among the water reducers, high range water reducing agents are very efficient for reducing bulk conductivity; accelerating water reducers are more efficient than normal setting water reducing agents. Setting retarding water reducers increase bulk conductivity in the early hydration process due to their setting retardation. Air entraining agents also reduce the conductivity of mortar thanks to introducing the micro bubbles to separate the connective conductivity path.

4.2.2 Different addition of chemical admixtures

Based on above results, 5 chemical admixtures were selected to test the effect of different addition on conductivity of samples. They are EUCON 75, EUCO 727, RHEOBUILD 1000, EUCO 37 and MICROAIR.

4.2.2.1 Consistency

Increasing the addition of admixtures caused the mixtures to exhibit a little plasticity, but the spreading of the flow table was not increased.

4.2.2.2 Conductivity

Type A (EUCON 75)

Table 4.9 and Figure 4.13 display the conductivity results of different additions of EUCON 75. It was clearly shown that the conductivity of high dosage addition mortar was lower than that of medium dosage mortar in the early hydration process.

Table 4.9 Conductivity of mixture WR (E75) II at different dosages

(W/C=0.35)

ASTM Specification	Mix	EUCON75 Dosage (ml/ 100 kg cement)	Conductivity (μS/cm)/ Relative to Blank II					
			1d	3d	7d	14d	21d	28d
Control I	Blank I	0	669	336	254	227	206	203
Control II	Blank II	0	1445	1247	1072	711	578	561
Type A	WR(E75) II-M	352	1027/ 0.7	891/ 0.7	683/ 0.6	389/ 0.5	341/ 0.6	317/ 0.6
	WR(E75) II-H	480	979/ 0.7	585/ 0.5	486/ 0.5	425/ 0.6	372/ 0.6	335/ 0.6

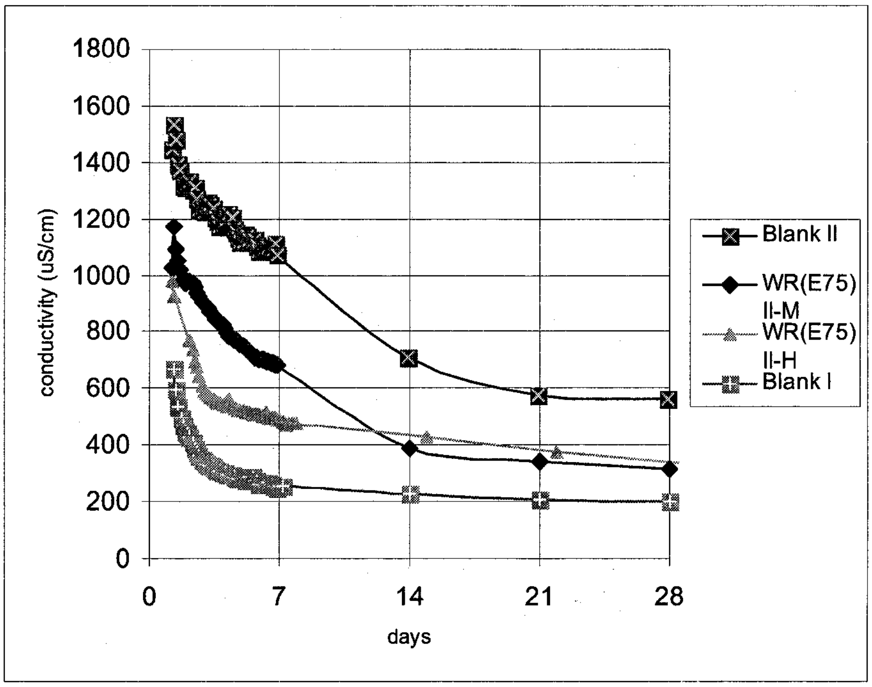


Figure 4.13. Conductivity of WR (E75) II

mixed with difference dosages of EUCON75

<u>Type D (EUCO 727)</u>

As expected, the conductivity of high addition of EUCON 727 was higher than that of the control sample during the early hydration process. However, it reduced quickly. After 3 days, it reached to the level of the control sample, reducing until the end of test. It makes sense that as set retarding water reducer, adding more EUCON 727 delayed the development of hydration and microstructure in the early hydration period therefore raised the bulk conductivity of mortars.

Table 4.10 Conductivity of mixture WR (E727) II at different dosages

(W/C=0.35)

ASTM Specification	Mix	EUCON 727 dosage (ml/ 100 kg cement)	Conductivity (µS/cm) / Relative to Blank II					
			1d	3d	7d	14d	21d	28d
Control I	Blank I	0	669	336	254	227	206	203
Control II	Blank II	0	1445	1247	1072	711	578	561
Type D	WR(E727) II-M	124	1743/ 1.2	700/ 0.56	527/ 0.49	542/ 0.76	572/ 0.99	503/ 0.9
	WR(E727) II-H	216	1846/ 1.3	1090/ 0.9	881/ 0.8	528/ 0.7	442/ 0.76	448/ 0.80

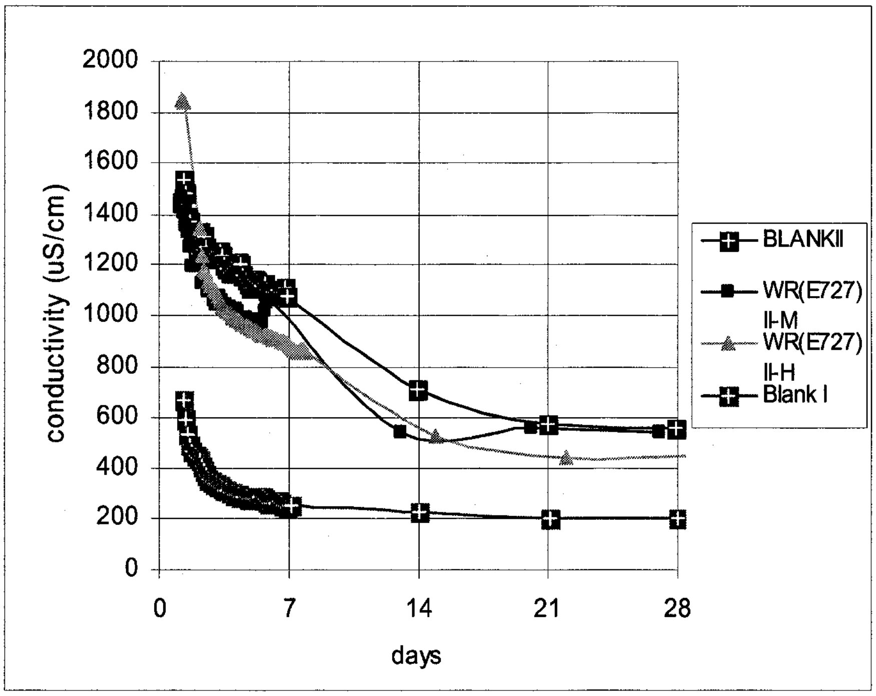


Figure 4.14 Conductivity of WR(E727) II mixed at different dosages of EUCON 727

Type F

RHEOBUILD 1000

Table 4.11 and Figure 4.15 display the conductivity results of HRWR II-M and HRWR II-H. Their conductivity behaviors were that increasing the addition of RHEOBUILD 1000 admixture decreased the bulk conductivity. This trend was on the contrary to that of the high water cement ratio mixtures. The conductivity of these two addition mixtures was much lower than that of the control sample, and even lower than that of blank I.

Table 4.11 Conductivity of mixture HRWR II at different dosages (W/C=0.35)

ASTM Specification	Mix	RHEOBUILD 1000 dosage (ml/ 100 kg cement)	Conductivity (µS/cm) /Relative to blank II					
			1d	3d	7d	14d	21d	28d
Control I	Blank I	0	669	336	254	227	206	203
Control II	Blank II	0	1445	1247	1072	711	578	561
Type F	HRWR II-M	1140	474/ 0.33	222 / 0.18	204 / 0.19	172 / 0.24	153/ 0.26	156/ 0.28
	HRWR II-H	1600	385/ 0.27	198/ 0.16	153/ 0.14	132/ 0.19	116/ 0.20	122/ 0.22

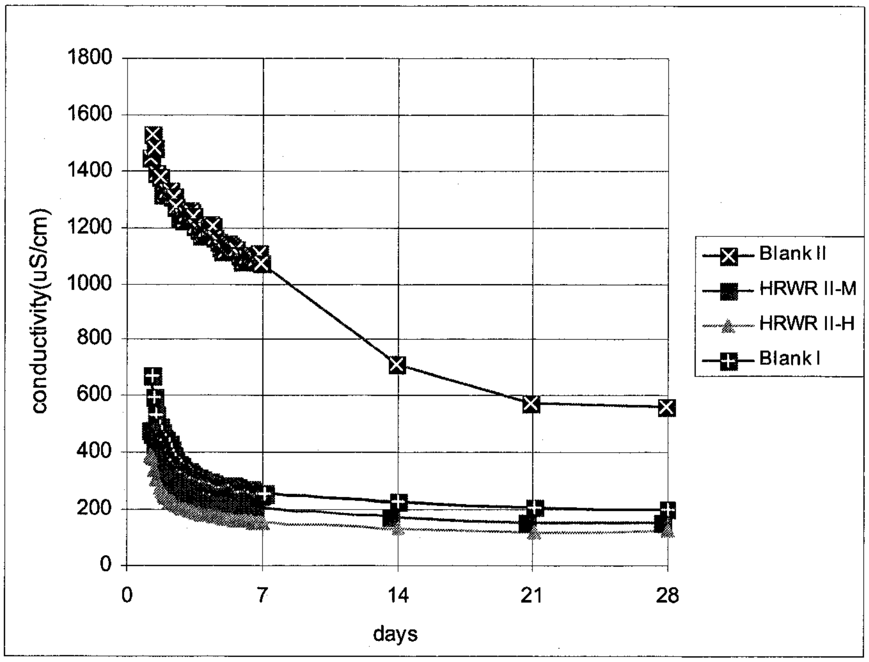


Figure 4.15 Conductivity of HRWR II mixed at

different dosages of RHEOBUILD 1000

EUCO 37

The conductivity results are listed in Table 4.12 and Figure 4.16. Both of the conductivity of SP (37) II-M and SP (37) II-L were markedly lower than that of the control sample. They were just 20%-30% of the one of the control sample. The conductivity of the medium dosage mixture (over- dosage) SP(37) II-M was a little higher than that of SP(37) II-L, especially at the early age. The results indicated that even in the low water to cement ratio condition, the over dosage addition of EUCON 37 still caused relatively high conductivity comparing with the conductivity of low addition mixture.

In the literature review section it was discussed that the conductivity of concrete, mortar or paste is the competing result of change of ionic concentration of pore solution and development of tortuous pore structure. It seems that under lower water to cement ratio condition, the latter factor is predominant. It is clear that in the low water to cement ratio, appropriate addition of PNS exhibits strong water reduction, it disperses mixing water efficiently and makes hardened samples less porous, hence lowing conductivity.

Table 4.12 Conductivity of mixture SP (37) II at different dosages (W/C=0.35)

ASTM Specification	Mix	EUCON 37 dosage (ml/100 kg cement)	Conductivity (μS/cm) /Relative toBlank II					
			1d	3d	7d	14d	21d	28d
control	Blank I	0	669	336	254	227	206	203
control	Blank II	0	1445	1247	1072	711	578	561
Type F	SP(37) II-M	2200	494/ 0.34	280/ 0.22	219/ 0.2	163/ 0.23	145/ 0.25	139/ 0.25
	SP(37) II-L	1120	365/ 0.25	192/ 0.15	146/ 0.14	130/ 0.18	122/ 0.21	125/ 0.22/

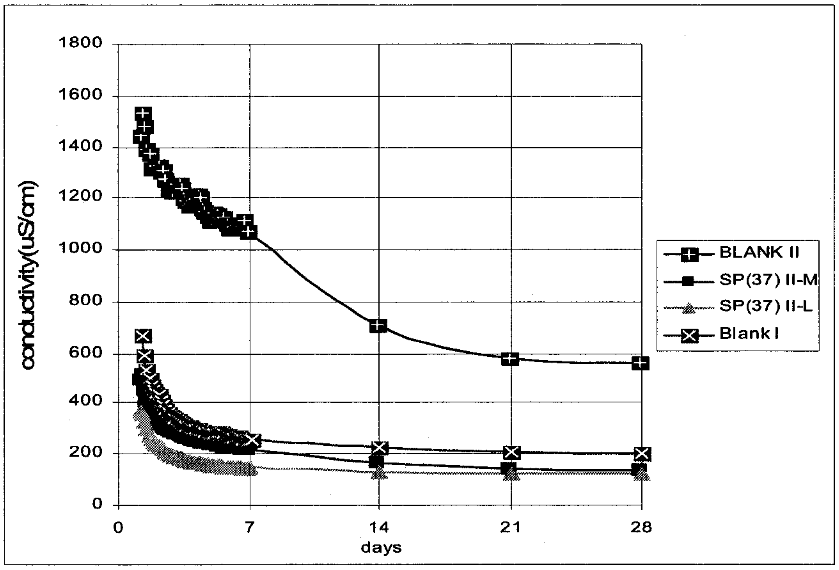


Figure 4.16 Conductivity of SP37 mixed at different dosages of EUCON37

AEAs (MICROAIR)

Adding MICROAIR, the bulk conductivity was reduced, and the higher addition, the lower the conductivity (Figure 4.17).

Table 4.13 Conductivity of mixture AE (M) II at different dosages (W/C=0.35)

ASTM Specification	Mix	MICROAIR Dosage (ml/100 kg cement)	Conductivity (μS/cm) /Relative to Blank II					
			1d	3d	7d	14d	21d	28d
Control I	Blank I	0	669	336	254	227	206	203
Control II	Blank II	0	1445	1247	1072	711	578	561
AEAs	AE(M) II-M	640	794/ 0.5	785/ 0.6	669/ 0.6	499/ 0.7	429/ 0.74	389/ 0.69
	AE(M) II-H	1200	783/ 0.54	736/ 0.59	588/ 0.55	480/ 0.68	ND	370/ 1.0/

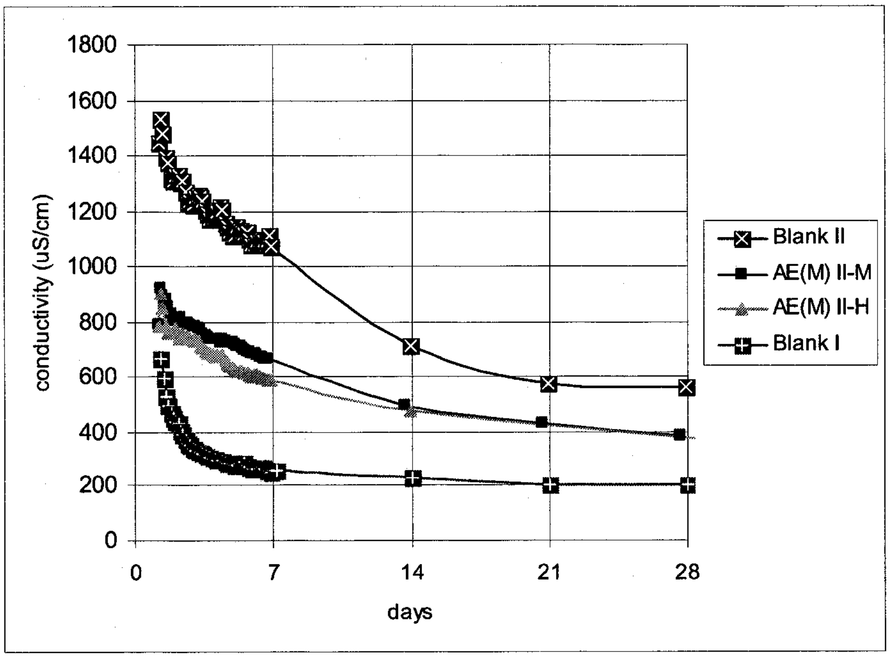


Figure 4.17 Conductivity of AE (M) II mixed at different dosages of MICRO AIR

4.2.3 Degree of hydration

Some samples were selected to test their degree of hydration. The selection was based on their conductivity performance, if both samples using same ASTM type of admixtures exhibited similar conductivity behavior, only was one of them chosen to test hydration. For example, samples of WR (E90) and WR (MP20) have similar conductivity curves, only WR (E90) was tested for hydration.

The ultimate hydration predicted by Mills (in Nokken, 2004) for Portland cement paste with W/C 0.35 was 0.663, the degree of hydration of blank II at 28 days was 0.659, which matched Mill's results very well. The degree of hydration of each admixture was not significantly different from its counterpart at the high water cement ratio. But the high addition of EUCON 727 did not show very low degree of hydration at the early hydration time as it did in the phase I experiments. For instance, the hydration value of WR(727) II-3 at 1 day was 36%, whereas WR(727) I-3 was only 17.5%. For the superplasticized mixtures, there was not a significant difference of degree of hydration between the high addition and the low addition, unlike the performance of the phase I experiment. It implied that the setting retardation of chemical admixtures did not play an important role in the lower water to cement ratio condition. Instead, the dispersion and water reduction make microstructure of samples develop quickly and dense, especially in the early hydration period.

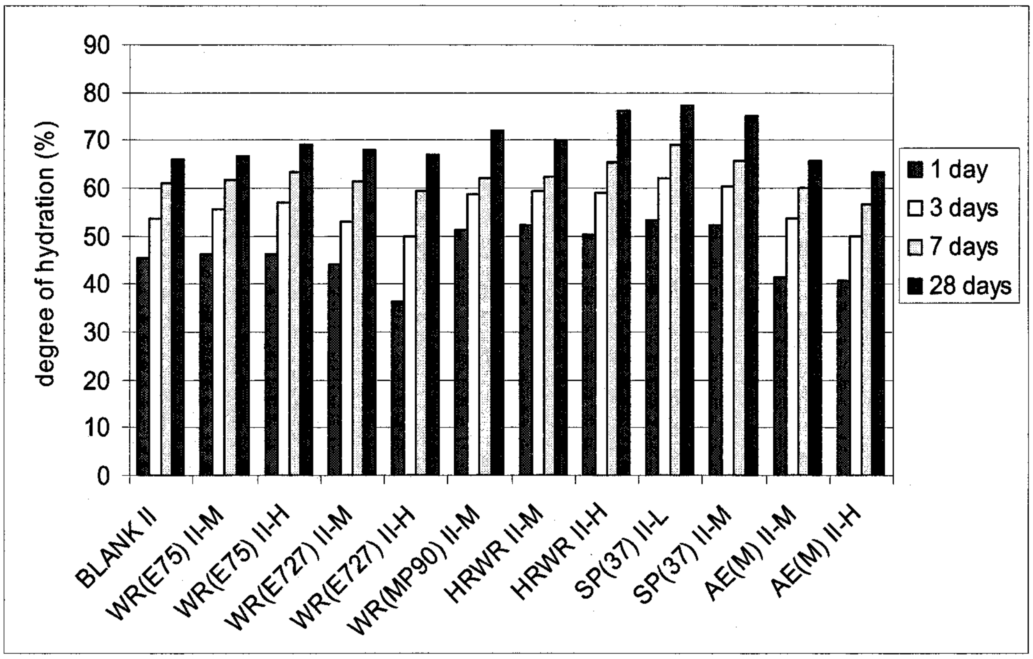


Figure 4.18 Degree of hydration

4.3 Gravimetric water porosity

The procedures of the gravimetric water porosity test was a modification of ASTM C642, the details were described in the test procedure section. The control samples and two species of Type F mixtures with two kinds of water to cement ratio were tested. Only the superplasticized mixtures were chosen for testing because they showed significant difference of conductivity in two water to cement ratios. The results are presented in Table 4.14.

Table 4.14 Gravimetric porosity (%)

MIX	W/C	Addition (ml/100 kg cement)	Gravimetric porosity (%)			
			1 day	3 days	7 days	28 days
Blank I	0.485	0	17.6	17.1	17.0	16.6
Blank II	0.35	0	23.4	23.3	22.8	22.1
HRWR I-M	0.485	1600	19.94	19.35	18.83	18.24
HRWR II-M	0.35	1600	15.50	14.79	14.41	14.35
HRWR I-H	0.485	1140	20.01	19.89	19.10	19.00
HRWR II-H	0.35	1140	14.0	13.96	13.78	13.55
SP 37 I-M	0.485	2200	19.63	19.2	19.0	19.35
SP 37 II-M	0.35	2200	14.7	13.9	13.6	13.58
SP 37 I-L	0.485	1120	18.81	18.2	16.6	16.44
SP 37 II-L	0.35	1120	14.35	14.1	14.1	13.95

The results revealed that for the control samples, high water to cement ratio resulted in lower porosity compared to low water to cement ratio. This phenomenon which is opposite to that normally attributed to extremely low water to cement ratio (without water reducers). As well, the relatively high sand to cement ratio caused sands not to be bound sufficiently by poorly dispersed (agglomerate) cement.

On the contrary, when adding Type F chemical admixtures, the samples of high water to cement ratio possessed the higher porosity than that of the control sample, the results showed that the higher the addition, the higher the porosity, whereas in the case of low water to cement ratio, porosity of samples reduced pronouncedly, the values were much lower than those of the control sample as well as those samples with high water to cement ratio.

4.4 Conductivity of chemical admixtures and ionic concentration of the pore solution in mixtures

The concentrations of Na^+, K^+ and OH^- of all chemical admixtures are presented in the Table 4.15. Concentrations were measured by flame photometry and pH meter. The conductivity was measured with a conductivity probe as outlined in the procedures.

4.4.1 Na^+ and K^+ concentration of the pore solution in mixtures

The alkali content of the cement used in this study is 0.23%Na_2O and 0.84%K_2O, respectively. In one specimen, cement content is 250g; mixing water is 121 ml for W/C 0.485. It is assumed that the immediately available sodium and potassium in the pore solution of cement are 40% and 75%, respectively (Mikanovic et al, 2000). If the water introduced by chemical admixtures is neglected, and all chemical admixtures are solubilized instantaneously and completely when mixed with water, based on the results of Table 4.15, the concentrations of Na^+ and K^+ in the pore solution of control sample and in the mixtures with different chemical admixtures can be calculated. The results are listed in Table 4.16.

It is revealed from Table 4.16 that concentrations of K^+ in all mixtures were nearly constant, around 277-278mM/L, whereas the concentrations of Na^+ varied; the mixtures of Type E and Type F possess relatively high sodium concentrations, and the rest of mixtures have the same level as that of the control sample. The highest Na^+ concentration was mixture WR (MP90) I-M, which was 237.2mM/L, around 4 times that of the control sample. The second highest Na^+ concentration was mixture SP (E37) I-M, was 143.4 mM/L. Mikanovic et al (2000) detected Ca^{2+}, SO_4^{2-}, K^+ and Na^+ concentrations in the pore solution of cement pastes with added PNS, the results show

Table 4.15 Conductivity and ionic concentration of chemical admixtures

Name of chemical admixtures	$[Na]^+$ (mM/L)	$[K]^+$ (mM /L)	$[OH]^-$ (mM /L)	pH	Conductivity (*m*S/cm)
EUCON 75	581	18	2.5 E-05	6.39	14.66
Pozzolith 210	6	0	4.9 E-03	8.69	0.18
EUCON CIA	9	7	3.7 E-04	8.95	92.10
RHEOCRETE CNI	19	1	3.4 E-05	6.53	93.80
EUCON 727	751	10	1.0 E-05	6.02	14.27
POZZOLITH 100XR	14	0.000	1.1 E-05	6.06	0.33
EUCON 90	2620	40	4.2 E-06	5.62	90.90
POZZUTEC 20+	509	2	1.2 E-06	5.09	80.00
EUCON 37	1808	0	3.7 E-04	7.57	44.90
RHEOBUILD 1000	1062	4	3.8 E-05	6.59	21.52
AIREXRA	22	253	4.2 E-05	9.62	12.23
MICRO AIR	83	301	8.9 E-03	12.8	23.56

4.16 The Concentration of Na^+ and K^+ in the mixtures of W/C =0.485

MIX	Type	Chemical admixtures			Cement		Mixtures	
		dosage	Na^+ (mM/L)	K^+ (mM/L)	Na^+ (mM/L)	K^+ (mM/L)	Na^+ (mM/L)	K^+ (mM/L)
Blank I	control	0	0	0	61.2	277.5	61.2	277.5
WR(E75)I-M	Type A	0.88	4.23	0.13	61.2	277.5	65.4	277.6
WR(E75)I-M		1.20	5.76	0.18	61.2	277.5	67.0	277.8
WR(M210P)I-M		0.65	0.03	0.00	61.2	277.5	61.23	277.5
CIA –M	Type C	14.30	1.03	0.80	61.2	277.5	62.2	278.3
CIA-L		7.2	0.52	0.40	61.2	277.5	61.7	277.9
CNI-M		16.10	2.46	0.16	61.2	277.5	63.7	277.7
WR(E727) I-M	Type D	0.31	1.92	0.03	61.2	277.5	63.1	277.5
WR(E727) I-L		0.19	1.18	0.02	61.2	277.5	62.4	277.5
WR(E727) I-H		0.54	3.35	0.04	61.2	277.5	64.6	277.5
WR(MP100)I-M		0.40	0.05	0.00	61.2	277.5	61.2	277.5
WR(MP20) I-M	Type E	7.74	32.56	0.13	61.2	277.5	93.8	277.6
WR(MP90) I-M		8.13	176.04	2.69	61.2	277.5	237.2	280.2
HRWR I-M	Type F	2.85	25.01	0.09	61.2	277.5	86.2	277.6
HRWR I-H		4.00	35.11	0.13	61.2	277.5	96.3	277.6
SP(E37) I-M		5.50	82.18	0.00	61.2	277.5	143.4	277.5
SP(E37) I-L		2.80	41.84	0.00	61.2	277.5	103.0	277.5
AE(M) I-M	AEA	0.16	0.11	0.40	61.2	277.5	61.3	277.9
AE(M) I-H		0.30	0.05	0.63	61.2	277.5	61.3	278.1

that the presence of 1% PNS increased the Na^+ concentration, and SO_4^{2-} concentration was increased slightly, K^+ concentration kept constant, and Ca^{2+} concentration reduced a few. Based on the calculation results and other references, addition of PNS based admixtures and other high content of Na^+ and K^+ admixtures results in raising the Na^+ and K^+ concentration of the pore solution of samples.

4.4.2. OH^- concentration of the pore solution in mixtures

Generally, the concentration of OH^- ions in the pore solution of concrete, mortar or paste is varied with cement chemical composition, water to cement ratio, etc. Usually, the pH value of the plain cement is around 13.4 (Liu et al, 2000). Nokken (2004) tested the concentrations of OH^- in the pore solution of mixtures with different water to cement ratios. The concentrations of OH^- in the samples with 0.35, 0.40 and 0.55 water to cement ratios are 0.673 mol/L, 0.485 mol/L, and 0.307 mol/L, respectively. The chemical composition of the cement Nokken used was different from the cement in this study. The alkali content of the cement she used was 0.11% Na_2O and 0.45% K_2O. Diamond and Penko (1988) proposed a linear relationship between OH^- ion concentration and cement alkali content (equiv. % Na_2O) (see Figure 4.19). In this study, the equivalent alkali content is 0.783%, corresponding to of OH^- concentration 0.56 mol/L. According to the results of Table 4.16, the concentration of OH^- of all chemical admixtures was several orders lower than that of the pore solution of the plain cement. Bonen and Sarkar (1995) used ICP and pH meter to measure the concentrations of Ca^{2+}, S^{2-}, OH^-, Na^+ and K^+ in the pore solution of 6 types of cement addition of sodium PNS. They found that the addition of sodium PNS always increases the S^{2-} and Na^+ concentrations, whereas K^+ to a lesser extent, and Ca^{2+} decrease. OH^- concentrations were affected by Ca^{2+} rather than addition of sodium PNS. Therefore, in this study, the contribution of OH^- by addition of chemical admixtures will be neglected.

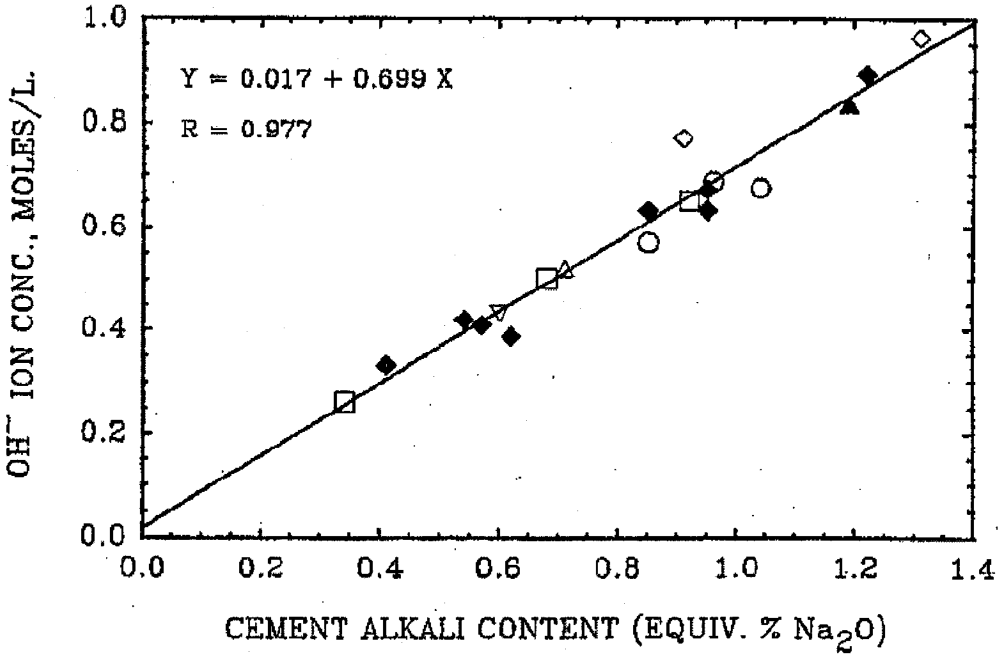


Figure 4.19 The relationship between cement alkali content and OH^- ion concentration in pore solution (Diamond and Penko, 1992).

4.4.3. Ca^{2+} concentration of the pore solution in mixtures

The calcium ion concentration of the original cement paste pore solution depends on various factors, such as water to cement ratio, cement type, chemical and mineralogical composition, fineness, and gypsum content (Mikanivic et al 2000). Generally, calcium ion concentration reduces with the hydration process and diminishes to negligible level (Shi, 2004; Snyder et al, 2003). Bonen (1995) gave the calcium ion concentration of 6 different types of cement pastes, for 0.35 W/C, it was around 20-40 mM/L at 120 min after the cement was mixed with water. Mikanivic et al (2000) measured Ca^{2+} concentrations of the low alkali cement and the high alkali cement with 0.4 W/C, the maximum values were between 35-50 mM/L in the very early hydration process, and addition of PNS superplasticizier did not alter them significantly. In this study, Ca^{2+} concentration was not measured because most of chemical admixtures are salt of sodium and potassium.

There is an exceptional case, Type C admixture which is a calcium nitrite based material. The results of Table 4.16 showed that Type C did not possess a high alkali concentration, but as discussed in Chapter 2, this kind of chemical admixture induces a large number of Ca^{2+} and NO_2^- ions to the pore solution, raising bulk conductivity. In Table 3.2, it was shown that the calcium nitrite concentration in EUCON CIA and RHEOCRETE CNI are more than 30%, and the addition of them (Table 3.3) were 5720ml and 6440 ml for 100 kg cement, respectively. It is assumed that all introduced Ca^{2+} and NO_2^- ions are unprecipitated in the pore solution. (Some of Ca^{2+} should participate in hydration and form CH crystals). It can be calculated that the calcium ion concentrations in pore solution of mixture CIE and CIA (W/C 0.485) were 207mM/L and 232mM/L, respectively; while the concentrations of nitrite ions were 414mM/L and 464mM/L, respectively. Comparing with the results of Bonen and Mikanivic et al, the calcium ion and nitrite ion concentration in the pore solution of samples adding calcium nitrite were one order higher than those of plain samples. Obviously, calcium nitrite based corrosion inhibitor did introduce a large number of calcium and nitrite ions into the pore solution, significantly changing the pore chemistry composition.

5.0 Discussion

As noted previously, the conductivity of the bulk paste, mortar or concrete is a function of the pore solution composition, the porosity and connectivity of the pore system. The conductivity of concrete, mortar or paste varies with the age of specimens; it decreases with time by microstructure development and variations in pore chemistry (Rajabipour, 2004). When cement mixes with water, available Na^+, K^+, Ca^{2+}, OH^- and SO_4^{2-} release onto the pore solution, forming the electrolytic solution; its conductivity generally increases over time. During the hydration process, the volume and size of the porosity decrease with hydration, reducing the conductive path. The competing result of these parts forms the bulk conductivity (Nokken, 2004). When cement is mixed with mineral and chemical admixtures, the soluble ingredients of these materials are released into the pore solution of cement and alter the pore chemistry (Shi, 2004; Liu, 2000; Jolicoeur, 1998). Chemical admixtures have their own ionic chains, for example, sulfonated naphthalene formaldehyde condensates superlasticizer (SNF) have Na^+, or Ca^{2+}, and hydroxycarboxylic water reducer possesses COO^- and OH^-. Most of the polymer water reducers contain alkali metals, like Na, K and Ca in order to improve solubility in water (Rixom et al, 1986). On the other hand, chemical admixtures can manipulate cement setting, change hydration rate and degree, and affect the porosity and its connectivity. For example, accelerators and setting retarders alter the structure development of cement pastes at the very early age by adjusting setting time; air entraining agents change air content, porosity and pore structure by intruding uniformly dispersed microscopic bubbles in concrete (Rixom et al, 1986). When cement is mixed with these chemical admixtures, both the pore chemistry and porosity are altered, the conductivity of cement paste, mortar or concrete is the result of the competition of these factors.

Based on above discussion, the conductivity of concrete, σ_t, is affected by several factors, which were expressed as equation 2.5 by Garboczi (1990)

$$\sigma_t = \sigma_0 \varphi \beta \qquad \text{Eq.2.5}$$

where σ_0 is the conductivity of pore solution, φ is the volume of porosity, and β is the pore connectivity factor. It has been found that σ_0 increases with the hydration process; φ and β decrease with time elapsing. The effects of chemical admixtures on conductivity of specimens will be discussed from these three factors.

5.1. Effect of pore solution chemistry composition on bulk conductivity

Generally, the composition of pore solution of hydrated cement includes primarily OH^-, Ca^{2+}, Na^+, K^+ and SO_4^{2-}. The concentration of these ions is varied with hydration time. When cement mixes with water, appreciable Na^+, K^+, OH^-, Ca^{2+} and $SO4^{2-}$ release to the mixing water. With the hydration process, the Ca^{2+} and SO_4^{2-} reduce to negligible values. Different ions possess different conductivity. The equivalent conductance of some ions at the infinite dilution in water at 25°C was listed in Table 2.2. As previously discussed, besides ions released by cement itself, chemical admixtures introduce certain ionic species into the pore solution. Most of chemical admixtures are salts of alkali or earth alkali metals; frequently sodium and potassium are used (Rixom et al, 1986). For instance, in this project, EUCON 75 is sodium glucoheptonate; EUCON 37 and RHEOBUILD1000 are sulfonated naphthalene formaldehyde condensates superlasticizer (PNS), containing sodium. Matsukawa and Diamond (in Xu et al, 2000) analyzed pore solutions of cement with and without PNS superplasticizer, they found that at 4 hours there was a 18% increase of the ionic concentration in the superplasticized paste, compared with the control paste.

5.2 Conductivity of Na^+ and K^+ ions in the pore solution

It can be seen from Table 2.1 that the most significant contributor to the pore solution conductivity is the OH^- ion due to its high equivalent conductivity at the infinite dilution condition, which is a factor of two greater than those of Na^+ and K^+. This study only considers the contribution of chemical admixtures to the pore solution conductivity, and OH^- concentration of all chemical admixtures is much lower than that of the original cement (Table 4.15). Therefore it is assumed that all mixtures have same level of conductivity of OH^- ion which is possessed by the original cement. The influence of OH^- ion by chemical admixtures is neglected, but it could be included for the cement (which is constant in this case).

Based on the results of Table 4.16, the conductivity values of Na^+ and K^+ in the pore solution of mixtures were calculated by equations 2.9 and 2.10, and the results are given in Table 5.1. The electrical conductivity values of K^+ in all mixtures were almost constant due to similar concentrations, and the electrical conductivity of Na^+ varied. The mixtures of Type E and Type F possess relative high pore solution conductivity. For example, WR (E90) I-M had Na^+ conductivity of 9490 μS/cm, much higher than the control sample; the Na^+ conductivity of SP (E37) I-M was 6005 μS/cm, which was the second highest Na^+ conductivity among all mixtures.

Table 5.1 Calculated electrical conductivity of high W/C mixtures at 25℃

MIX	Type	Electrical conductivity (μS/cm)			
		pore solution of mixtures			Bulk
		Na^+	K^+	Total	1 day
Blank I	Control	2718	16939	19656	669
WR(E75)I-M	Type A	2894	16946	19840	870
WR(E75)I-H		2958	16949	19907	783
WR(M210P)I-M		2719	16939	19658	863
CIA –M	Type C	2761	16984	19744	925
CIA-L		2739	16961	19701	636
CNI-M		2821	16948	19768	1136
WR(E727) I-M	Type D	2798	16940	19738	876
WR(E727) I-L		2767	16940	19707	871
WR(E727) I-H		2858	16941	19799	1627
WR(MP100)I-M		2720	16939	19658	1053
WR(MP20) I-M	Type E	4054	16946	20999	685
WR(MP90) I-M		9490	17089	26579	658

Table 5.1 Calculated electrical conductivity of high W/C mixtures at 25°C

(continued)

MIX	Type	Electrical conductivity (uS/cm)			
		pore solution of mixtures			Bulk
		Na^+	K^+	Total	1 day
HRWR I-M	Type F	3749	16944	20693	845
HRWR I-H		4156	16946	21102	1155
SP(E37) I-M		6005	16939	22944	1001
SP(E37) I-L		4426	16939	22365	821
AE(M) I-M	AEA	2722	16961	19683	803
AE(M) I-H		2720	16974	19694	821

Mixtures of Type A, C, and D admixtures and air entraining agents have slightly higher Na^+ conductivity than the control sample. The results indicated that Na^+ ion concentration in Type E and Type F chemical admixtures contributes much more to the pore solution conductivity than that of Type A, C, and D does. This can partially explain the phenomena of high addition of these chemicals causing increased bulk conductivity except Type E.

The mixtures of Type E, especially WR (MP90) I-M which has very high Na^+ ion concentration in the pore solution, but its bulk conductivity was not very high compared to other mixtures. In this case, the fast development of microstructure and hydration at the early age dominates the bulk conductivity.

Another exceptional case is air entraining agents. The two types of air entraining agents contain Na^+ and K^+ ions according to the chemical composition results, when adding more the bulk conductivity reduced. This phenomenon is other reasons than altering pore chemistry composition.

The Type C admixtures, as calculated results in section 4.4.3, the concentrations of Ca^{2+} ions and NO_2^- ions induced to the pore solution were 207-232 mM/L and 414-464 mM/L, respectively. Using the same calculation method, the conductivity of Ca^{2+} ion induced by CIA medium and lower dosages and CNI medium dosage were 8163 uS/cm, 4540 uS/cm and 8975 uS/cm, respectively. There is less data for calculation of the conductivity of NO_2^- ion. However, it is known that calcium nitrite is a strong electrolyte (Duffey, 2000), only Ca^{2+} ions can cause so high conductivity of the pore solution, therefore its high ionic concentration overwhelmed its accelerating hydration rate. It is not doubt that addition of calcium nitrite based corrosion inhibitors increases the bulk conductivity.

Figure 5.1 illustrates the relationship of the bulk conductivity and Na^+ and K^+ ions' conductivity in the pore solution. Some samples had higher bulk conductivity but lower ionic (Na^+ and K^+) conductivity, like WR(E727) I-H; other samples exhibited reverse, such as WR(E90) I-M. As discussed previously, the bulk conductivity is the competition results of pore solution conductivity (total ions), porosity and pore connectivity. They compete each other in the hydration process; a particular factor dominates the result in the specific condition. Beyond all doubt, introduction of the strong electrolyte to the cement system increases bulk conductivity in certain degree.

For the case of the low water to cement ratio, the change of the pore solution chemistry composition follows the same rule. However, the conductivity results showed that the addition of chemical admixtures resulted in lower bulk conductivity. This implied that in the condition of low water to cement, pore solution chemistry of mixtures added by chemical admixtures did not dominate the bulk conductivity. Instead of that, degree of hydration and low porosity play the key roles, which will be discussed in the next two sections.

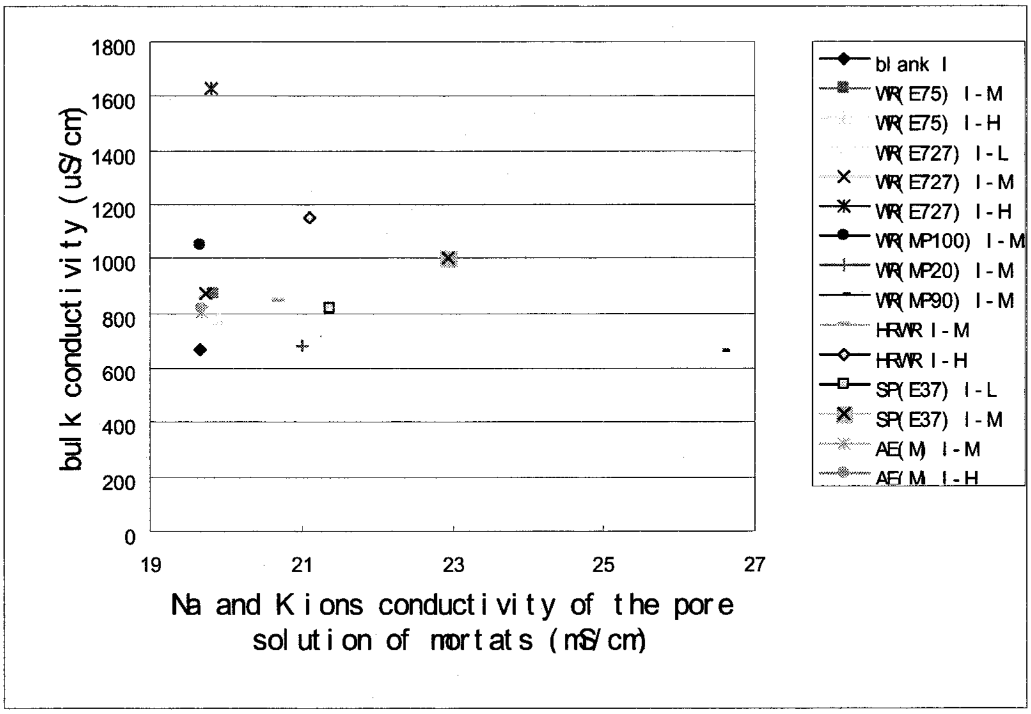


Figure 5.1 Bulk conductivity versus pore conductivity of Na^+ and K^+ ions

5.3 Degree of hydration

In this study, the degree of hydration refers to the amount of CH and CSH in the mortars. It can be related to the development of microstructure, the pore geometry, tortuosity, and connectivity of mortars. Because when cement hydrates, the nuclei of hydration products grow and precipitate in the capillary pores, resulting in the decrease volume and connectivity of the capillary pores. In the results chapter, Figure 4.11 and Figure 4.13 illustrated the degree of hydration of mixtures with different addition of chemical admixtures with the two water to cement ratios. Generally speaking, the higher water to cement ratio, the higher degree of hydration. The lower degree of hydration for the pastes at lower water to cement ratio can be attributed to the insufficient space available to accommodate more hydration products (Lam et al, 2000). In the case of the high water to cement ratio, Types A, D, F and air entraining agents all showed setting retardation at the early hydration period, whilst Type C and Type E exhibited marked acceleration in the whole hydration period. For the low water to cement ratio, this setting retardation and acceleration did not make that much difference between various additions. Figures 5.1 to 5.7 graphically exhibit the relationship of resistance (inverse of conductivity) versus degree of hydration. Each curve includes 4 points corresponding to the hydration ages of 1 day, 3 days, 7 days and 28 days. Interestingly, most of curves can be expressed as linear relationship with good correlation. Table 5.2 lists the equations of the trend lines for mixtures and their R-square values. This linear relationship can be expressed as:

$y = kx - C$

where y is bulk resistivity (Ω.m)

x is degree of hydration (%)

k and C are constants.

Table 5.2 The relationship of bulk resistivity versus degree of hydration

Mix	Type of admixtures	Equation of trend line	R^2
Blank I	control	$y= 1.386x - 52.194$	0.9898
Blank II		$Y=0.953e^{0.0412}$ / $y=0.462x-15.597$	0.7766/ 0.6905
WR(E75)I-M	Type A	$Y= 1.175x-40.239$	0.9431
WR(E75)I-H		$Y= 1.075x-40.333$	0.7854
WR(E75)II-M		$Y= 0.92x-36.203$	0.6714
WR(E75)II-H		$Y= 0.92x-36.203$	0.6714
CIA -M	Type C	$Y=0.77x-31.859$	0.9753
CIA-L		$Y=1.209x-43.479$	0.9969
WR(E727) I-M	Type D	$Y=0.52x- 3.276$	0.8990
WR(E727) I-L		$Y=1.115x-38.553$	0.9152
WR(E727) I-H		$Y= 0.505x- 4.732$	0.9158
WR(E727) II-M		$Y= 0.153x+ 0.504$	0.6910
WR(E727) II-H		$Y= 0.259x- 3.941$	0.9969
WR(MP90) I-M	Type E	$Y= 1.465x-61.722$	0.9769
WR(MP90) II-M		$Y= 1.279x-54.504$	0.9558

Table 5.2 The relationship of bulk resistivity versus degree of hydration (continued)

Mix	Type of admixtures	Equation of trend line	R^2
HRWR I-M	Type F	$Y= 0.979x-33.279$	0.9487
HRWR I-H		$Y= 0.784x-22.931$	0.9717
HRWR II-M		$Y= 2.808x-115.43$	0.9904
HRWR II-H		$Y= 1.581x-55.774$	0.9117
SP(E37) I-M		$Y= 0.961x-28.269$	0.9882
SP(E37) I-L		$Y= 1.7x-81.573$	0.9845
SP(E37) II-M		$Y= 2.255x-99.34$	0.9864
SP(E37) II-L		$Y= 2.236x-89.154$	0.9772
AE(M) I-M	AEA	$Y= 1.276x-50.803$	0.9900
AE(M) I-H		$Y= 1.352x-43.413$	0.9267
AE(M) II-M		$Y=0.3791e^{0.0258x}$	0.6347
AE(M) II-H		$Y=0.2224e^{0.0377x}$	0.9244

The slope, k controls the rate of growth of bulk resistivity, and C may be seen as the other factors affecting bulk resistivity besides degree of hydration. From Table 5.2 and Figures 5.2 to 5.8, it can be seen that for most of mixtures with high water to cement ratio, when the addition of chemical admixtures increases, their k reduces, which means the development of bulk resistivity gradually becomes slower than that of the control sample. If the chemical admixtures possess setting retardation, the growth of bulk resistivity is delayed (bulk conductivity increase), the most noticeable examples are mixtures WR (E727) I-M and WR (E727) I-H (Fig. 5.4), their k values exhibited pronounced reduction compared to that of the control sample. However, there are two exceptional mixtures, which k increases when chemical admixtures are added, they are mixtures WR (E90) I-M and SP (37) I-L. This makes more sense because WR (E90) I-M is a set accelerator, which has positive effect on development of hydration. SP (37) I-L possesses the lowest bulk conductivity, and not very low degree of hydration which implies this amount of addition maybe the optimized dosage of this admixture. The optimized dosage refers to the efficient adsorption on the cement particles and dispersing each other without severely influencing hydration (Flatte et al, 2001). Xu et al (1999) explained the set retardation of water reducers by delaying the precipitation of $Ca(OH)_2$ and CSH hydrates, and they work

- by adsorption onto cement particles, partially blocking reactive surface sites
- by altering the nucleation and growth of $Ca(OH)_2$ and CSH particles.

In the linear relationship, the constant C changes with mixtures by adding different admixtures and additions. The factors influencing of this constant may include porosity, pore solution chemistry composition, etc.

For the low water to cement ratio, the control sample showed the poor correlation for the linear relationship (R^2=0.6905), but a little better for an exponential relationship (R^2=0.7766). However, when adding chemical admixtures, especially high addition, the exponential relationship converted to the linear relationship noticeably. For the cases of addition of superplasticizers (Type F), k increases markedly with addition.

The slopes of lines of these mixtures are very steep, which means the growth of the bulk resistivity dominates the relationship, and hydration also has positive contribution to the bulk resistivity.

Xu and Beaudoin (2000) used AC impedance spectroscopy to detect the effect of PNS superplasticizer on the interfacial transition zone. They found that with 0.45 water to cement ratio and 2.5 silica sand to cement ratio, the superplasticized sample showed low resistivity with high addition of PNS. On the contrary, in the case of 0.35 water to cement ratio and the same sand to cement ratio, the resistivity raised with increase the addition of PNS. The results are very similar with this study although the tests were carried out by different method. Xu and Beaudoin (2000) referred to deflocculation, bleeding and segregation to explain this phenomenon.

For 0.35 water to cement ratio, the trapped water released by the deflocculating action of the superplasticizers sufficiently wets the deflocculated cement grains for hydration without a thick water film forming around cement and sand particles which will delay hydration. It was observed by higher degree of hydration of HRWR II-M, HRWR II-H, SP37 II-M and SP37 II-L.

For 0.485 water to cement ratio, the released trapped water may further dilute the paste system, and increased the thickness of water layer around the sands resulting in delayed hydration. This "extra" water also increases the mobility of the ions in the pore solution cause high conductivity. An excessive dosage of superplasticizer (SP37 I-M, HRWR I-M) resulted in the cement paste too fluid. The sands were no longer maintained in suspension and bleeding and segregation occurred, observed by high porosity of mixtures which will be discussed in the next section.

Xu and Beaudoin (2000) pointed out the improvement of the superplasticized samples would depend on the balance between the positive action of deflocculation, high dispersion, more efficient hydration and the negative effect of increased water layer thickness, bleeding and segregation.

Not only can the superplasticizers be explained by this theory, the results of other water reducers also follow this rule except for the water reducing-accelerators. Because of their high accelerating function, the rapid hydration development of samples overwhelms the effects of their fluidity.

The mixtures of air entraining admixtures, in the high water to cement ratio condition, the resistivity versus degree of hydration followed the linear relationship; for the low water to cement ratio mixtures, this relationship changed to the exponential. The presence of AEAs result in decrease in the mechanical properties has been reported in many papers (Rixom et al, 1986). Figures 4.11 and 4.13 also showed that the high addition of AEAs lead to lower degree of hydration than those of the control samples, not only in the high W/C samples, but also in the low W/C samples. AEAs are surfactants, they can improve the consistency of fresh cement meanwhile they induce large numbers of micro-air-bubbles to the cement system. Therefore, the hardened samples possess lower degree of hydration but higher resistivity. Appropriate addition of AEAs can reduce bulk conductivity.

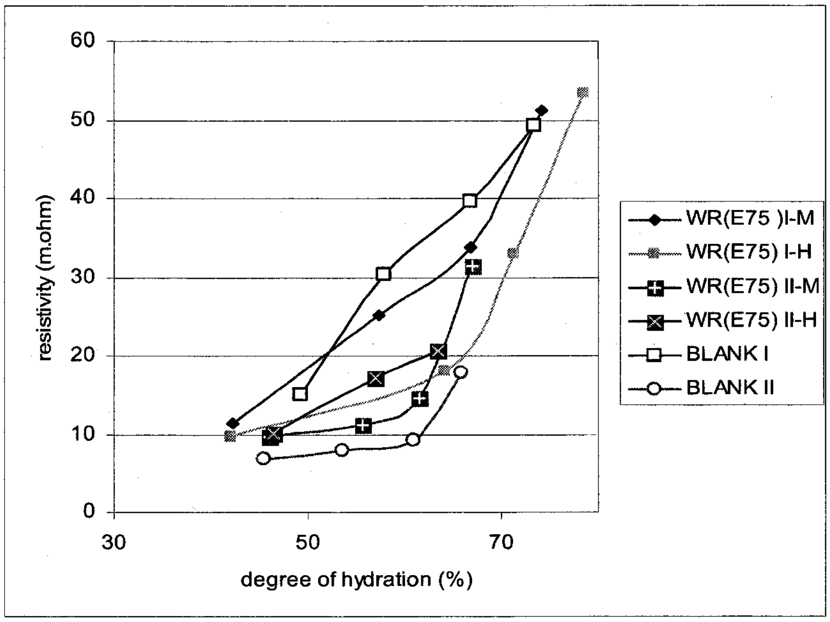


Figure 5.2 Degree of hydration versus resistivity of mixture WR (E75)

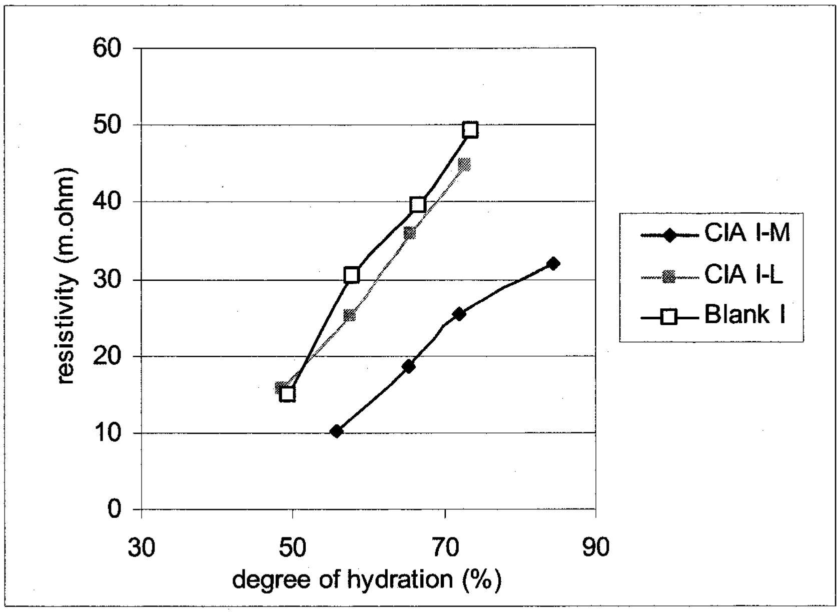


Figure 5.3 Degree of hydration versus resistivity of mixture CIA

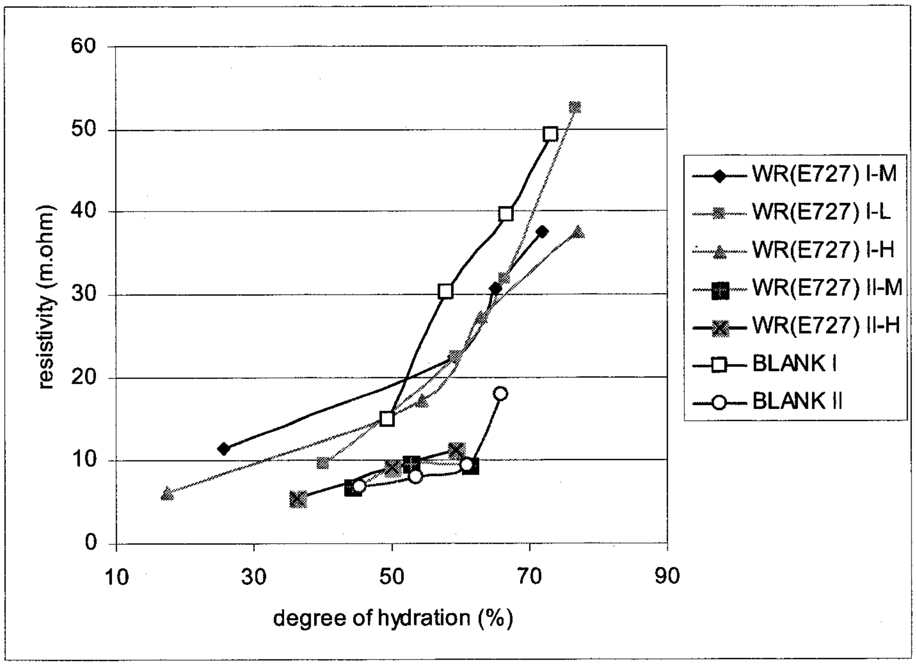


Figure 5.4 Degree of hydration versus resistivity of mixture WR (E727)

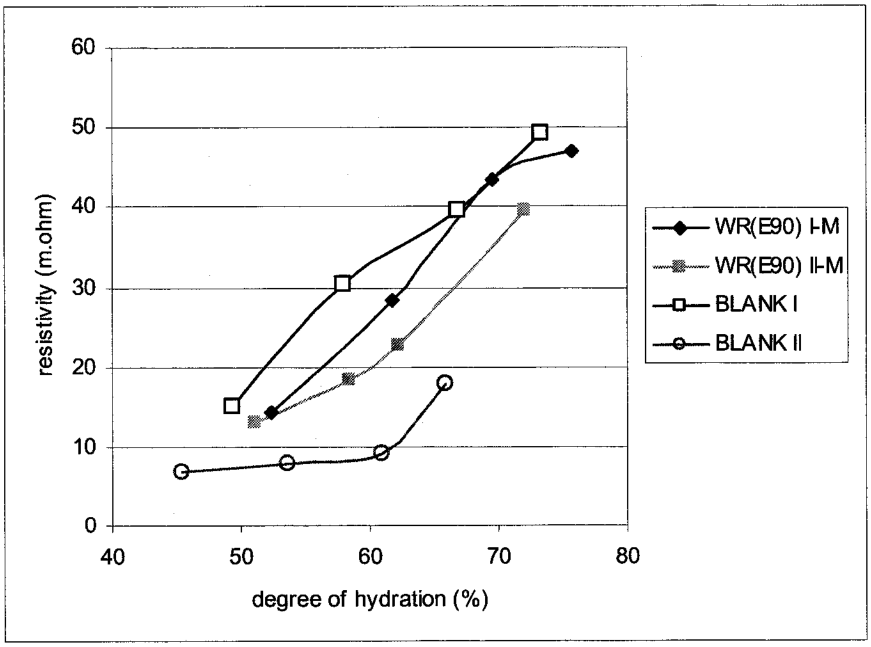


Figure 5.5 Degree of hydration versus resistivity of mixture WR (E90)

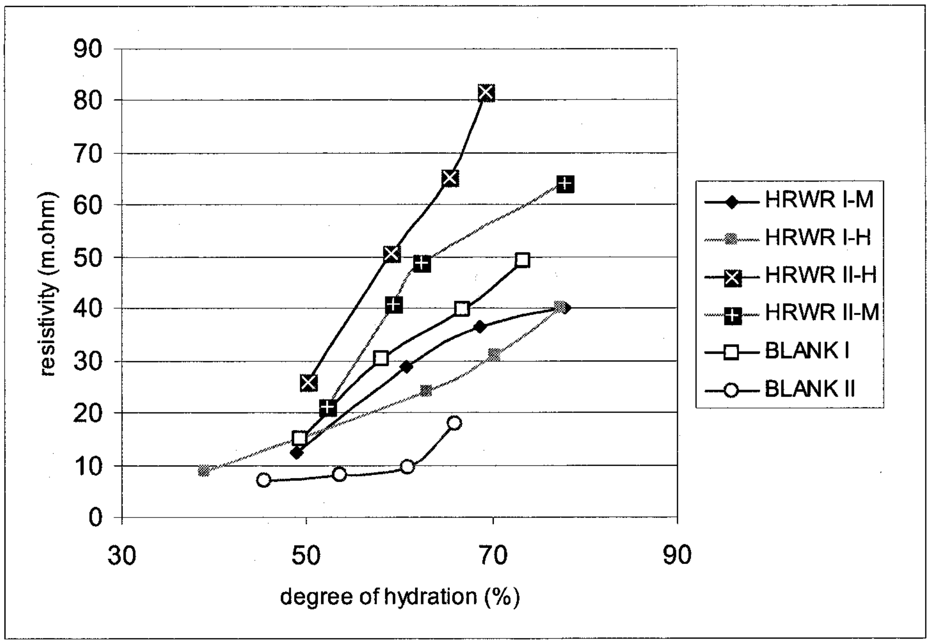


Figure 5.6 Degree of hydration versus resistivity of mixture HRWR

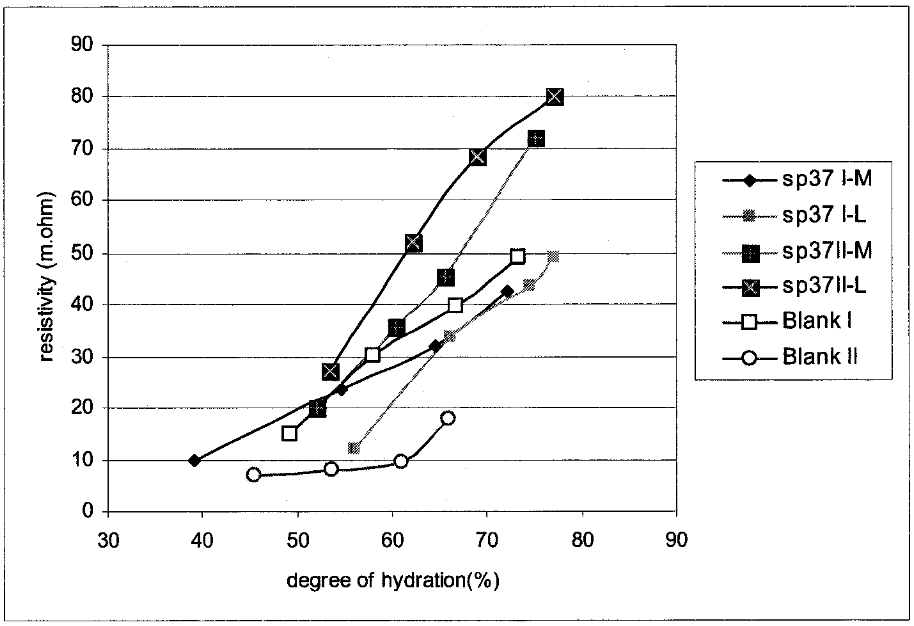


Figure 5.7 Degree of hydration versus resistivity of mixture SP37

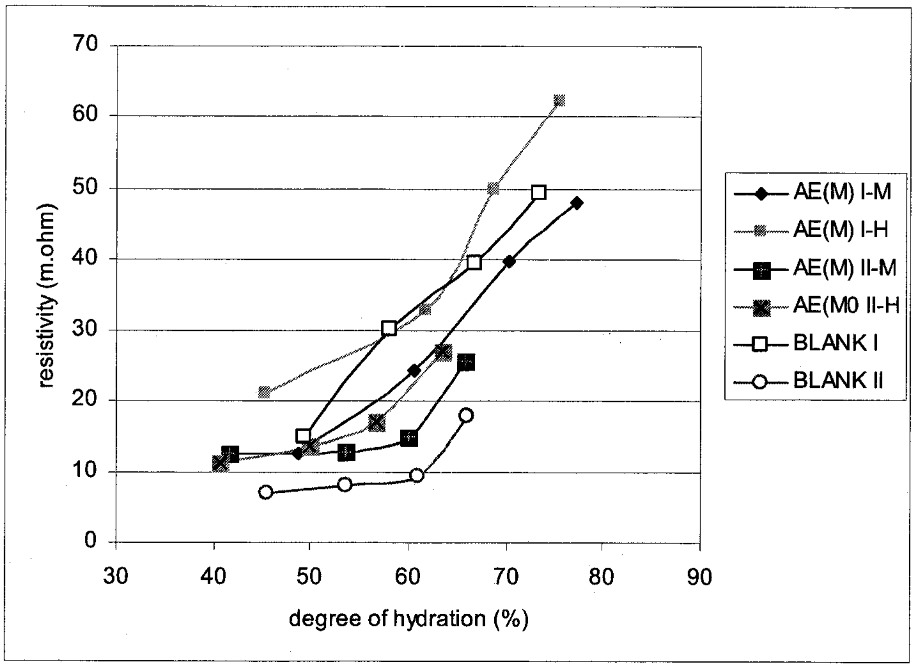


Figure 5.8 Degree of hydration versus resistivity of mixture AE (M)

5.4 Porosity

The porosity results of the plain samples with at the two water to cement ratios given in Table 4.14 displayed that the high water to cement ratio resulted in low porosity, and low water to cement ratio caused high porosity. This was owing to high water to cement ratio provided sufficient mixing water to disperse cement particles and these particles are surrounded by water, hence the hydration could develop to a greater extent. In the case of low water to cement ratio, such less mixing water could not disperse and wetting cement particles, therefore these particles tend to aggregation. This phenomenon was observed by the samples exhibiting poor consistency, lower degree of hydration and high bulk conductivity.

For the superplasticized samples, the results were on the contrary. For the low water to cement ratio, as discussed above, the trapped water was released and wetted cement particles, and a greater amount of hydrates were produced. The cement particles are more evenly distributed, allowing a more efficient packing of the cement grains around sand, thus reducing the number of large pores, hence, lowering the overall porosity of mortars. This was confirmed by Xu et al (2000) by using AC impedance technique, SEM and MIP to investigate mortars at 0.35 water to cement ratio with 0.1% to 1.5% PNS additions. They found that the measurement of "interfacial excess conductance" showed that the interfacial transition zone in the superplasticized mortars was denser than that in the control samples. Their SEM results showed that there was an abundance of C-S-H fibers or needles located in the fracture surface of superplasticized specimens. The MIP results showed that the appropriate dosage of superplasticizers caused mortars to have lower porosity, finer pore size distributions and smaller threshold pore diameters. Consequently, the microstructural features of mortars predominantly controlled the bulk conductivity.

For the high water to cement ratio, the trapped water release causes the mortar system to have more fluidity, these extra water and entrapped bubbles introduced by impure superplasticizers form capillary pores in the hardened specimens, which results in high porosity and high bulk conductivity. In the real world, high workability superplasticized concrete always contain fine materials, such as fly ash, silica fume or some gum to prevent from bleeding, segregation and generation of extra water. A lot of cases can be found in self-consolidating concrete (SCC), high-performance concrete (HPC). This part is beyond of study of this project.

Figures 5.9 and 5.10 display the relationship of the gravametric porosity and the bulk conductivity of superplasticized mixtures and the control samples. It can be seen that the porosity reduced with the decrease of bulk conductivity, and obviously the high water cement ratio samples possessed high porosity compared to those of low water cement ratio. Gu et al (2000) have shown that for a plain cement paste, the overall resistance is an inverse function of porosity, mean pore size, and ionic concentration of the pore solution. Nokken (2004) found a poor exponential relationship (R^2 was 0.58) between bulk conductivity and porosity for samples with different water to cement ratios, from 0.30 to 0.90. Table 5.3 lists the exponential equations of the trend line for mixtures and their R-square values. It can be seen that the values of R^2 are not low except SP37 I-M (a linear function gives slightly better correlation, R^2 is 0.61). For other water reducers, the dispersion and water reduction play the similar roles to superplasticizers in samples with two kinds of water to cement ratios. However, the efficiency of dispersion and water reduction is not as strong as superplasticizers, and combined with their setting adjusting function, their effect on porosity maybe complicated.

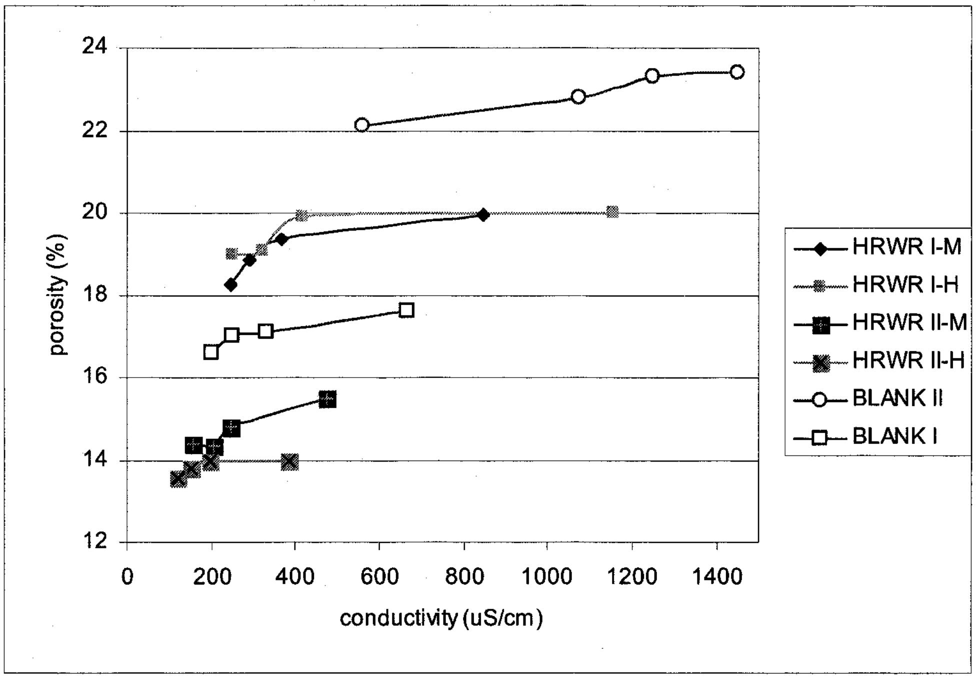


Figure 5.9 Conductivity versus porosity of HRWR

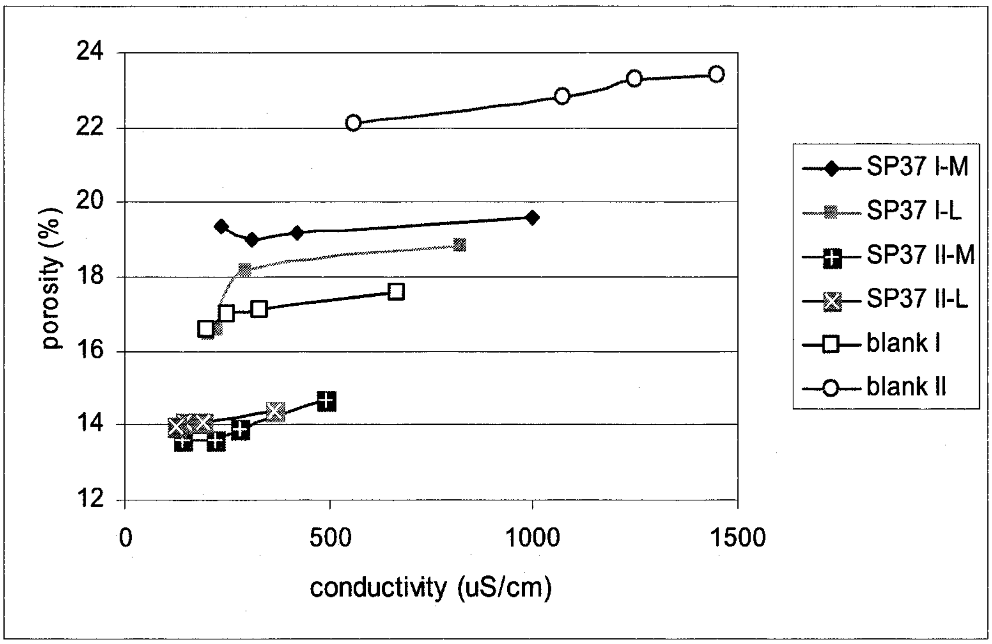


Figure 5.10 Conductivity versus porosity of SP (37)

Table 5.3 The relationship of bulk resistivity versus porosity

Mix	Type of admixtures	Equation of trend line	R^2
Blank I	control	Y=0.7733ln(x) +12.6	0.9454
Blank II		Y=1.393ln(x) + 13.25	0.9578
HRWR I-M	Type F	Y= 1.2376ln(x) +11.716	0.8659
HRWR I-H		Y= 0.6506ln(x) +15.535	0.6977
HRWR II-M		Y= 1.0726ln(x) +8.8528	0.9197
HRWR II-H		Y= 0.3529ln(x) +11.962	0.7274
SP(E37) I-M		Y= 0.2926ln(x) +17.528	0.4782
SP(E37) I-L		Y= 1.6181ln(x) +8.1504	0.7671
SP(E37) II-M		Y= 0.9157ln(x) +8.8719	0.8553
SP(E37) II-L		Y= 0.3379ln(x) +12.354	0.9274

In the case of AEAs, as discussed in chapter 2, the mechanism of AEAs in pastes or concrete can be simply described by Figure 2.5. At the appropriate dosage, AEAs generate microscopic bubbles, and with the appropriate water content, the hydrophobic tails and hydrophilic heads connect cement particles and bubbles to form connecting system like bridge. This system makes bubbles separate and stable in pastes or concrete. If there are not enough AEAs, the system would not be stable. In this test, the water to cement ratio was fixed, when AIR MICRO dosage was increased, more air bubbles were generated, and the mixture became more fluid (AE(M) I-H had higher consistency than AE(M) I-M; AE(M) II-H was more plastic than AE(M) II-L) by more microscopic bubbles lubricating the surface of aggregates or sand particles, hence that “connecting system” is built up. Usually, if maintaining the same workability, a reduction in the water can be made of 5-15 % (Ramachandran, 1984). Maintaining the water to cement ratio resulting in high workability can be seen as adding extra water to the original mixture. Ramachandran (1984) indicated that the additional water played the role to bind the sand and created more space for the accommodation of bubbles. The result is that conductivity paths of samples are blocked by separated micro-bubbles.

6.0 Conclusions

- This method directly uses conductivity as parameter to express migration of all ions in the pore solution of hardened samples instead of total coulombs. The testing duration is 5 minutes at every 3 hours to avoid the Joule effect and it allows monitoring the long term performance of samples.
- Addition of chemical admixtures to mortars alters the pore solution chemistry; the effect depends on genetic nature of chemicals. EUCON 90 and POZZUTEC 20+ (Type E), EUCON 37 and RHEOBUILD 1000 (Type F) raise the Na^+ concentration in the pore solution of mortars compared with other chemical admixtures because they induce much more Na^+ to the pore solution of mortars; EUCON CIA and RHEOCRETE CNI (Type C) introduce large amount of Ca^{2+} and NO_2^- ions to the pore solution of mortars.
- Electrical conductivity of mortars is the competitive result of ionic conductivity of the pore solution, hydration development and porosity. In the different conditions, chemical admixtures exhibit pronounced different influences on the electrical conductivity of cement mortars.

  In the high water to cement ratio:

  ○ Type A (EUCON 75), Type D (EUCON 727) and Type F (EUCON 37 and RHEOBUILD 1000) have negative effects on bulk conductivity due to their set retardation (all of these three chemicals), high Na^+ concentration and the increase in porosity (EUCON 37 and RHEOBUILD 1000). These negative effects become more severe with increased dosage. It can be explained that the released trapped water which resulted from the addition of water reducers may further dilute the paste system, and increased water layer thickness around the sands result in hydration delay. This "extra" water will also increase the mobility of the ions in the pore solution causing high conductivity.

- Type C (EUCON CIA and RHEOCRETE CNI) calcium nitrite based chemical admixtures noticeably increased bulk conductivity as also observed in ASTM C 1202 test. The mainly reason is that the significant effect of altering pore solution chemistry in mortars of this kind of chemical admixture overwhelms its accelerating effect.
- Type E (EUCON 90 and POZZUTEC 20+) has no significant change of bulk conductivity. The high Na^+ concentration in EUCON 90 is offset by its accelerating function.
- Type F (EUCON 37 and RHEOBUILD 1000) increases the porosity of mortars, and the higher addition, the higher porosity of mortars. The over dosage of EUCON 37 caused bleeding in mortars. The high dosage of Type F results in a mortar system with more fluidity; this extra water and entrapped bubbles introduced by impurity of these chemicals form capillary pores in the hardened specimens, bleeding and segregation occurred as well.
- Increased dosage of MICRO AIR (AEAs) reduces bulk conductivity due to its introduction of microscopic separate bubbles cutting the conductive path in mortars.

In the low water to cement ratio:

- All chemical admixtures have positive effect on bulk conductivity of mortars except the high dosage of EUCON 727 (Type D). Type F pronouncedly reduces conductivity of mortars; the conductivity values were only 20-30 % of the control samples. Alteration of the pore solution chemistry does not play the important role in these mixtures.
- The set retardation of Type A, Type D and Type F is not as obvious as the mortars with high water to cement ratio. The reasons are that the trapped water released by the deflocculating action of the water reducers sufficiently wets the deflocculated cement grains for hydration without thick water film forming around cement and sand particles which delays hydration.
- Type F chemical admixtures reduce porosity of mortars pronouncedly due to their high water reduction. The cement particles are more evenly distributed, allowing a more efficient packing of the cement grains around sand, thus reduce the number of large pores. Hence, reduce overall porosity of mortars.
- The behavior of AEAs (MICRO AIR) follows the same trend as samples with the high water to cement ratio.

7.0 Recommendations

- In this study it is proved by calculation that chemical admixtures do alter the pore solution chemical composition. It is necessary to measure the concentration of Na^+, K^+ and compare to the calculated results. For the ionic concentrations, such as SO_4^{2-}, OH^-, Ca^{2+} should be measured in order to obtain the overall effects of chemical admixture on the pore solution of mortars.
- In this study, the porosity was measured by modified ASTM C 642-97, which is gravimetric water porosity. The results showed that type F admixture could change the total porosity of mortars significantly, either in high water to cement ratio or low water to cement ratio. It is necessary to measure the pore distribution, the threshold of pore and other information of porosity of sample added by various chemical admixtures in order to reveal how these chemical admixtures change porosity as well as bulk conductivity. It is pity that there is no porosity data of mortar added by AEAs in this study.
- It is well known that addition method PNS and PNM based superplasticizers influences their absorption and dispersion in cement systems. In this study, the addition sequence followed the procedure of standard mortar. The delayed addition can improve the absorption and dispersion of this species significantly (Rixom et al, 1986; Ramachandran, 1984) because it relates with optimized dosage and absorption. It is suggested to test the effects of delayed addition of chemical admixtures on the pore solution, bulk conductivity and porosity of mortars.

- This study was conducted on mortars. The influence of admixtures should be studied in concrete. Supplementary cementitious materials (SCM) have been increasing use in concrete in the real world due to their improvement on the durability of concrete. It has been proven that silica fume reduces pH value of pore solution, and increases bulk conductivity in the very early hydration process and then decreases. The combined effects of SCMs and chemical admixtures should be studied further. This is normal mixture design for concrete in the real world. Therefore, it is necessary to figure out the effects of combination of chemical admixtures and SCM on conductivity /durability of concrete.

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