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Durability of concrete exposed to sulfuric acid attack

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DURABILITY OF CONCRETE EXPOSED TO SULFURIC ACID ATTACK

By

Seyed Mahmoodreza Joorabchian, B.Eng.

Azad University of Tehran Central, Tehran, Iran, 2005

A thesis

Presented to Ryerson University

In partial fulfillment of the
requirements for the degree of
Master of Applied Science
in the program of
Civil Engineering

Toronto, Ontario, Canada, 2010

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Durability of Concrete Exposed to Sulfuric Acid Attack
Master of Applied Science, 2010

Seyed Mahmoodreza Joorabchian
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Abstract

This thesis investigates the effects of aggressive sulfuric acid attack on the concrete mixtures prepared with metakaolin (MK) and limestone filler (LF) at various replacement levels. In addition, rapid chloride permeability (RCPT), water sorptivity, water porosity and rapid freezing and thawing tests were also performed on the concrete samples. Three sulfuric acid solutions with concentrations of 3%, 5% and 7% were used for examining the resistance of concrete specimens for a total exposure period of eight weeks. The performance of the degraded specimens was evaluated by measuring the weight loss, change in strength and visual assessment. The results of the weight loss and visual assessment reveal that the increase in amount of MK would enhance the performance of concrete, while inclusion of LF into MK concretes has shown positive results in terms of resistance against sulfuric acid attack. The mixtures with ternary binders of OPC, MK and LF experienced the lowest strength loss after exposure to high concentrations of sulfuric acid. Measuring the change of weight was found to be a better way to evaluate the resistance of concrete specimens immersed in sulfuric acid solutions as the results of the load bearing capacity can be affected by several parameters such as the variable geometry of degraded specimens. The rate of the water absorption of concrete with MK and LF was lower than the reference mixture with only Portland cement. The RCPT results also showed that the reference mixture had considerably higher permeability than other concrete mixtures. The results of the water porosity on degraded samples indicate that the inner parts of the concrete (not in contact with sulfuric acid) have remained sound and maintained their original pore structure after different exposure periods.

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I would like to thank Dr. Franck Cassagnabere, who provided me with his practical experiences and worthy advice throughout this project. And I also offer my kind regards to Nidal Jaalouk and Mohamad Aldardari for their technical assistance throughout this research work.

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List of Notations

AEA	Air entraining admixture
ASR	Alkali Silica Reaction
BOD	Biological oxygen demand
CH	Calcium hydroxide
CP	Corrosion protection systems
CSA	Canadian Standards Association
C-S-H	Calcium Silicate Hydrate
GGBS	Ground granulated blast furnace slag
ITZ	Interfacial transition zone
LF	Limestone filler
LMC	Latex modified concrete
LOI	Loss on Ignition
MIC	Microbial induce corrosion
MK	Metakaolin
OCI	Organic corrosion inhibitor
OPC	Ordinary Portland cement
PMC	Polymer modified concrete
RCPT	Rapid Chloride Permeability Test
SAE	Styrene acrylic ester polymer
SBR	Styrene butadiene rubber
SCC	Self consolidated concrete
SCM	Supplementary Cementitious Materials

SL	Strength Loss
SP	Super Plasticizer
SRB	Sulfate reducing bacteria
VPV	Vinyl copolymer
WL	Weight Loss
XRD	X-Ray diffraction

Chapter 1. Introduction

1.1 General

According to the U.S Geographic Service in 2006, approximately 7.5 cubic kilometres of concrete is produced every year, and thus, it is the most used human made construction material in the world. It is interesting to note that the word ‘concrete’ comes from the Latin word ‘concretus’ which means compact or condensed. This material is generally highly durable and can be made to possess superior mechanical properties, such as high compressive and flexural strengths. It is typically made out of Portland cement, supplementary cementitious material, water, aggregates, and depending on its application and the requirements of a specific project, different types of chemical and mineral additives may be used in its production.

When it comes to resistance to different types of chemicals, the durability of concrete is quite influenced by its manufacturing process (curing methods, finishing, etc.) and the materials that are used. Moreover, if sufficient research and studies have not been previously performed, the produced concrete may not meet the durability parameters for specific environmental conditions and subsequently, the result of its application may be disastrous. Although most concrete structures have considerable long life expectancies, there are also a significant number of infrastructures in the world, such as wastewater systems, which are constantly under corrosion from different types of chemicals, such as sulfuric acid. Unfortunately, this continuous invasion and ingress of acidic ions into concrete can ultimately lead to serious damages to structures, which will consequently result in costly repairs or in some cases, complete replacement of the whole structure.

Sulfuric acid is one of the most destructive acids to concrete and depending on its concentration and formation manner, can cause severe degradation and damage to concrete structures which come into contact with it. This acid may be produced in soils and groundwater through the oxidation of iron sulfide minerals in the form of pyrites or marcasite (Richardson 2002). In the steel and iron industry, waste acids, which are used for surface preparations, may be disposed into wastewater systems which will consequently result in attacks to underground concrete facilities. Sulfuric acid may also cause degradation on the floor of food processing plants.

The most commonly known type of sulfuric acid corrosion in concrete takes place in sanitary sewer system infrastructures. This type of corrosion is also known by different names, such as biogenic sulfuric acid corrosion, hydrogen sulfide (H_2S) corrosion and microbial induced corrosion (MIC). All of these names clearly imply the nature of the corrosion process. In the United States, around 40% of the 20,000 wastewater systems are made of concrete and considerable repair and reconstruction costs are being induced by MIC in these structures. In Germany, the cost of the maintenance of private and public sewage systems runs about 100 billion US\$ and almost 40% of the damages can be related to biogenous sulfuric acid attacks (Kaempfer and Berndt 1999).

MIC typically occurs in concrete sewer pipes, treatment plants, manholes, pumping stations, junction chambers, etc. These environments have the capability of providing suitable conditions for the production of H_2S gas which will consequently oxidize into corrosive sulfuric acid and attacks concrete.

The substantial and rapid destruction of concrete sewer systems which convey sulfide-bearing sewage has been observed to occur as early as 1900. It was also noticed that the degraded concrete is highly acidic due to the existence of sulfuric acid. In 1945, Parker discovered strong acid forming bacteria from samples of deteriorated concrete sewer pipes and named them *Thiobacillus concretivorus* (Sand et al. 1994). After this discovery, researchers started to recognize that concrete damages in sewers primarily result from sulfur oxidizing bacteria.

According to various studies and investigations, the corrosion in sewer pipes is initiated by the actions of particular bacteria. The process is attributed to the sulfur cycle, which in contrast to the carbon cycle (global warming), has not significantly elicited public interest, although the development of biogenous sulfuric acid corrosion is considerably attributed to the life style of the population (Sand et al. 1994). It is important to acknowledge that, the amount of sulfur in the earth atmosphere has been significantly increased as the result of burning coal, natural gas and fossil fuels which will consequently disturb the sulfur cycle in nature. Therefore, the effect of this interruption in the sulfur cycle must be seriously taken as the carbon cycle, which again, is due to the rapid production of carbon dioxide (CO_2) in which the earth is unable to maintain its natural carbon balance, means that the concentration of CO_2 in the atmosphere constantly increases and will ultimately lead to global warming.

Under special circumstances, anaerobic conditions are found in sewers which will consequently lead to the reduction of dissolved sulfate to sulfide by anaerobic bacteria or otherwise known as sulfate reducing bacteria (SRB) (Bertolini et al. 2004). These microorganisms may be present in the mud at the bottom of sewer pipes or in the slime layer (biofilm) that coat the surface of concrete pipes below and above sewage water (Vincke et al. 1999). The H_2S that was produced by the SRB is released into the atmosphere in the sewer which is caused by various processes, such as the turbulence of the effluent and also dissolution of the H_2S in the sewage under alkaline conditions which subsequently will reduce the pH.

H_2S easily converts to a gas phase, even at low concentrations (Sand et al. 1994). As soon as the H_2S is emitted into the atmosphere, it may react with oxygen to produce elemental sulfur which is deposited onto the concrete surface. At this point, a reduction of the pH level means that biological colonization of Thiobacillus bacteria will take place. These bacteria (exist at the $pH \leq 7$) are capable of converting H_2S gas into sulfuric acid in the presence of oxygen. Various species of these aerobic bacteria colonize on the surface of concrete, decrease the pH and die out, leaving the production of acid to the next generation of more aggressive bacterium species (Ramsburg 2004). The severe corrosion and degradation of concrete infrastructures and in some cases, their total collapse, can be the ultimate result of this corrosion process.

In order to avoid the huge costs of repairs, maintenance or replacement of concrete sewer infrastructures, different solutions have been suggested for various cases of MIC over the past years. It is obvious that it would be more desirable to construct a new concrete sewage system with the capability of withstanding sulfuric acid corrosion during a long period of time without any major rehabilitation. However, in many cases, replacing an old sewage system with a new one is not an option due to the lack of sufficient funds. Hence, looking for efficient ways to protect existing sanitary facilities from further damage or possibly even increase their life span is a more realistic approach.

As previously stated, anaerobic conditions must be provided for the SRB to produce H_2S gas. These conditions are made possible by the long retention times of wastewater and uneven settlement, in which wastewater in the entirely filled mains becomes anaerobic after being transported. Thus, one of the best design approaches is to avoid long retention times (Bertolini et al. 2004).

A conventional method is to prevent the anaerobic conditions by addition of oxygen, hydrogen peroxide or nitrate to sewage. This method has been successful before, but is expensive and not considered a permanent solution.

Other protection systems, such as coatings and liners, can be used to protect the concrete surface from colonization of *Thiobacillus* bacteria and subsequently, serious damage. The problem with the coatings is that they are costly and must be applied with great skill and accuracy. Thus, avoiding any uncovered areas that may be susceptible to the ingress of sulfuric acid ions, which would cause further degradation is crucial.

It has been proven that liners are effective in corrosion protection and frequently used in the past, but they have some limitations depending on the diameter and design of the sanitary utilities. The problem with liners is that the installation must be done very carefully with great accuracy; otherwise, they can be completely useless. As depicted in Figure 1.1, liners may also delaminate and grow thin over time, which result in huge expenses in repairs and restorations (Ramsburg 2004).

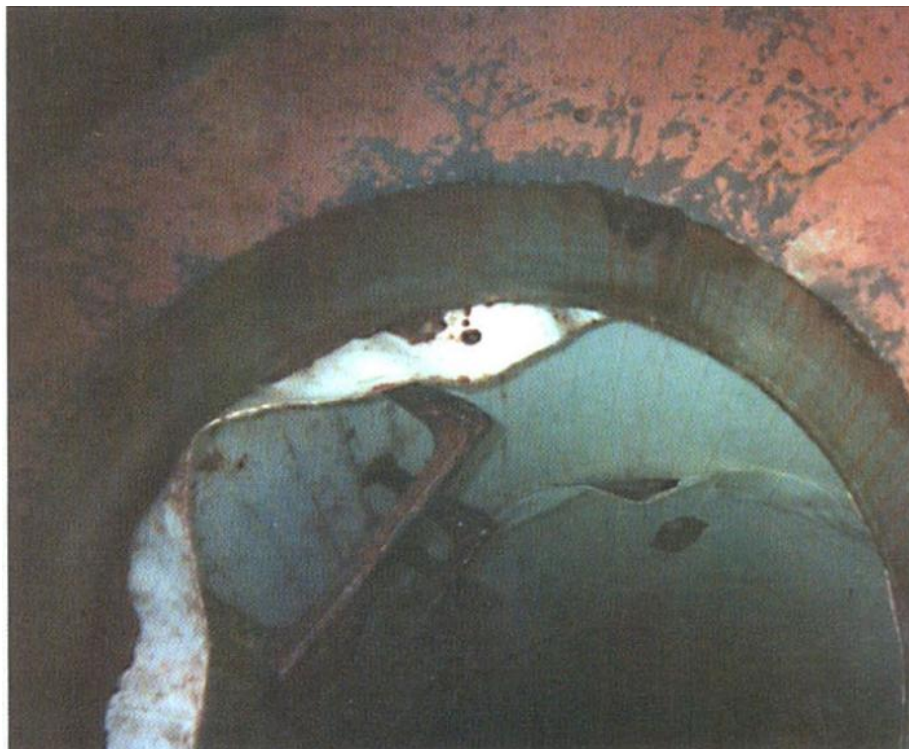


Figure 1.1 Delaminated liners of a sewer manhole (Ramsburg 2004).

Producing concrete which has good resistance against chemical and microbiological sulfuric acid corrosion can also be a solution. This goal can be achieved by using different kinds of supplementary cementing materials, chemical admixtures and mineral additives. Afterwards, the concrete specimens can be tested by using different methods in research labs to evaluate their performances in terms of strength, mass loss, appearance, etc.

It should be noted that the performance of concrete mixtures in the lab do not necessarily mean that they would behave the same way in the field as there are a wide range of parameters that can play crucial roles on concrete performance, such as the presence of other kinds of aggressive chemicals which may not be used in experimental procedures in a lab.

Anti-microbial agents have proven to be very effective in protecting concrete sewers from MIC. They were introduced in 1996 which resulted in reduction of Thiobacillus bacteria on and in concrete. Haile and Nakhla (2008) studies showed that the antimicrobial zeolite coatings inhibit the growth of A. Thiooxidans bacteria in suspension. Hewayde et al. (2007) also studied the coating of concrete pipes with copper oxide and silver oxide (metals used as antimicrobial agents) to reduce the corrosion caused by microorganisms named D. desulfuricans.

1.2 Objectives

The main objective of this study is to enhance the durability of concrete against the invasion of sulfuric acid ions by incorporating different kinds of supplementary cementing materials, mineral admixtures and polymers. The effects of binary and ternary binders when using metakaolin (MK) and limestone filler (LF) on the chemical resistance of concrete to sulfuric acid solutions has been thoroughly investigated in the experimental program of this study.

Different methods, such as measuring the change of strength, mass loss and visual inspection, have been employed to examine the resistance of concrete specimens to aggressive sulfuric acid solutions and subsequently, the advantage of each method over the other can be determined.

A more in-depth understanding of the degradation procedure and penetration of sulfuric acid into concrete specimens will be achieved by performing a phenolphthalein colour test, water sorptivity and porosity tests on deteriorated concrete samples.

It should be noted that the testing procedure which is used here is considered as a chemical resistance of concrete to sulfuric acid (Monteny et al. 2001). To evaluate the microbiological resistance of concrete, a complex testing method may be employed, which consists of growing bacteria and sometimes using an environmental chamber to simulate real life sewer conditions.

It is commonly known that the pore structure of concrete plays a crucial role on its durability in different environmental conditions. Therefore, another aim of this study is to examine the permeability characteristics of original concrete specimens from different mixtures by performing various tests, such as rapid chloride penetration, water sorptivity and water porosity. These tests together will provide a better understanding of the pore structure of concrete mixtures that contain different quantities of supplementary materials.

In addition to examining the performance of concrete exposed to sulfuric acid attacks, the effects of including different quantities of MK and LF on concrete resistance to repeated freezing and thawing cycles are also investigated.

1.3 Thesis Outline

The first chapter is an introduction to the study which provides a brief background on the corrosion of concrete sewage systems and the factors involved in their degradation process. The formation of sulfuric acid and its detrimental effect on concrete infrastructures is discussed. The solutions which have been used to improve the life span of concrete sewage structures are briefly reviewed in this chapter.

Chapter 2 is a comprehensive review of previous studies on the durability of concrete in terms of resistance to sulfuric acid attacks which is the main aspect of this research. The production and different types of sulfuric acid attacks are discussed. The effect of various kinds of supplementary cementing materials, such as silica fume, blast furnace slag, MK, etc. on concrete resistance to sulfuric acid is reviewed. The incorporation of polymer modifiers and their effects on the performance of concrete exposed to aggressive sulfuric acid is discussed. In this regard,

the role of other concrete constituents, such as aggregates, Portland cement and water, is also presented in this chapter.

Two case studies and previously used corrosion protection (CP) systems are described. Finally, the pore structure of concrete and the significant role that it plays on durability properties is presented which is then followed by a brief study of the freezing and thawing effects on concrete.

Chapter 3 represents the experimental program of this study. Introductory studies are provided on the resistance of concrete specimens from different mixtures that contain acrylic latex polymer, fly ash and Xypex to a solution with 3.5% concentration of sulfuric acid. The materials of the study and their properties are introduced. The mix designs, placing and curing of concrete specimens are presented. In the experimental program, concrete cylinders from 5 different mixtures are subjected to three sulfuric acid solutions with concentrations of 3%, 5% and 7% for a total period of 8 weeks and several measurements are taken to evaluate their resistance in this period. The procedure for all of the experiments is thoroughly described in this chapter.

The results of the experimental program of this study are provided in Chapter 4. There will be an in-depth analysis and discussion of the test results. The results of the introductory studies are also presented and discussed. The fresh and hardened properties of five different concrete mixtures are presented, followed by the results of the strength change, mass loss and visual inspection of specimens subjected to different sulfuric acid solutions. The results of the rapid chloride permeability test, rapid freezing and thawing, water sorptivity, and water porosity are presented and analyzed. In the degradation section, the results of a phenolphthalein test, water porosity, and sorptivity on concrete specimens exposed to sulfuric acid attacks for different periods are thoroughly analyzed.

Chapter 5 is dedicated to the conclusions and recommendations derived from an analysis of the results in this research program.

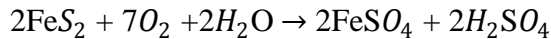
Chapter 2. Literature Review

This chapter reviews previous studies and investigations on the durability of concrete in terms of resistance to sulfuric acid attacks and also contains a brief review of permeability properties and frost resistance of concrete.

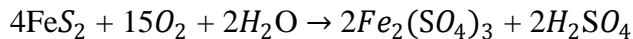
2.1 Sulfuric Acid Attacks

Sulfuric acid can be present or produced in different environments that surround concrete infrastructures. The places in which sulfuric acid can exist and have detrimental effects on concrete are as follows.

Groundwater usually contains many different sulfates and free sulfuric acid may also be one of the products. Free sulfuric acid can be produced by oxidation of pyrite (FeS_2) or other sulfides which may exist in soils with the help of air oxygen under weathering circumstances.



Or



It should be noted that the rate of the deterioration of concrete structures close to groundwater is dependent on the concentration of the sulfuric acid and the amount of water that can reach the concrete surface. The permeability of the soil that is in contact with concrete also plays an important role (Skalny et al. 2002).

Industrial waste can contain a considerable amount of sulfuric acid. For example, in the iron and steel industry, strong mineral acids, such as hydrochloric and sulfuric acids, are used to remove rust and prepare the surface in the final treatment before the iron and steel are sold to manufacturers. Therefore, the wastewater that is usually discharged into the underground sewage

system can contain waste sulfuric acid that is very hazardous for concrete pipes and may cause severe corrosion in the short or long term period.

The environment of concrete sewer structures and bacterial reactions, which take place in the pipes, may lead to the creation of sulfuric acid, in which due to its formation process, can be more harmful and destructive than regular acid. The deterioration of concrete caused by this process is commonly known as MIC. This microbiological process is the reason for billions of dollars in expenses for maintenance, repairs and finally, in some of the worst conditions, complete replacement of sewer pipes. Hot climates can be a favourable place for microbial growth and the underground sanitary system of these places has been frequently subjected to this kind of corrosion. However, it should be noted that there has also been substantial damage in concrete sewage systems in the northern parts of the United States and Canada, which have really cold weather for the majority of the year.

Sulfuric acid may also be present in acid rain, which is formed by oxidation of sulfur dioxide (SO_2), a product of the combustion of coal and petroleum or other industrial processes. This rain can be harmful to concrete infrastructures in some situations where its pH is around 3, but in comparison to other deteriorations caused by sulfuric acid, it has a somewhat weak effect on concrete and in most cases, damage can be avoided by producing good quality concrete.

2.1.1 Microbial Induced Corrosion (MIC)

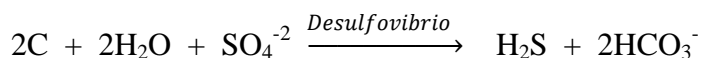
Around 40% of the sanitary sewer infrastructure systems in the United States are made of concrete and the degradation of these structures has resulted in billions of dollars in maintenance and reconstruction.

According to previous studies, there are two different types of corrosions caused by sulfuric acid. One is biogenic and the other one is simply chemical. The concrete sewer structures that have been constructed for a life span of at least 30 years, in some cases, collapse and fail in a few years due to biogenic sulfuric acid attacks.

It is interesting that the corrosion of sewer pipes has been falsely called a corrosive gas problem after almost 60 years since the discovery of MIC by Parker in 1945. However, the real issue in the sewer pipes is not the gas itself as it is the reaction that takes place between the H_2S and the Thiobacillus bacteria that can be very destructive for concrete (Ramsburg 2004).

Concrete structures, such as manholes, treatment plants and sewer pipes, contain considerable amounts of liquid waste which make them suitable places for anaerobic bacteria to convert dissolved sulfate into H₂S. The species responsible for the formation of sulfide gas in the sewer atmosphere are called SRB which reduce the oxidized sulfur compounds into H₂S (Vincke et al. 1999).

The reaction that takes place for the production of H₂S gas by the SRB in sewer pipes is as follows (Kaempfer and Berndt 1999):



The question that comes to mind is to determine how anaerobic conditions are provided for the SRB to perform its work. The response is that these conditions may happen in the sewers as the result of long term storage of wastewater that becomes anaerobic in the entirely filled pressure mains (Bertolini et al. 2004). It should be noted that the SRB grows in the bio film or slime layer that covers the inside surface of the concrete pipes and usually oxygen is not able to permeate this layer, therefore an anaerobic area is formed which is the perfect place for sulfides to be produced (Kaempfer and Berndt 1999). The temperature, retention time, high biological oxygen demand (BOD) levels and turbulence are factors that contribute to rapid bacterial growth in underground sewage systems (Ramsburg 2004).

With the turbulent overflow of anaerobic wastewater to the aerobic sections of the sewers, more H₂S gas is released into the sewer environment, and this phenomenon usually happens in lift stations and manholes. It should be mentioned that another reason for the emission of H₂S gas into sewer pipes is the acidification and reduction of the pH level.

Thiosulfuric and carbonic acids that are produced by CO₂ and H₂S will reduce the pH level of the concrete surface by reacting with calcium hydroxide (Ca(OH)₂), but these acids hardly create any problems for concrete pipes. As soon as the pH of the concrete is dropped to a certain amount, the colonization of different kinds of Thiobacillus bacteria takes place on the surface (Vincke et al. 1999). These bacteria are capable of transforming H₂S gas into sulfuric acid. A type of bacteria that is called Thiobacillus thiooxidans, also known as concretivorus, is able to produce sulfuric acid with very high concentrations of up to 10% in mass that can severely corrode a

concrete structure (Bertolini et al. 2004). The production of H_2S and its conversion into sulfuric acid in concrete sewer pipes is shown in Figure 2.1.

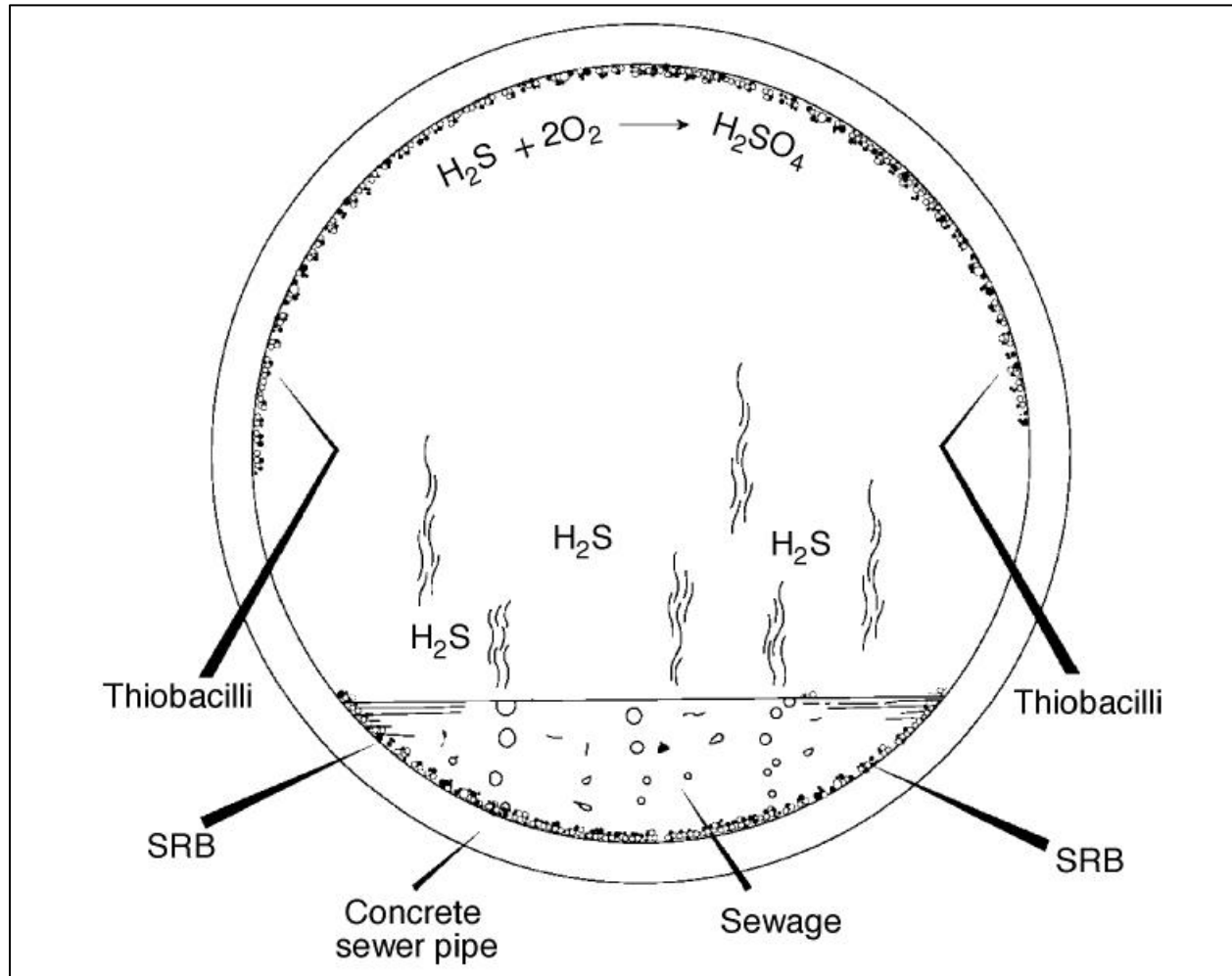


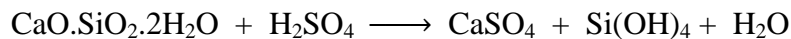
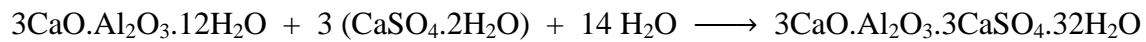
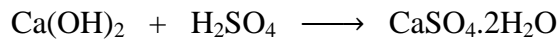
Figure 2.1 Illustration of sulfur cycle taking place in the sewer pipes (Little et al. 2000).

When the sulfuric acid begins to react with concrete, the result of this reaction is believed to be more harmful than a regular sulfate attack as it combines both sulfate and acid. The hydration products in regular concrete are in an equilibrium state with the pore solution which has a high pH value due to the existence of hydroxide ions. As soon as the reaction between the sulfuric acid solution and hydration products takes place, the dissolution of hydrated composites by

hydrogen ions will occur. The rate of this action is dependent on factors such as concrete porosity and pore structure, and most importantly the pH and concentration of the sulfuric acid (Li et al. 2009).

It should be noted that sulfuric acid migrates from the outside surface of the concrete to the interior. Therefore, the outer surface of concrete, which mostly consists of mortar, plays an important role in neutralizing and preventing the solution from penetrating the inside core of the concrete. In this regard, products such as Ca(OH)_2 , calcium silicate hydrate (C-S-H) and limestone aggregate are the neutralizing forces that can help provide the concrete with better resistance against acidic corrosion (Li et al. 2009).

Gypsum is the initial product of the reaction between sulfuric acid and hydration composites which is followed by an expansion in volume of the concrete. The production of gypsum and other compounds, which result from the reaction of concrete with sulfuric acid, are illustrated as follows (Monteny et al. 2000).



The increase in volume which is initially caused by the formation of gypsum will result in tensile stresses in concrete and ultimately spalling of the concrete surface. As the reaction of gypsum with calcium aluminate phases continues, the production of ettringite takes place which will cause an expansion in volume by a factor of about 7, which is significantly higher than the volume increase caused by gypsum. The internal stresses that result from the previously mentioned reactions will eventually lead to a considerable amount of cracking in the concrete microstructure (Monteny et al. 2000). Sulfuric acid may also cause the decalcification of C-S-H and will ultimately transform the C-S-H into amorphous hydrous silica.

The white gypsum (a by-product of sulfuric acid attacks) which covers the surface of concrete can act as a protective layer to prevent more degradation of the concrete matrix, but can be easily removed or washed off by floods in the sewer pipes, which results in the exposure of the concrete bare surface to more sulfuric acid attacks.

2.2 Prevention of Sulfuric Acid Attacks

Concrete durability in terms of resistance to sulfuric acid attacks can be improved in a number of ways. As previously stated, sulfuric acid may exist in different places, such as in underground water and industrial waste, and can be very harmful for concrete structures that come into contact with it. The most common and destructive corrosion problem is in the underground concrete sewer structures of North America which is caused by biogenic sulfuric acid attacks.

There has been much work and many studies around the world to avoid the severe deterioration of concrete that results from this type of acidic attack or at least improve the performance and extend the life span of the concrete structures with this problem. This special type of degradation that is mostly observed in sewer pipes, junction chambers, manholes and sumps, can be treated in different ways. For example, one way to treat this issue is to look at the initial stage of the microbiological process, which is the activation of the SRB under anaerobic conditions induced by long retention times in the sewage systems. This process can be avoided by adding oxygen, hydrogen peroxide or nitrate into the sewage which will cause resistance against anaerobic conditions. Another solution is to connect rain drainages to raise the flow in sewer pipes or in other words, avoid long storage times in the system (Bertolini et al. 2004).

It should be noted that the usage of chemicals, such as potassium permanganate, chloride and oxygen in the sewage to reduce the amount of H_2S gas, is costly and will only serve as temporary solutions (Ramsburg 2004).

Another way to improve the life expectancy of concrete infrastructures subjected to severe sulfuric acid corrosion is to use different types of CP systems, such as sheet liners, which will be described in the upcoming parts.

Improving the quality of the concrete by using different types of supplementary cementing materials, mineral additives, chemical admixtures and polymeric modifiers, is also a good way to increase resistance to sulfuric acid attacks.

Another method to decrease the deterioration of concrete pipes in a sewage system is to prevent the formation of Thiobacillus bacteria. This can be done by using different kinds of antimicrobial agents.

2.2.1 Role of Supplementary Cementing Materials

There are many reports on the usage of different types of supplementary cementitious materials (SCM) in the concrete mix to evaluate their effects on the durability of concrete in terms of resistance to sulfuric acid attacks. It should be noted that in most of these studies, the most popular method of exposing the concrete specimens to sulfuric acid solutions with different concentrations and pH has been used. According to previous studies, there has not been a total agreement between researchers on the effects of different kinds of SCMs on concrete performance against sulfuric acid attacks. In the following sections, different SCMs and their effects on the resistance of concrete against sulfuric acid will be thoroughly discussed.

2.2.1.1 Silica Fume

Silica fume is the by-product of silicon metal and ferrosilicon alloys. This product, which is also known as microsilica, is famous for its great fineness and high silica content. Silica fume has a very high surface area and from a pozzolanic point of view, is very active. It has been many years since this product was used for the first time in concrete and it has successfully enhanced the properties of concrete, such as strength, abrasion and microstructure. It should be noted that in terms of resistance to chloride ion penetrations, silica fume will significantly improve the concrete performance.

However, when it comes to concrete resistance to sulfuric acid, there are different opinions about the effectiveness of this type of SCM. For example, Durning et al. (1991) reported that silica fume would improve the resistance of concrete against a 1% sulfuric acid solution by refining the pore structure and reducing the amount of Ca(OH)_2 . They also found that the C-S-H formed in the concrete which contains silica fume is more stable in low pH conditions.

Mehta (1985) reported that replacing Portland cement with 15% silica fume would improve the resistance of concrete to a 1% sulfuric acid solution. In this study, cylindrical specimens were submerged into a sulfuric acid solution and their weight was measured every week after the removal of loose particles from their surfaces by using a steel wire brush. A better performance of the concrete which contains micro silica was attributed to less Ca(OH)_2 and more C-S-H phases in its structure.

On the other hand, the studies of Monteny et al. (2003) on different concrete mixtures showed that concrete mixture with 8.6% silica fume does not perform very well in terms of resistance to 0.5% sulfuric acid. In their studies, a special kind of apparatus was used to expose the concrete cylinders to the 0.5% sulfuric acid solution. As illustrated in Figure 2.2, concrete cylinders were subjected to cycles of immersion in sulfuric acid solution and dried in air by rotation on horizontal axes at the pace of 1 RPH. Each cycle would last around 12 days and subsequently, rotary brushes are used to eliminate the loose particles found on their surfaces.

The study of Chang et al. (2005) demonstrated that concrete mixtures with both fly ash and silica fume as SCMs perform very well against a 1% sulfuric acid solution after a specific immersion period.

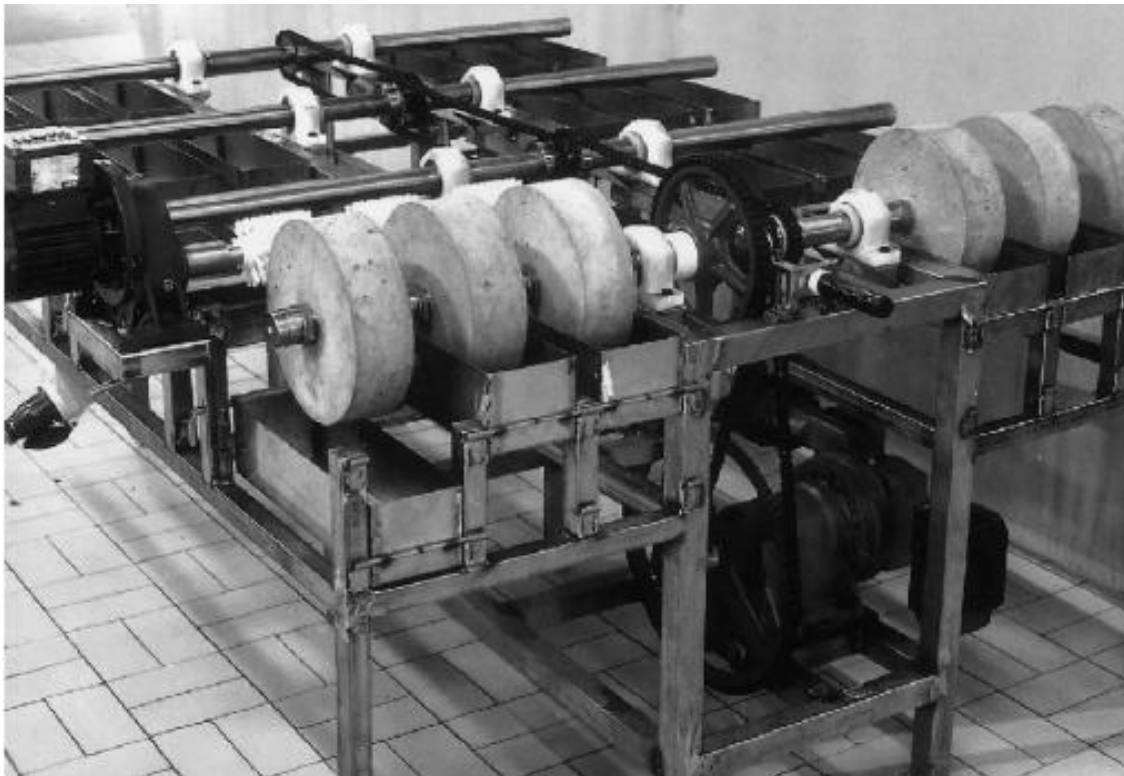


Figure 2.2 Apparatus for accelerated degradation testing (De Belie et al. 2002).

2.2.1.2 Ground Granulated Blast Furnace Slag

Ground granulated blast furnace slag or simply GGBS is another SCM that has been widely used in the concrete industry to improve concrete durability. GGBS is the by-product of steel and iron manufacturing. It is made by cooling melted iron slag from a blast furnace in water or steam and grounding the granular glassy product to a fine powder afterwards. This product has been successfully used all around the world and occasionally, has improved the lifespan of concrete from 50 to 100 years. However, according to previous research and studies, it is generally not accepted as an appropriate SCM when it comes to resistance to sulfuric acid exposure.

For instance, Monteny et al. (2003) reported that concrete samples made with slag cement have superior behaviour in comparison to the ones made with regular Portland cement in terms of durability against a 0.5% concentration of sulfuric acid solution. On the other hand, the studies of Bassuoni and Nehdi (2007) on the resistance of self consolidating concrete (SCC) to a 5% sulfuric acid solution showed that concrete cylinders with 45% slag and 5% silica fume had the highest mass loss in comparison to other mixes. However, it should be noted that the mixture with GGBS and silica fume had less weight loss than the reference mix with only Portland cement, but its performance was inferior to the other mixtures with different kinds of supplementary cementing materials.

In this regard, Chang et al. (2005) reported that concrete specimens with 60% slag content do not display a satisfactory improvement against a 1% sulfuric acid solution after the end of their testing period.

2.2.1.3 Fly Ash

Fly ash is one of the several by-products of coal combustion in electric generating plants or power stations. This fine product is generally captured from the chimneys of coal burning power stations and consists of inorganic matters that have been fused during combustion into a glassy, amorphous structure. It has been used as a replacement for ordinary Portland cement (OPC) to improve concrete durability and mechanical properties over the years. Two classes of fly ash are defined by ASTM C618. Class F has less than 10% lime content and good pozzolanic properties, but no cementitious nature. Class C usually has more than 20% lime content and unlike Class F, has some cementitious properties, but its pozzolanic activity is lower.

In the Canadian Standards Association (CSA) Standard A3001-A23.5, fly ash is classified into F, C and CH (high CaO content) classes which contain less than 8%, between 8% and 20%, and more than 20% calcium oxide (CaO) by mass, respectively.

According to the literature, in most cases, fly ash improves the behaviour of concrete against exposure to sulfuric acid attacks. Aydin et al. (2007) studied the effects of incorporating Class C fly ash into concrete on its resistance to a 5% sulfuric acid solution in a period of 60 days of total immersion. They used different replacement levels of 10% to 70% fly ash and also employed two methods of curing: in lime water and steam curing. For steam cured cylinders, the concrete with 70% fly ash had 37% less strength loss (SL) than the ones without any fly ash. Moreover, the weight loss of the concrete (standard cured) with no fly ash has reduced from 5% to 3.3% by replacing Portland cement with 70% fly ash. It should be noted that the overall trend of weight loss (WL) versus fly ash content of different concrete mixtures demonstrates improvement of concrete durability against a 5% sulfuric acid solution by using various percentages of high calcium fly ash. Figure 2.3 represents the SL and WL versus fly ash replacement levels for different concrete mixtures cured in lime water (Aydin et al. 2007).

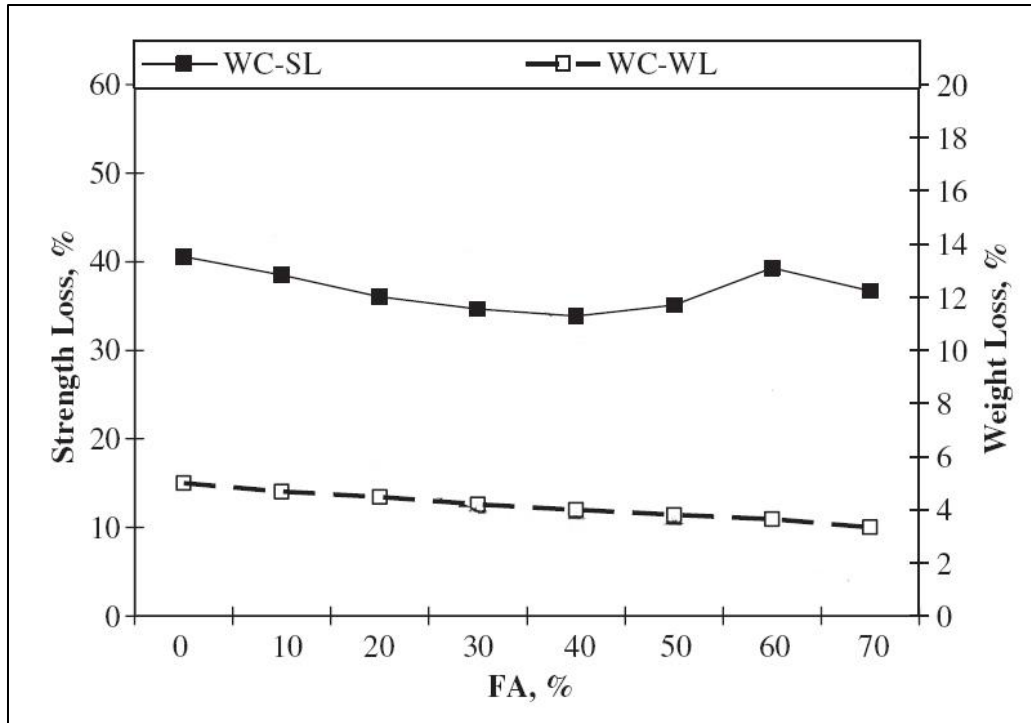


Figure 2.3 Strength loss and weight loss percentages of water cured specimens with different quantities of fly ash (Aydin et al. 2007).

In the Bassuoni and Nehdi (2007) studies on SCC resistance to sulfuric acid solution, the concrete mixture with a quaternary binder of 50% cement, 20% slag, 15% LF and 15% low calcium fly ash performs the best in terms of mass loss at the end of a certain immersion period in a 5% sulfuric acid solution. Roy et al. (2001) studied the effects of incorporating low calcium fly ash and other types of supplementary cementing materials into mortars on their resistance to 1% and 5% sulfuric solutions. They used fly ash in percentages of 7.5% to 30% to replace Portland cement. Their results showed that mortars with fly ash had the best performance between all the mixtures in terms of mass loss after a 28 day immersion period. Roy et al (2001) showed that the WL increases as the amount of replacement with fly ash increases from 0-10% to 15-30%.

2.2.1.4 Metakaolin

The characteristics of thermally activated alumino-silicate called MK and its effects on concrete mechanical and durability properties are discussed in this section.

At 650-800°C, the calcination of kaolinite (a clay mineral) takes place by a process called dehydroxilation. This process will produce a reactive amorphous pozzolan called MK. MK is in the form of a white powder and usually contains 50-55% of silicon dioxide (SiO_2) and 40-45% of aluminum oxide (Al_2O_3) and very little calcium oxide and alkalies, hence, it needs a cementitious material to hydrate. The particle size is around 2 μm , which is smaller than the 10 μm particle size of regular Portland cement, but compared to silica fume, the size of its particles is larger (Zhang and Malhotra 1995). As a cement replacement, MK starts to react with CH and produces C-S-H gel after mixing with concrete, and in addition to that, the alumina phases in MK also react with $\text{Ca}(\text{OH})_2$ which will result in the formation of extra alumina containing phases, such as C_4AH_{13} , C_2ASH_8 and C_3AH_6 (Kim et al. 2007). MK has a significant advantage over other kinds of supplementary cementing materials because it is a primary product rather than a by-product, such as fly ash. Therefore, the properties of MK can be controlled and adjusted to a desirable quality (Poon et al. 2006).

According to the literature, MK has the following influences on concrete properties: increased compressive and flexural strength, improved workability and finishing of the concrete, less shrinkage, better resistance against Alkali Silica Reaction (ASR), reduced permeability and an overall enhancement in concrete durability.

In the Republic of Korea, silica fume is normally used as a replacement for Portland cement to produce high performance concrete. However, the high price of imported silica fume has significantly increased the cost of construction; therefore, some studies have been done on the use of MK in high performance concrete which has similar effects as silica fume and is more economical at the same time (Kim et al. 2007).

One of the other advantages of MK over silica fume is that although concrete with 10% MK in lieu of cement has less slump than concrete with 100% Portland cement, it consumes 25-35% less high range water reducer admixture than concrete with the same percentage of silica fume. Therefore, finishing and placing of MK concrete is more painless than concrete with silica fume (Caldarone et al. 1994).

In concrete that contains different quantities of MK, the strength increases more rapidly at the early ages than concrete with silica fume, but after a long term curing, their strengths become the same. This behaviour is the result of a higher degree of pozzolanic reaction at the initial stages of curing of MK concrete, but the pace of the hydration will eventually slow down (Poon et al. 2006).

Several reports on the porosity and chloride permeability of concrete that contains different amounts of MK can be found in the literature. It is generally accepted that the incorporation of MK will result in better resistance against chloride ion penetration and also lower porosity. Poon et al. (2006) used 5-20% MK in their production of high performance concrete and compared its pore structure with concrete that contained silica fume and a reference mixture that contained only Portland cement. Mercury intrusion porosimetry was used in their study to determine the porosity and average pore diameter of different concrete specimens. The final results of their studies illustrated that MK concrete has less porosity and smaller pore size in comparison to the control and silica fume concrete. It can be observed from Figure 2.4 that the cumulative mercury intrusion curve of 20% MK is lower than the control mixture, which verifies a finer pore size distribution of this mix after 28 days of water curing.

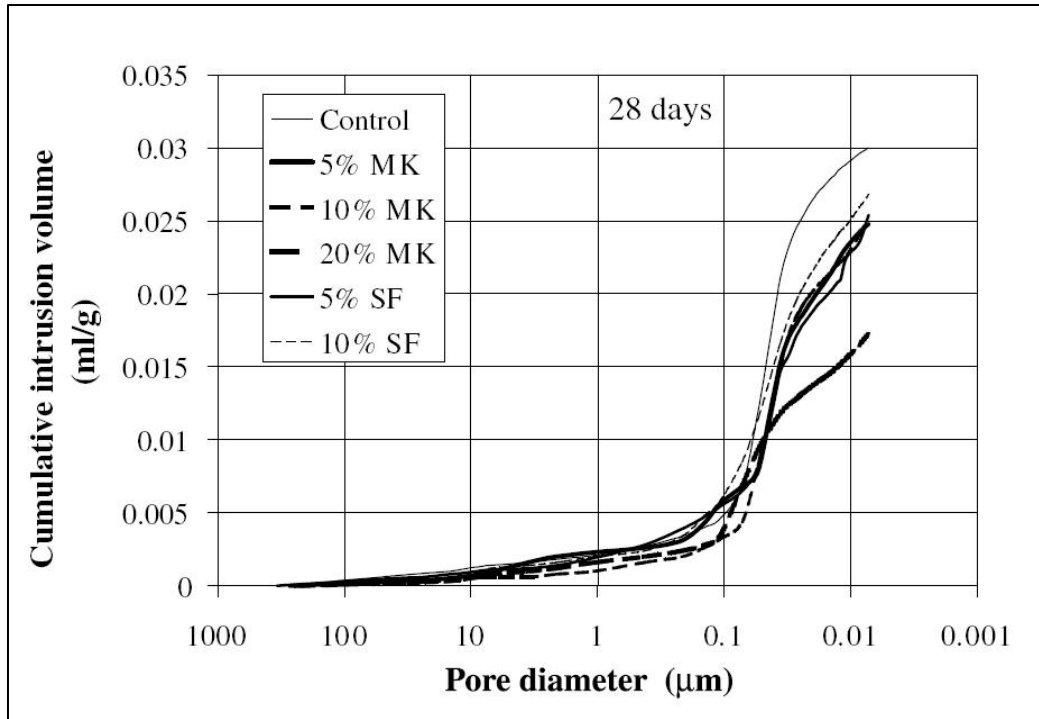


Figure 2.4 Pore size distribution of different concrete mixtures after being water cured for 28 days (Poon et al. 2006).

There is limited information in the literature on the resistance of concrete with MK to sulfuric acid attacks. Akhras (2006) studied the use of MK as a replacement for cement in percentages of 5-15% in concrete exposed to sulfate attacks. A 5% sodium sulfate solution was used in which concrete prisms were immersed for a period of 18 months. It was reported that the prisms that contained 10% and 15% MK with a water-binder (w/b) ratio of 0.5 have the maximum expansion of 0.10% and 0.07% after the 18 month immersion period. By replacing regular Portland cement with different amounts of MK, the tricalcium aluminate hydrate phase will be diminished in the concrete matrix and aside from that, more CH is consumed by the pozzolanic reaction of MK and more C-S-H will be produced in the hydration phase. Thus, all of these will ultimately result in an enhanced resistance of concrete to the sulfate solution (Al-Akhras 2006).

A study has been implemented by Daczko et al. (1997) on the durability of concrete bars against sulfuric acid solutions with different pHs of 1, 2.5, 4 and 7. MK, silica fume and an organic corrosion inhibitor (OCI) were used in this study as admixtures to improve concrete performance. The replacement level for MK and silica fume was 8% in two separate mixes. The bars were submerged into containers for a total period of 100 days and the acid solution was refreshed every two weeks to keep the pH constant. The specimens were removed at 7, 14, and 28 days and after that, every 4 weeks until the end of the testing for weight and length measurements. It is interesting that the final results of their experiments demonstrate improved performance of silica fume and OCI concrete, but no such improvement was noticed for MK concrete. It was observed that concrete that contained 8% MK performs the same as concrete with only type I Portland cement as the binder. This result is mostly evident for specimens in an acid solution with pH 1. Daczko et al. (1997) believed that the presence of Al_2O_3 in the MK may cause further reaction and corrosion of concrete that is exposed to sulfuric acid, but it should be noted that this result must be further investigated.

The results of Roy et al. (2001) study on mortars which consisted of different SCMs, and subjected to 1% and 5% sulfuric acid solutions, entirely contradict the results of Daczko et al. (1997). The mortar specimens were completely submerged into the solutions and also other kinds of acidic solutions throughout a period of 28 days. The specimens immersed in a 1% sulfuric acid solution were not very affected after the exposure period, but on the contrary, all of the specimens (with and without SCM) had inferior performances against a 5% sulfuric acid solution. Roy et al. (2001) investigation showed that concrete specimens which consisted of MK with a 7.5-22.5% replacement levels had better resistance against a highly aggressive sulfuric acid solution than the reference mix and the mixture with the same quantity of silica fume. It is important to note that WL was used as an indicator of the performance evaluation and the pH of the 5% sulfuric acid solution increased from the initial 1.03 to 6.95 at the end of the 28 day period. The curing regime in this study was 28 days moist curing in 95% relative humidity and w/b ratios of 0.36 and 0.40 were used for the mortars with MK.

2.2.1.5 Limestone Filler

Although LF is considered a mineral additive and not a SCM, its properties and contributions to the mechanical and durability attributes of concrete will be discussed in this section.

High consumption of energy and the production of a large number of environmentally hazardous products is the most crucial issue for cement producing plants. Hence, in order to distribute less CO₂ and consume less energy, cement manufacturers are blending mineral admixtures, such as slag, natural pozzolans and LFs, after the burning stage (Kenai et al. 2004). In France, the total consumption of LF has increased to 2.4 million tons in the cement producing industry. Moreover, 470,000 tons of LF were used in ready mixed concrete plants compared to 350,000 tons of fly ash in 2004 (Kenai et al. 2004).

The technical advantages of using LF in concrete are the increase of early strength, low sensitivity to the inadequacy of curing, and control over bleeding. Furthermore, as previously stated, there is the economic benefit of using less cement for the same strength development. Many studies have been carried out on the performance of concrete, mortars and pastes which contain different amounts of LF. Generally speaking, LF increases the hydration rate of cementitious components and thus, improves the strength at the early ages. It is important to note that LF does not have pozzolanic properties, but it is not inert either (Bonavetti et al. 2003).

It is believed that LF has a dual reaction in concrete. First, there is the acceleration effect. The particles perform as nucleation areas, which improve the likelihood of encounter between the C-S-H and the solid particles, and then they precipitate. This behaviour is only notable at the early ages and insignificant after 28 days of curing. Second, if the cement contains a considerable amount of aluminate phase (AFm), carboaluminate components will be created which have some cementing potential (de Larrard 1999).

It should be noted that the major influence of LF is on the physical properties, as it results in the improved packing of the cement granular structure and greater dispersion of cement grains (Bonavetti et al. 2003).

In this study, an LF with a specific fineness has been used. Hence, it is appropriate to mention that when it comes to LF fineness, there are some associated effects. First, the acceleration

effect is controlled by the specific surface of this mineral additive. Second, as the fineness of the filler increases, the water demand of the binder also increases to reach the required slump, and if the particle size of the LF is around 1 μm or less, large quantities of super plasticizer (SP) must be used (de Larrard 1999).

The durability of concrete mixtures with LF in terms of resistance to sulfuric acid attacks has been studied by very few researchers. One study has been performed on the resistance of SCC that contained 47% LF to 1% sulfuric acid (Al-Tamimi and Sonebi 2003). Cylindrical specimens that were 45 mm in diameter and 90 mm in height were immersed into a 1% acidic solution for a period of 18 weeks. Mass loss and visual inspection were used as indicators of the performance of the different specimens. It should be noted that these results were compared to the results of conventional concrete which contained only Portland cement subjected to the same testing method. The final results showed that conventional concrete had experienced severe degradation and lost 21% of its mass while the SCC mix with limestone powder lost only 9% of its mass at the end of the immersion period. The better performance of the LF concrete was attributed to the sacrificial effect of limestone powder (Al-Tamimi and Sonebi 2003).

In the studies of Bassuoni et al. (2007), different groups of concrete mixtures were subjected to a sulfuric acid solution with a concentration of 5%. One of their mixtures comprised 50% Portland cement, 15% LF, 20% slag and 15% fly ash (B4-N-50). The SRPC mixture was made with type V Portland cement, OCI mixture contained organic corrosion inhibitor and OPC, B1-N-50 mixture contained 100% Portland cement as the only binder, B2-N-50 was a binary binder mixture with 8% silica fume, B3-N-50 was a ternary binder mixture with 5% silica fume and 45% slag and B5-N-50 was quaternary binder mix with 5% silica fume, 20% fly ash and 25% slag at different replacement levels of OPC.

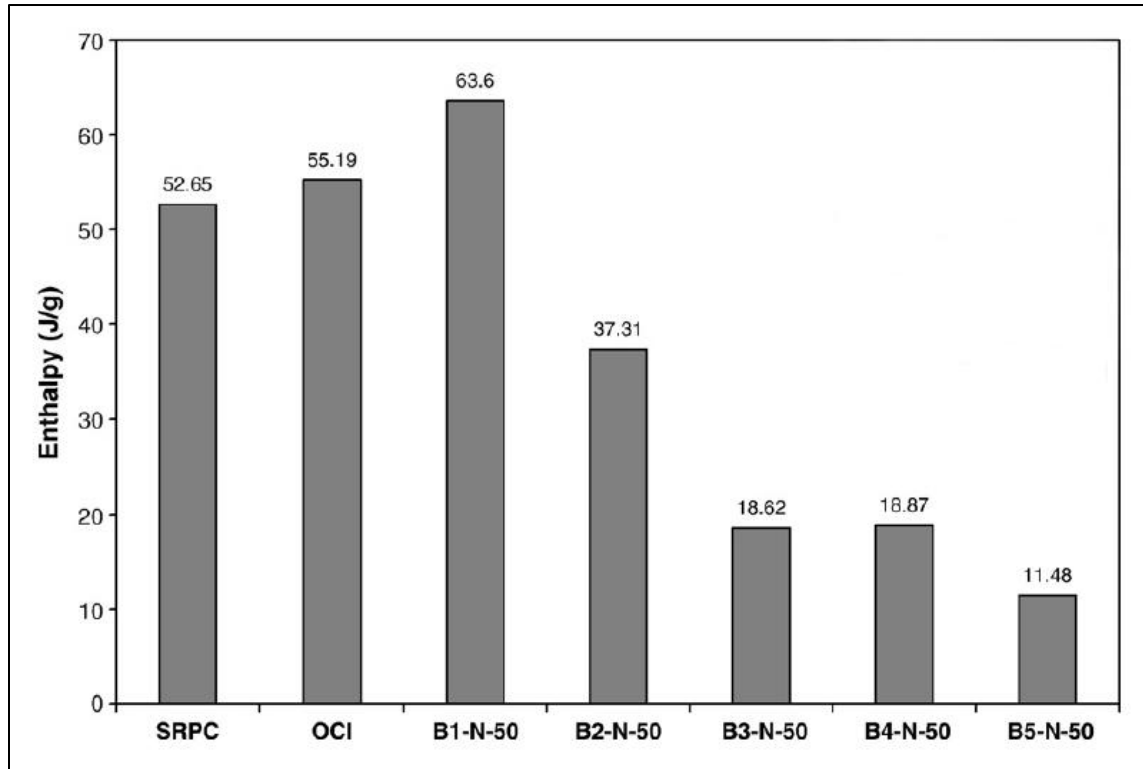


Figure 2.5 The $\text{Ca}(\text{OH})_2$ heat flow peaks of non air entrained mixtures after 56 days of moist curing (obtained by DSC) (Bassuoni and Nehdi 2007).

This quaternary binder mix was made three times with different properties. One was air entrained, the second had no air, and the third had steel and polypropylene fibers. Cylinders that were 75 mm × 150 mm in size were moist cured for 56 days in 95% relative humidity before being submerged into the solutions. The air entrained and no air mixtures had a similar trend in mass loss after six weeks of exposure. The quaternary mixture had an average of a 66% decrease in mass loss in comparison to the control mixture at the end of phase I with a pH threshold of 2.5. At the end of phase II (6 weeks with pH threshold of 1), the mixture with four binders which contained 15% LF, had a 42% reduction in mass loss in comparison to the control mixture (the best performance). For phase I with a higher pH, this performance was attributed to the consumption of $\text{Ca}(\text{OH})_2$ by the high amount of SCM. Figure 2.5 demonstrates the results of differential scanning calorimetry on the different mixtures after the moist curing period. It can be observed that the enthalpies of CH in B3 (ternary binder) and B4 (quaternary binders) is considerably less than the mixture with no SCM (Bassuoni and Nehdi 2007).

For phase II with a lower pH of 1, the superior performance of concrete that contains LF was considered to be the result of the buffer layer made by the LF around the surface of the concrete. An X-ray diffraction (XRD) analysis showed strong peaks of calcium magnesium carbonates for LF concrete which may demonstrate the existence of this protective layer (Bassuoni and Nehdi 2007).

2.2.2 Portland Cement

Various types of cement are produced in different parts of the world with a wide range of compositions and characteristics. The most widely used cements are the Portland cements. These types of cement have hydraulic properties, or in other words, they set and gain strength by reacting with water and their main constituents are hydraulic calcium silicates. The name Portland originated as a trade name and does not reflect the composition or properties of the cement. Currently, the name applies to various types of cements that are produced to meet different chemical and physical requirements for specific usages, but it is important to note that the overall properties are very similar (Mindess et al. 2003).

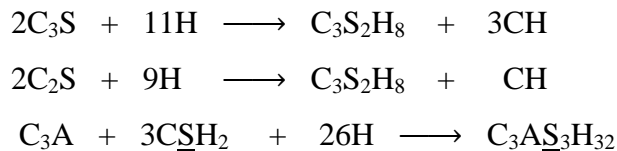
In Canada, the CSA has identified six types of Portland cement under Standard A3001. These six types of cement are as follows: general use (GU), moderate sulfate resistance (MS), moderate heat of hydration (MH), high early strength (HE), low heat of hydration (LH), high sulfate resistance (HS), and white Portland cement. The ASTM C1157 has equivalent designations for the five types of Portland cement used in the United States.

Type GU (Type 10) cement is for general usage and most commonly employed in the construction of concrete structures in which no particular or exceptional requirements are needed. MS cement was developed with a higher rate of strength development as it contains more tricalcium silicate (C_3S) than LH cement and at the same time, has some resistance against sulfate invasion.

HS cement, formerly known as Type V, has a low quantity of tricalcium aluminate (C_3A) which makes it durable in terms of resistance against different kinds of sulfate attacks. It is important to note that reducing the C_3A phase by converting it into calcium aluminoferrite (C_4AF) has been

considered as a very efficient way to combat sulfate attacks. According to previous studies, keeping the C_3A content under 5% by weight has proven to be very successful in the performance improvement of concrete in aggressive environments (Mindess et al. 2003).

The outcome of the reaction between Portland cement and water in concrete are hydration products. Among these products, $Ca(OH)_2$ and ettringite are responsible for concrete deterioration when it is subjected to environments that contain aggressive sulfates. The following equations represent the reactions which take place between the cement compounds and water and will consequently result in the generation of hydration products (Mindess et al. 2003). The $C_3S_2H_8$ or C-S-H is the primary product of cement hydration. The composition of this compound is changeable over an extensive range and this formula is only approximate. The CH is a fine crystallized material with a well defined structure. This product is completely vulnerable to sulfate attacks as it reacts with sulfates and produces gypsum.



The last equation demonstrates the formation of $C_3AS_3H_{32}$ or simply, ettringite. It is important to note that in this equation, the \underline{S} represents sulfate and CSH_2 is obviously the gypsum that is provided by the cement. Similar to CH, ettringite also crystallizes in the form of hexagonal crystals, but in the shape of needles with a higher aspect ratio. Ettringite is a solid or stable hydration compound as long as there is a sufficient supply of sulfate. When the sulfate is used up before the complete hydration of C_3A , ettringite will convert to a compound called mono sulphoaluminate ($C_3A.CS.H_{12}$). When $C_3A.CS.H_{12}$ comes into contact with a new source of sulfate ions, then the secondary ettringite will form, which will eventually cause expansion and cracks in concrete structures (Mindess et al. 2003).

Now it is clear that the C_3A content of the cement needs to be reduced to avoid these chains of reactions that will subsequently result in the degradation of concrete. It should be mentioned that the main subject of this research is sulfuric acid intrusion which is mostly more acidic than sulfate attack, but the expansion caused by secondary ettringite formation is also a part of

sulphuric acid attacks, therefore providing this information is considered to be essential for a complete understanding of the whole process.

Various studies have been carried out on the resistance of concrete to sulfuric acid attacks with only Portland cement as the binder. In most of these Studies, concrete with no additives is used as the reference mixture. Moreover, as previously stated, concrete with cement as the sole binder has shown inferior performance compared to the mixes with SCMs and different types of mineral admixtures. Fattuhi and Hughes (1988) studied the resistance of concrete and cement pastes to a 2% sulfuric acid solution. Different concrete mixtures were prepared with only Portland cement and water-cement (w/c) ratios of 0.4 to 0.7. The specimens were cast as 100 mm × 102 mm cubes and cured in water until the day of the testing. The concrete cubes were lightly brushed to remove loose particles before weighing and returning to the acid solution. The pH of the solution was kept constant at 1.67 throughout the testing period.

The final results of this research concluded that the ages of the concrete specimens do not have any significant effects on their WL after the exposure period. They also discovered that with a reduction of the w/c ratio, the WL of the concrete cubes unexpectedly increases, as the WL of concrete with a w/c ratio of 0.4 was three times more than that with a w/c ratio of 0.7. This behaviour was considered to be the outcome of a reduction in the cement content of the concrete mixture. It should be noted that the total length of the exposure period was 49 days and different brushing methods were used. In this regard, it was found that less brushing or brushing twice a week does not have considerable effects on the trend of the WL (Fattuhi and Hughes 1988).

The effect of cement quantity used in concrete on its performance in regards to sulfuric acid exposure was evaluated by Hewayde et al. (2007). In this study, concrete mixtures with cement content of 310 kg/m³ to 570 kg/m³ were prepared with the same w/c ratio of 0.35. The mixtures had a slump of around 50 mm and were cast in cylindrical moulds of 75 mm × 150 mm in size. They were moist cured for 28 days prior to the testing. Sulphuric acid solutions with a wide pH range of 0.3 to 3.0 were made in which the 0.3 pH represents a sewer environment with high temperature and humidity.

The period of exposure was 13 weeks for solutions with a pH that was higher than 1, and 8 weeks for those with lower pH. It was reported that the mass loss of the specimens subjected to solutions with pH of 0.3, 0.6 and 1 increases 72%, 35%, and 66%, respectively, as the cement content increased from 310 kg /m³ to 570 kg /m³. It was also determined that the concrete samples did not experience any significant reduction in their weight after 13 weeks of exposure to sulfuric acid solutions with a pH over 1.5. An important note about the studies of Hewayde et al. (2007) is that they dried the specimens in an oven (105°C) before every measurement and therefore, the consequence of this method must be considered while studying their results.

With regards to HS cement, the studies of Monteny et al. (2003) involved a concrete mixture with type V cement which showed a better performance against a 0.5% sulfuric acid solution than concrete that contained silica fume, but the resistance of this mixture (used as the reference in their study) was inferior to concrete made with slag cement and some other polymer modified concretes that will be discussed in the following sections of this literature review.

It was reported that SCC made with 100% OPC has approximately similar behaviour as SCC made with sulfate resistance Portland cement (SRPC) after exposure to a 5% sulphuric acid solution (Bassuoni and Nehdi 2007). The reason for the results was explained as the existence of a large amount of CH and C-S-H which are most vulnerable to low pH acidic solutions. Bassuoni et al. (2007) stated that both OPC and SRPC mixtures had similar prevalent phases of gypsum on the surface of concrete surrounded by a sulfuric acid solution. These results can be confirmed by the XRD analysis that is presented in Figure 2.6.

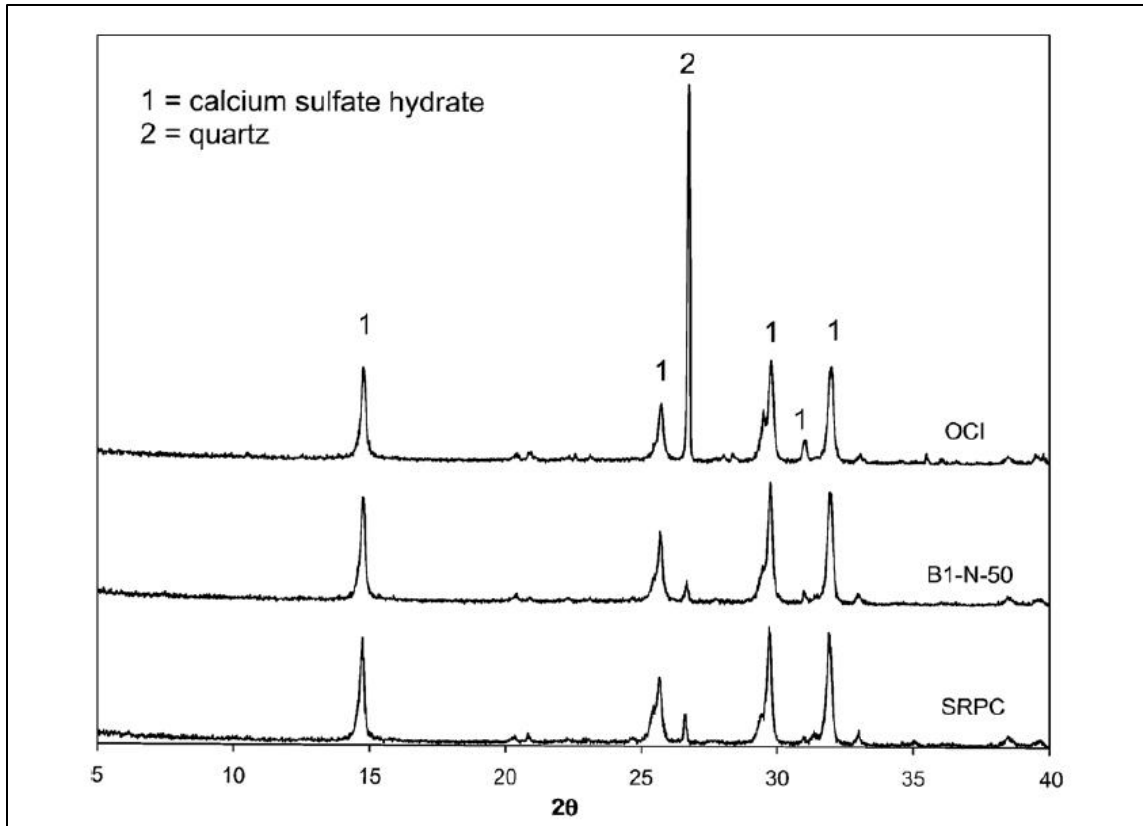


Figure 2.6 XRD of concrete samples that contain OPC, SRPC and OCI after 12 weeks of immersion in a 5% sulfuric acid solution (Bassuoni and Nehdi 2007).

It should be noted that OCI is a mix with an organic corrosion inhibitor, and B1-N-50 represents the mix with 100% OPC. The XRD in this research was conducted on powder form compounds that were removed from the surface of the degraded concrete specimens. Ettringite was not present on the concrete surface which was subjected to a low pH sulfuric acid, but was noticed in the deeper sections of the OPC with a higher pH of around 11 while they could not be detected in concrete with HS cement due to less C_3A content (Bassuoni and Nehdi 2007).

2.2.3 Polymer Modifiers

Whenever different types of organic polymers with various forms (dispersed or redispersible in water) are mixed with concrete, the outcome of this action produces polymer modified concrete (PMC). Other forms of the name may be found in the literature, such as latex modified concrete (LMC) and polymer Portland cement concrete (PPCC). An organic polymer is produced by polymerization of thousands of simple molecules (monomers) into large molecules. Whenever polymer is made by polymerization of one monomer, it is called homopolymer. If it is made by the polymerization of two or more monomers, it will be a copolymer.

This product is available in three different forms: dispersed in water (latex), redispersible powder, and liquid that is soluble in water. Dispersed polymers in water are commonly known as polymer modifiers and their dispersions are called latexes (ACI 548.3R-03). The latexes that are used as modifiers for concrete are generally produced by a process known as emulsion polymerization. Basically, the process consists of mixing the monomers with water, a surfactant and an initiator. The initiator creates a free radical that polymerizes the monomers by chain addition. It should be noted that a wide range of latexes are commercially available, but only around 5% of them are appropriate for usage in concrete and the rest do not have the required properties to be used as a modifier for cementitious mixtures. Each type of latex may have different properties and any variations in their components can result in dissimilar behaviour in concrete or mortar, therefore discussing the production, reactions, components and properties of different types of polymer modifiers is out of the scope of this study.

The reactions and process of polymer modification in concrete should be discussed to understand the reasons behind certain behaviours of these composites. This process is illustrated in Figure 2.7.

As soon as the latexes are mixed with concrete, they are uniformly distributed in the cement paste phase. At first, these products are partially placed on the surface of the cement gel and unhydrated cement constituents. As the hydration process continues and subsequently, the capillary water is removed from the capillary pores, the polymer begins to flocculate to create a continuous, closed packed layer of polymer particles on the outside surface of the cement gel and hydrated cement constituents.

Eventually, with further reduction of water by evaporation and hydration of cement, the polymer particles come together to form a polymer film that is interwoven in the hydrated cement phase, producing a uniform comatrix that covers the aggregates and lines the voids (Chandra and Ohama 1994).

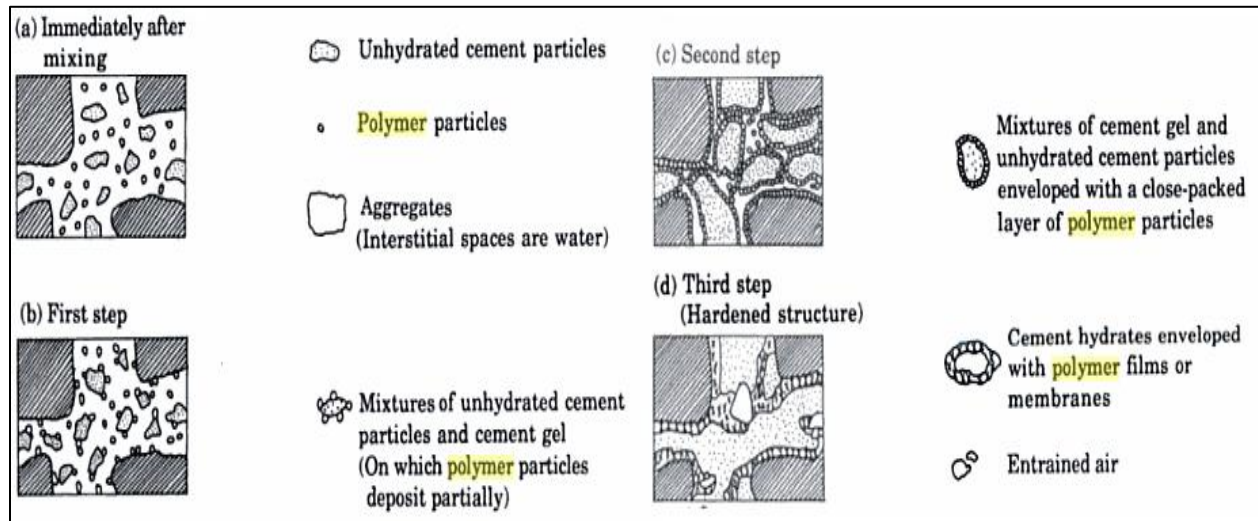


Figure 2.7 A basic model of the polymer modification process in a hydraulic cementitious matrix (Chandra and Ohama 1994).

As the name of the PMC implies, polymer modifies some properties of concrete by the formation of a polymer film in the cementitious matrix and the interpenetrated network that is constructed between them. One of the differences between PMC and regular unmodified concrete is that unlike conventional concrete, there is no bleeding water in the fresh state of the LMC. The side effect of the high consumption of water in PMC is that the risk of plastic shrinkage cracking is higher; therefore necessary steps such as covering the surface of the concrete must be taken to prevent any damages to the concrete.

When it comes to drying shrinkage or other stresses caused by water evaporation, polymers can help in two ways. Polymer modifiers reduce the rate and range of water movement by obstructing the passages. This behaviour will also give the concrete more resistance against the penetration of different chemicals and improve the durability in terms of freezing and thawing (Chandra and Ohama 1994).

The other improvement is the bridging of microcracks by polymer strands in the cementitious matrix, which will consequently lead to better tensile and flexural strength. Another beneficial effect of polymer modification is air entrainment. PMC does not require any air entraining admixtures (AEA) as it normally entrains a minimum of 6% air into the concrete structure (Chandra and Ohama 1994).

The optimum replacement level of polymer solids for cementitious content is in the 7%-20% range. Usually, latex polymers have 47% of polymer solids and the rest is water. It should be noted that the curing process of LMC can have significant effects on its strength and other properties. The most efficient curing regime for these types of concretes is moist curing for a couple of days after casting, followed by dry curing in air for the development of polymer films.

Different types of polymers are used for different purposes. Therefore, in choosing a polymer for a concrete mixture, the required properties and its application must be considered beforehand to determine if the polymer can provide the specific requirements and enhance the performance of the concrete or otherwise. Styrene Butadiene Rubber (SBR) copolymers are suitable when high bond strength and low permeability are the preferred properties. Acrylic polymers and copolymers (PAE) and styrene acrylic copolymers can provide colour fastness aside from permeability resistance and bond strength. Vinyl acetate copolymers also provide some bond strength and lower permeability, but they are not as effective as the ones that were previously mentioned. One of the issues, which must be taken into consideration before using polymers as admixtures in concrete, is their cost. Most polymers are more expensive than other types of additives and modifiers. Therefore, all of the requirements, specifications, and more importantly, the magnitude of the project must be studied before using any type of polymer modifiers.

In terms of resistance to sulfuric acid attacks, different kinds of polymers may improve or may not have any considerable effects on the performance of concrete. There are limited published articles about the durability of PMC exposed to a sulfuric acid invasion. A study was performed at Shantou University in China on the resistance of different mortars that contained fly ash, soluble soda glass and polyvinyl acetate to sulfuric acid attacks. Four groups of mixtures were prepared and fly ash was used in all of the mixtures with the same replacement level of 15%.

Nine prisms sized 4 cm x 4 cm x 10 cm were made for the WL measurements after exposure to a 1% sulfuric acid solution. All the specimens underwent the same curing regime of 28 days in 95% relative humidity. After 25 weeks of immersion in sulfuric acid, the mortar that contained 5% polyvinyl acetate had a 29.5% WL which was around 62% of the unmodified mortar without any polymers (Xiong et al. 2001). It is important to note that in this research, the mix with 7% soluble soda glass and 3% polyvinyl acetate performed superior to other mixes. In another study, Monteny et al. (2003) made various concrete mixes with different types of polymers, such as SBR, styrene acrylic ester (SA) polymer, acrylic polymer and vinyl copolymer. These mixes were subjected to a 0.5% sulfuric acid accelerated test. All of these mixtures had the same polymer solids/cement ratio of 7.5% and the amount of water content was adjusted to take into account the quantity of water in the polymer modifiers. The testing apparatus for accelerated degradation testing (described in previous sections) was used in this study. The specimens were subjected to 9 cycles of exposure to 0.5% sulfuric acid. Monteny et al. (2003), used laser sensors to measure the corrosion of the samples. These measurements were used to calculate the change in radius of the different cylinders before and after brushing.

The aforementioned method was used to determine the average change of radius of the cylinders due to the mechanical action of brushing as well as the chemical reaction of concrete and sulfuric acid solution. In their opinion, the greatest expansion of the concrete does not usually mean the largest WL due to brushing. Therefore, it was considered necessary to evaluate both parameters for a better understanding of the behaviour of the mixtures.

Figure 2.8 shows the results of the measurements of the radius of the cylinders before and after brushing. The trend of the graphs illustrates continuous increase and decrease of the radius which result from expansion by chemical reaction, and loss of material by brushing the degraded cylinders. As determined by a statistical analysis of the results, it was concluded that the first 4 cycles did not have any considerable effects on the specimens, but based on the performance of the mixtures after the fifth cycle, they were divided into two groups. The first group consisted of the reference mixture, SA polymer, vinyl copolymer, etc. The second group contained acrylic polymer, and SBR polymer mixes.

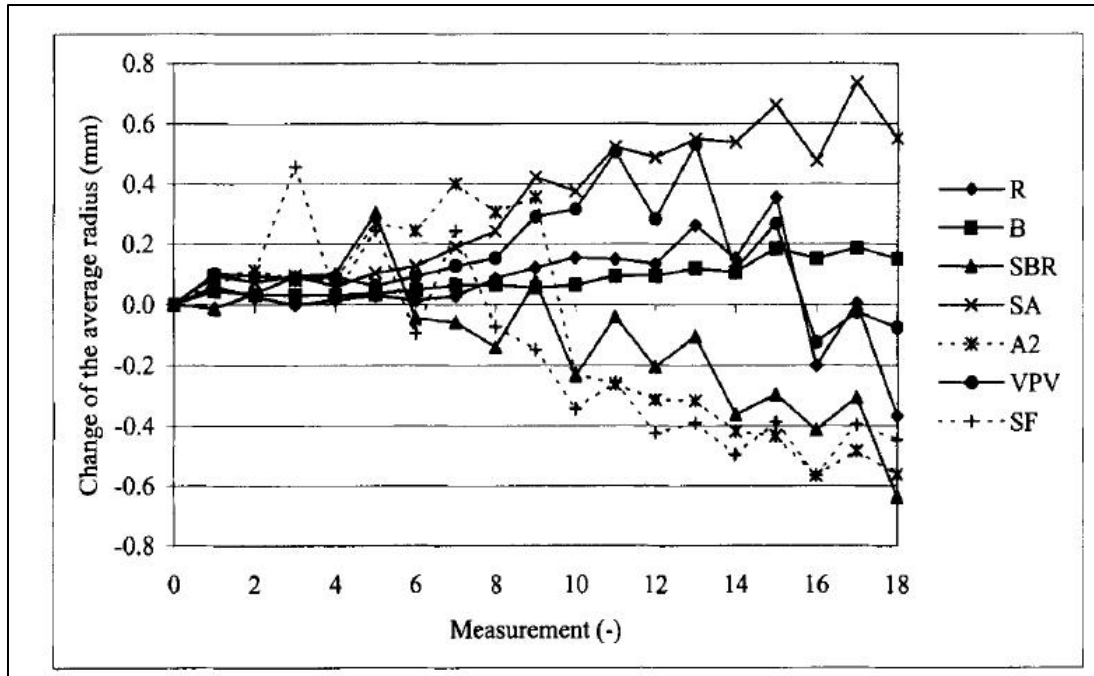


Figure 2.8 Average change of radius of the different concrete mixtures versus the number of measurements (Monteny et al. 2003).

As illustrated in Figure 2.8, the mixture that contains SA polymer has experienced an increase in radius even after nine cycles of exposure to sulfuric acid, followed by brushing for measurements. The mixture with vinyl copolymer (VPV) had a decrease in dimension after eight cycles which was considered a fine performance. On the other hand, the styrene butadiene (SBR) polymer and acrylic polymer (A2) mixes experienced reduction in their dimensions only after 3 and 5 cycles, respectively. It is important to note that after all the measurements and analyses of the data, it was concluded that in general, a large expansion of the specimens was associated with a higher loss of surface particles for all the mixes except one, which was the mix with SA polymer. The SA mix experienced a considerable expansion of about 1 mm, but the particle loss was only 0.4 mm. This behaviour was considered to be the result of a higher ability of plastic deformation of this mix due to the action of polymers that subsequently led to better resistance to internal pressures caused by the creation of expansive sulfate products. In all, the results showed that the SA and VPV mixture demonstrate better performances than the reference mixture (with only HS cement as the binder) and all other polymer modified mixtures in terms of resistance to sulfuric acid intrusion.

2.2.4 Role of Aggregates

The performance of concrete in terms of durability, such as chemical resistance and freeze/thaw behaviour or mechanical characteristics such as flexural and compressive strength, is significantly affected by the properties of the aggregates. Aggregates are one of the three main components of concrete which are produced from many different resources around the world with a wide range of properties. The properties of the aggregates such as maximum size, shape, type, and grading have a considerable effect on the overall concrete behaviour. Therefore, it is necessary to discuss the role of coarse and fine aggregates in the resistance of concrete to sulfuric acid attacks in this part of the literature review.

Few researchers have studied the effects of aggregate properties on concrete behaviour in aggressive acidic environments, such as sewage systems. The most popular types of aggregates in the concrete industry are limestone (calcareous) and siliceous aggregates. In this regard, a study was conducted by Chang et al. (2005) on the resistance of concrete mixtures, which contained different types of aggregates, to sulfuric acid exposure. Twenty-five millimetres graded limestone and 20/10 mm siliceous crushed gravels were used as coarse aggregates, and silica and 4 mm limestone graded sands were used for the fine aggregates.

Six concrete mixtures were designed with four that contained limestone coarse and fine aggregates. Two reference mixtures in this research were prepared with siliceous aggregates. It should be noted that in addition to Portland cement, supplementary cementing materials such as fly ash, silica fume and 60% slag blended cement were used as binders. Eight cylinders (100 mm x 200 mm) were made from each mix to resist a 1% sulfuric acid solution. The concrete performances were evaluated by measuring the change in mass of the specimens every week for the first four weeks and every month until the end of the testing period which was 168 days.

The results of this study demonstrated that all the concrete samples experienced mass gain in the first 21 days and afterwards, the reference mixture (C1) which contained siliceous aggregates and Portland cement as the binder started to lose weight, while the mix with the same properties, but limestone aggregates (C2) instead, experienced WL after 56 days. The mixes with ternary and binary binders had very little mass loss even after 140 days of immersion regardless of the aggregate type. At the end of the immersion period, the C1 mix had lost 10.6% of its mass while the C2 mix had lost only 2.8%.

Chang et al. (2005) determined that the reason behind early age mass gain and later mass loss was due to the effects of sulfate ion reaction and hydrogen ion dissolution, respectively. As stated before, these behaviours change with differences in the properties of the concrete mixtures. The concrete that contained limestone aggregates also showed superior performance in terms of crushing load capacity over the ones with siliceous aggregates. The crushing load was measured at 28, 56 and 168 days of immersion and compared to the original specimens which were cured in lime water for 7 days, followed by 21 days of air curing.

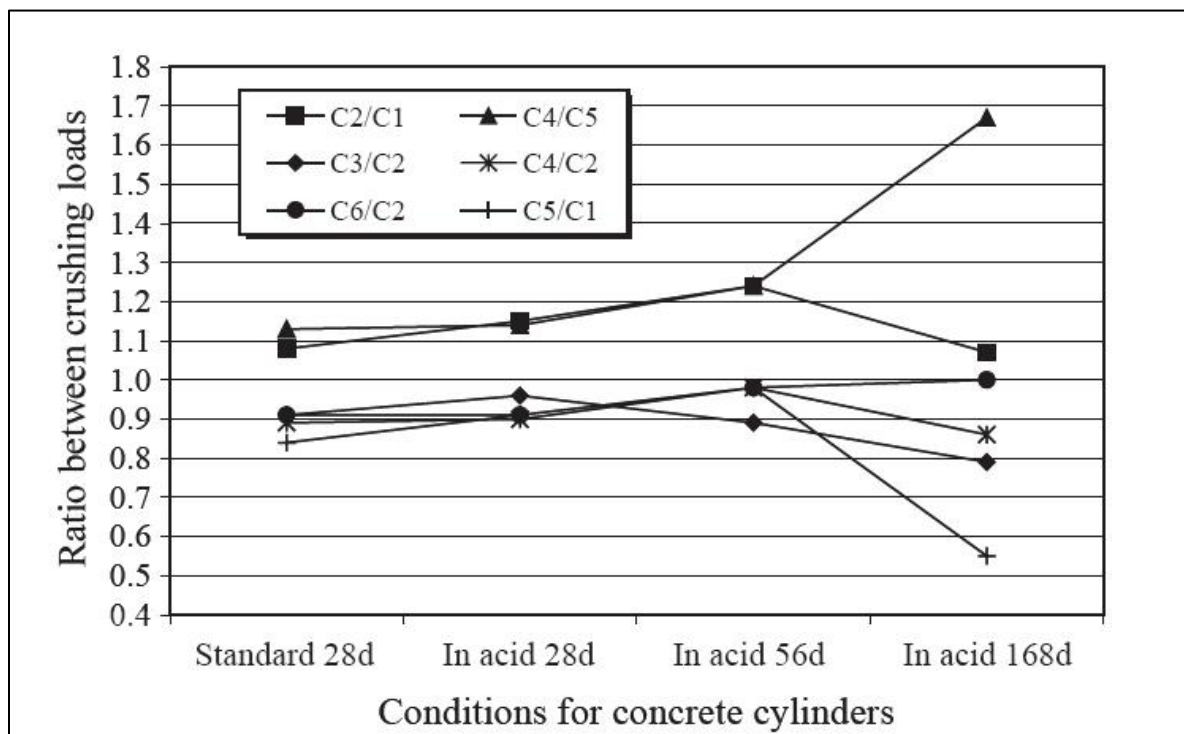


Figure 2.9 Ratios of the crushing load capacity of different concrete mixtures with various types of aggregates and cementitious materials (Chang et al. 2005).

It can be observed from Figure 2.9 that the C2 and C4 mixes (with limestone aggregates) have better crushing loads than their counterparts C1 and C5 (with siliceous aggregates) after different periods of immersion in a 1% sulfuric acid solution. The ratio of C4/C5 was recorded as 1.67 after the end of the 168 days. It should be noted that both C4 and C5 had the same amount of silica fume and slag as their SCM.

The reason behind this behaviour was explained by the fact that the acid soluble fraction of silica sand is only 3% and siliceous gravels is only 0.1% in comparison to the 99.5% acid soluble

fraction of limestone aggregates. This property will enable limestone aggregates to work as a neutralizer and increase the pH of the solution in the areas close to the surface of the concrete. Chang et al. (2005) also used SEM to gain a better understanding of the interfacial transition zone (ITZ) in the degraded concrete mixes. It was reported that the ITZ of the C1 mix consisted of cracks between the paste and aggregates while no discontinuity was noticed in the ITZ of the C2 mix. This behaviour was attributed to the uniform degradation of the limestone aggregates and the cement paste.

In the studies of Hewayde et al. (2007), the effects of the coarse aggregate content on the behaviour of concrete that was exposed to sulfuric acid solutions with different pH were investigated. Siliceous aggregates with a maximum size of 14 mm were used and the specimens were cylinders (75 mm x 150 mm) which were moist cured for 28 days prior to the testing. The range of coarse aggregate content was from 745 to 1010 kg/m³. The role of the aggregates was more pronounced in the solutions with lower pH. For example, the mix with 1010 kg/m³ of coarse aggregates had a mass loss of 32% in comparison to the mix with 745 kg/m³ of aggregates which experienced a mass loss of 19% after 8 weeks of immersion in a 0.3 pH sulfuric acid solution. The same results were also observed for specimens in a 0.6 pH solution, but on the contrary, the concrete cylinders subjected to a pH of 1 underwent a similar mass loss, although they contained different quantities of coarse aggregates. Therefore, it was concluded that the coarse aggregate content is an issue for concern, whenever the concrete is subjected to more severe sulfuric acid attacks with higher concentrations and $\text{pH} \leq 1.0$.

The results of this study was justified by the fact that with an increase in the quantity of coarse aggregates, less cement or mortar will be available to react with the sulfuric acid solution on the surface of the concrete. Hence, the aggressive solution can penetrate deeper into the structure of the concrete and subsequently, the dissolution of cement paste around the coarse aggregates will result in more degradation and aggregate loss over time (Hewayde et al. 2007).

2.2.5 Corrosion Protection Systems

Years of studies and observations of the various cases of corruptions in concrete sewer pipes have provided civil engineers and construction companies with a better understanding of the related degradation processes and the parameters which take part in them. The knowledge and experiences that come from these studies have led to the development of a wide range of corrosion protection (CP) systems which may help to increase the life expectancy of concrete structures that are subjected to severely aggressive environments. It is important to note that due to different restrictions, installation issues and economical considerations, there are limited number of new sewer systems that have used a CP system to improve the performance of their structures.

The most commonly known CP systems are as follows:

1. coatings: this type of CP system has been frequently used in the older days and has extensive performance and evaluation data, but its usage has been significantly reduced in new sewage systems due to its high price, low efficiency and grave effects of human error on its performance;
2. glass fiber reinforced polymer pipes: as the name implies, these pipes are made of polymer and reinforced with glass fibers. They are lighter than an ordinary concrete pipe with the same diameter and are more expensive at the same time. They have been successfully used in past projects by providing a good protection system. Currently, their maximum diameter is around 10 feet, but some progress has been made to overcome this deficiency in the future;
3. polymer concrete: this type of concrete may be used for small to medium size pipes and no reinforcement is provided in it. As the result of the usage of resin, the strength and other mechanical performances are superior to regular concrete. However, its economical impacts must be seriously considered before usage. Some additional work and studies are still needed before this type of concrete is used in the precast industry as normally reinforced concrete is used; and
4. polymeric sheet liners: a type of these liners is made with integral profile anchors on one side to be casted onto the surface of precast concrete pipes. The most commonly known

liner is made from polyvinyl chloride (PVC), with a linear T-shaped anchorage on one side which has been frequently used on precast concrete sewer pipes. Other types of liners are produced with high or linear low density polyethylene which may contain cone-shaped, X-shaped or T-shaped anchorage systems in the grid pattern on one side.

The previously stated information on CP systems is provided from the Chapman and Frank (2005) article on the design considerations of CP systems in a large diameter sewer tunnel. It should be noted that other protection systems, such as mechanically-anchored polymer liners and chemically attached systems, are available, but due to their limited or somewhat unsuccessful applications, they have not been discussed here.

2.3 Two Case Studies

Before performing an investigation on a concrete sewer pipeline, the reasons for doing so must be explained. The purpose of pipe inspections may include structure failure due to corrosion of different compounds or simply the observation of degradation. Nevertheless, the aim of the inspections and analyses will be to discover the causes of corruptions and determine the most efficient way to solve the problems.

The first case which will be discussed here is a reinforced concrete pipe that is 60 inches in diameter. The location of the investigation is in the municipal utilities of northeastern United States. First, the investigators had observed signs of pipe deterioration. In some regions, coal tar epoxy was entirely missing and in others, it could easily be removed from the surface above the waterline (Gebler 2003). Traditional indicators of H_2S corrosion, such as soft and white layers which cover the concrete, were noticed under the coatings. These findings can be easily observed in Figure 2.10. It was considered necessary to measure the pH level on and around the deteriorated areas for a better understanding of the corrosion process. It was found out that the pH was in the range of 1-7 and mostly close to 1 (high acidity) on the pipe walls (Gebler 2003).



Figure 2.10 Hydrogen sulfide corrosion on the crown of a concrete pipe and the remains of the coal tar epoxy coating on the crown (Gebler 2003).

Microbial studies have demonstrated that a considerable number of sulfur oxidizing organisms were present in the pipe which can only perform under low pH conditions. These analyses proved the presence of an H_2S invasion which eventually leads to the production of sulfuric acid which attacks the concrete structure and changes its hydrated cement to gypsum. The aggressive CO_2 gases in the effluent did not cause any considerable degradation. If the interior concrete envelope of the prestressed concrete cylinder pipe loses a significant amount of material, this may lead to the total collapse of the structure. Hence, it was concluded that instead of coal tar epoxy coatings, other kinds of protection systems, such as PVC liners, should have been used.

The second case is a sanitary sewer line in a municipality in the midwest United States. A petrographic study was performed and splits, cracks and tears were discovered in the different thickness of coatings. The investigations also showed that the concrete pipes had a degraded surface which was covered with gypsum as a result of an H_2S attack. Figure 2.11 clearly shows the removal of the coatings which was caused by gypsum expansion. A considerable amount of sulfur oxidizing organisms was noticed from the results of a microbial analysis on the scrapings of the pipes and manhole walls. These organisms grow in low pH environments where a sulfur source is present (Gebler 2003).

Immersing different kinds of concrete specimens into the pipeline at various depths was suggested to evaluate the severity of the nature of the sewer pipe environment. For this purpose,

fundamental frequency, and weight and length changes of the concrete samples can be periodically monitored.

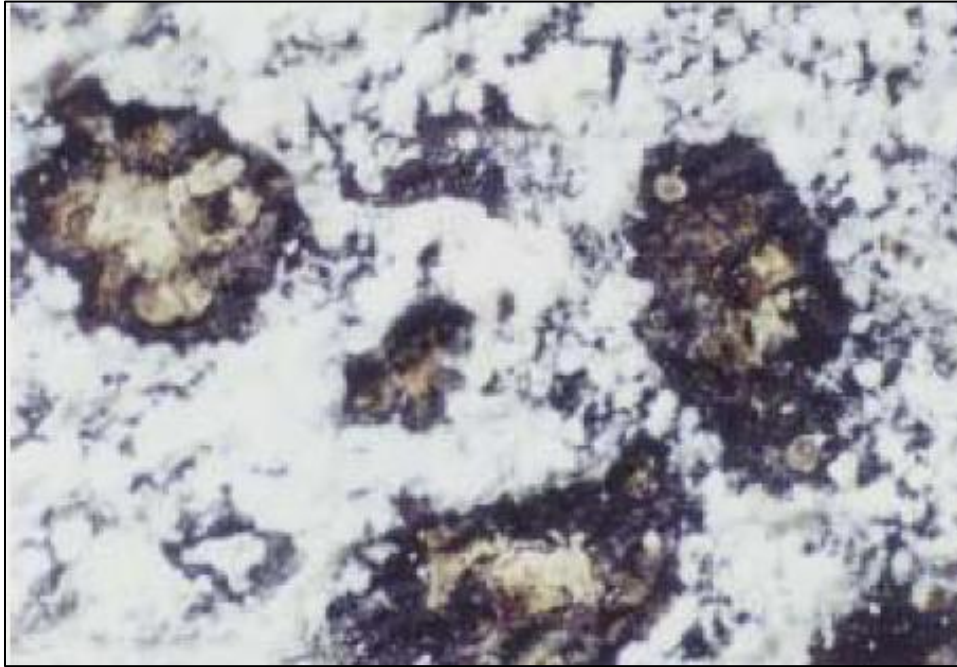


Figure 2.11 White deposits of gypsum underneath a coal tar epoxy coating, magnified 10 x (Gebler 2003).

2.4 Concrete Pore Structure and Permeability

It is commonly known that concrete permeability is one of the most important parameters, if not the most influential one, in regards to durability aspects, such as resistance to chemical and physical attacks. The permeability and pore structure of concrete can be influenced by various factors, such as w/b ratio, aggregate properties and the use of SCM. Reducing the w/c ratio and efficient moist curing will decrease the paste permeability of concrete which greatly influences the overall concrete performance.

Permeation characteristics and transport procedures are highly crucial for intrusion, internal redistribution or loss of materials which may be detrimental for concrete, its compounds or reinforcements (Newman and Choo 2003).

Two primary parameters are involved in almost all chemical and physical processes that affect the durability of concrete structures. These factors are transport in pores and cracks, and water. Pore structure, which indicates the pore size distribution and amount of pores, plays an important role on the extent and effect of the transport. Permeation of concrete is influenced to a large extent by the pore structure of the cement paste.

The open porosity and pore size distribution are two important factors that characterize the open pore structure with regards to the transport of elements within the porous concrete (Rostam 1992). Open porosity signifies interconnected pores which make the transport of liquids and exchange of dissolved substances possible. Pore size distribution is a factor which influences the rate of the transport. The pore size of cement paste can have a wide range with different magnitudes. Different types of pores exist in the concrete, which include compaction, air, capillary, and gel pores. They also can be called macro, capillary, and micro pores. Generally, the durability of concrete in terms of resistance to chemical attacks can be significantly affected by capillary pores (Rostam 1992).

The permeability of concrete can be evaluated by different procedures or testing methods. Hence, it is considered appropriate here, to provide a brief description and history of the rapid chloride permeability test (RCPT) and also other permeability tests which are used in this study.

Since measuring the permeability of concrete by using the flow of water based on Darcy's law is very challenging and does not provide dependable results, the RCPT can be a good replacement. It should be noted that the ingress of chloride ions in concrete structures subjected to chloride attacks, such as bridges and coastal structures, is a worldwide problem. Therefore, measurements of chloride penetrability of concrete can give good information to civil engineers on concrete resistance to chloride penetration and subsequently, prohibit the corrosion of reinforcements. The traditional way to measure concrete durability in terms of resistance to chloride ions is the famous salt ponding test with sodium chloride (NaCl), but the diffusion of chloride ions in concrete takes too much time. This test would take at least 4 months to produce useful and reliable results.

For this reason, the RCPT was introduced by Whiting (1981) as an alternative. According to ASTM C 1202, this test is an electrical indication of concrete ability to resist chloride ion penetration.

Researchers have not reached an agreement on the correlation of the RCPT test results and the results of the ponding test. According to Chindaprasirt et al. (2005), there is a good agreement between the RCPT and full and partial immersion testing methods for concrete that contains fly ash with different fineness, but they felt that the coulomb charge test is more effective as the immersion methods take too long to obtain good and reliable results for high strength concrete. In another study by Hooton et al. (2000), it was found that there is a good relationship between the results of the RCPT and the ponding test for different concrete mixtures that contained fly ash, silica fume, etc. On the other hand, there are reports from other studies that there lacks any good or obvious correlation between these two tests. For example, according to Miller and Darwin (2000), the lower values from the RCPT for silica fume concrete overlays may be the outcome of the effect of silica fume on the pore solution and it does not completely indicate high resistance against chloride ions. According to previous studies, concrete specimens with a smaller w/b ratio and older age will have better chloride resistance based on the RCPT. Therefore, it is recommended to test concrete at the age of 56 days rather than 28 for more representative results of actual field conditions.

The water sorptivity test is another method to understand the porosity characteristics of concrete. The primary parameters which determine the absorption of concrete are temperature, water content, porosity, water properties, pore size distribution and connectivity of pore space (Ball 1999).

In the concrete porous medium, the system of pores with various sizes may be identified as a system of capillaries. As soon as the concrete surface comes into contact with water, the capillary forces start to take water into the porous medium. The rate of the absorption of water can continuously be measured at different time intervals and subsequently, the water sorptivity of the concrete mixtures can be compared to each other. Water porosity tests are also used in this study as another method to evaluate concrete porosity characteristics. This test provides an idea of the percentages of the concrete pores which can be penetrated by water.

2.5 Concrete Resistance to Freezing and Thawing

Repeated freezing and thawing cycles are considered as a physical attack which can cause serious damages to concrete structures. In cold climates, such as northeastern United States and Canada, concrete structures are most vulnerable to this type of deterioration. It is important to note that if the produced concrete has a sufficient amount of entrained air, the damage caused by this type of attack can be considerably reduced.

In saturated concrete, water stays in different pores with a wide range of dimensions. This water will not freeze at the same time; for example, water in 10 nm pores will freeze at temperatures below -5°C , while in smaller pores with a diameter of 3.5 nm, freezing takes place at below -20°C . When the freezing temperature is reached, most of the water in the concrete is cooled down, but does not freeze, as for the creation of ice, a seed or nucleus is required (Mindess et al. 2003). With the continuous reduction of temperature, seeds will form in the large voids that permeate the cement paste. Eventually, the water on the C-S-H surface which forms the micropores may move to the capillary pores (ice locations), but will never freeze. If the paste is not properly protected and contains no air entrainment, severe expansion may happen which will cause a significant amount of tensile stress and cracking (Mindess et al. 2003).

Description of all the mechanisms of frost attacks is considered unnecessary and instead, may be found in various published literature. Here, it will be acknowledged that in freezing, the generation of ice crystals may create pressure on the pore walls and also cause the movement of water from the pores in the paste to the closest air voids, hence if water has to travel far, it could result in tensile stresses. The drawing of unfrozen water to the ice crystals during freezing can also occur. The slow growth of the crystals will in turn, cause internal stresses and subsequent cracking (Newman and Choo 2003). It should be noted that the pore structure of the concrete plays an important role in its resistance against frost attack.

Chapter 3. Materials and Experimental Procedures

The first part of this chapter provides information on the properties of different materials which are used in the preparation of the concrete specimens in this study, followed by a comprehensive description of the preliminary studies, experimental program and testing procedures.

3.1 Materials

Information on the aggregates, cement, SCM, and chemical admixtures used in the development of different concrete mixtures in this research is as follows.

3.1.1 Coarse Aggregates

The coarse aggregates were mixed siliceous/calcareous aggregates with a maximum size of 19 mm (3/4 inch) and specific gravity of 2.74. These aggregates were supplied from the Caledon quarries in Ontario, Canada. The water absorption of the aggregates was 1.5%. It can be seen in Figure 3.1 that the grading of the coarse aggregates satisfies the requirements of ASTM C33.

3.1.2 Fine Aggregates

The fine aggregates were well graded siliceous/calcareous sands which were provided from the same quarries as the coarse aggregates. The specific gravity and water absorption of the sands were 2.66 and 0.46%, respectively. The grading of the fine aggregates is shown in Figure 3.1.

3.1.3 Portland Cement

GU hydraulic cement (Type 10) which conforms to CSA-3001-03 was supplied from Lafarge Canada Inc. The properties of the Portland cement are illustrated in Table 3.1.

3.1.4 Metakaolin

MK was provided by Whitemud Resources Inc. in Canada. The characteristics of the MK, which are shown in Table 3.2, satisfy the requirements of CSA A3001-03 and ASTM C618 as a type N supplementary cementitious material.

3.1.5 Limestone Filler

OMYA Canada Inc. was the provider of the LF in this study. The calcium carbonate products are manufactured from marble in Perth, Canada. The name of the product is Betocarb 12-PT. The chemical composition and other properties of this mineral additive are shown in Table 3.3. The grading curves of all the materials are depicted in Figure 3.1.

3.1.6 Fly Ash

Class F fly ash, which has a CaO content of less than 8%, was used in accordance to CSA A3001-A23.5. The specific gravity of the fly ash was 2.3 g/cm³.

3.1.7 Latex Polymer

Latex 412 is an acrylic emulsion polymer which is specifically developed for the polymer modification of Portland cement and other hydraulic cementitious composites. It has a solid content of 48% and its minimum film forming temperature (MFFT) is 13°C.

3.1.8 Xypex

Xypex is an odourless product with a grey colour and has the form of a solid powder. It is designed to improve the mechanical properties and durability of concrete. Xypex admix C-5000 consists of Portland cement, very fine treated silica sand, and different kinds of active chemicals. It has a specific gravity of 2.604 g/cm³ and its maximum dosage rate is 10% of the cement content.

Table 3.1 Portland Cement GU (Type 10) Properties

Chemical Composition (% by wt)		Bogue Composition (% by wt)		Other Properties
CaO	61.80	C ₃ S	54.40	Specific gravity 3.15 g/cm ³
SiO ₂	19.40			
Fe ₂ O ₃	2.30	C ₂ S	14.70	Blaine fineness 4300 cm ² /g
Al ₂ O ₃	5.30			
SO ₃	3.80	C ₃ A	10.16	
MgO	0.95			
K ₂ O	1.10	C ₄ AF	6.99	Clinker (% Weight) 100
Na ₂ O	0.20			
LOI	2.10	Gypsum	6.46	

Table 3.2 Metakaolin Properties

Chemical Composition (% by wt)		Other Properties
CaO	0.36	Specific gravity 2.56 g/cm ³
SiO ₂	60.30	
Fe ₂ O ₃	1.11	
Al ₂ O ₃	31.60	BET surface area 139000 cm ² /g
SO ₃	-	
MgO	-	
K ₂ O	-	Strength Activity 1.16
Na ₂ O	1.81	
LOI	1.00	

Table 3.3 Limestone Filler Properties

Chemical Composition (% by wt)		Other Properties
CaO	53.90	Specific gravity 2.71 g/cm ³
SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ & K ₂ O	-	Blaine fineness 2100 cm ² /g
LOI	43.20	Strength Activity Index 0.78

3.1.9 Chemical Admixtures

ADVA CAST 575 from Grace Canada Inc. was used in this study as the SP. An AEA was also used to incorporate specific amounts of air into the concrete mixtures. The properties of these admixtures are provided in Table 3.4.

Table 3.4 Properties of the Chemical Admixtures

Name	Nature	Chemical Id	Content Range (% by cement wt)	Density	Solid Content (%)
SP	Super Plasticizer	Carboxylated Polyether Copolymer	0.13 - 0.46	1.06	40.0
AEA	Air Entraining Admix	Sulfonated Salts of Hydrocarbon	0.03 - 0.50	1.007	5.0

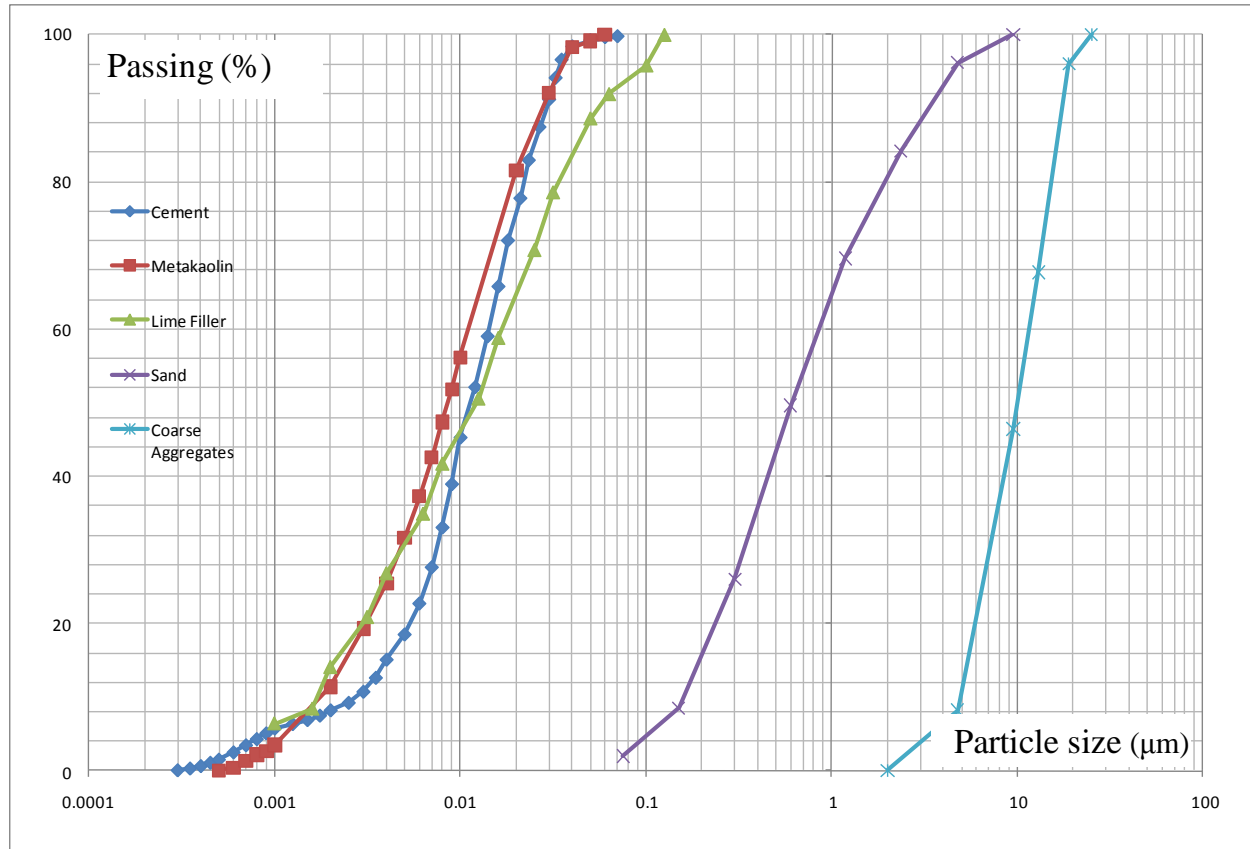


Figure 3.1 Particle size distribution of the materials

3.2 Preliminary Studies

In order to produce a desirable concrete mixture which meets the requirements of a specific project, trial mixes must be made with different amounts of binders and chemical admixtures. Producing these mixes will help to find suitable quantities of SP and an air entraining agent to reach the specified slump and air content. It should be noted that the trial mixes also help to realize if the types and amounts of aggregates and binders in the mixes satisfy the requirements of the study. In the first part of this section, the process and results of water demand tests on mortars will be described and the second part is dedicated to a preliminary study performed to evaluate the sulfuric acid resistance of different concrete mixtures that contained various kinds of materials, such as Latex polymer and Xypex.

3.2.1 Water Demand Tests on Binders

Before preparing the trial and actual mixtures, a brief water demand study was performed on Portland cement, MK and LF.

The water demand test for mortar is a straight forward test, designed to understand the behaviour and water requirements of different binders with various cementitious materials and combinations when they are mixed with water and an SP in a specific way (Sedran 1999). By performing this test, the amount of water can be determined for each binder to reach a specific consistency with a homogenous structure. Eventually, the results will be used to make the actual concrete mixture. This test will help the researcher to predict the fresh properties of concrete more comfortably and quantity adjustment of chemical admixtures will become a simpler task. Therefore, less material and energy will be wasted in making many trial mixes before producing the actual concrete mixtures.

The test requires a mortar mixer, squirting bottle and a scale with 0.01 g of precision. The test procedure is quite simple. First, the required amount of cementitious materials, chemical admixtures and water must be prepared. It should be noted that preliminarily, the quantity of water can be freely decided. The SP and air entraining agent can also be added to the water before mixing.

To start the mixing, the mixer is turned on and the speed is fixed on 2 (slow mixing) and then the pre-measured water and chemical admixture are slowly added to the binder. Afterwards, the water is slowly added by using the squirting bottle. At the start of the mixing, the binder consists of little dry pellets and then, as water is continuously added, the pellets change into wet pellets, then into a smooth paste, and finally, a flow paste. The mixer is turned off when the consistency of the mortar changes from little pellets to a smooth paste and subsequently, the water demand will be calculated. It is important to note that the mixing procedure must be the same for all the binders and the different combinations.

Figure 3.2 illustrates the water requirements of the raw binders with no admixtures. As expected, the water demand of MK is higher than the others. Figure 3.3 represents the water demand test results of different binders that contained no SP or AEA. It can be easily observed that the control binder with 100% Portland cement requires the lowest amount of water to reach the desired consistency in comparison to mixes with MK and LF. It can also be concluded that an increase in the replacement level of MK has resulted in an increase in the w/b ratio to achieve a satisfactory fresh state.

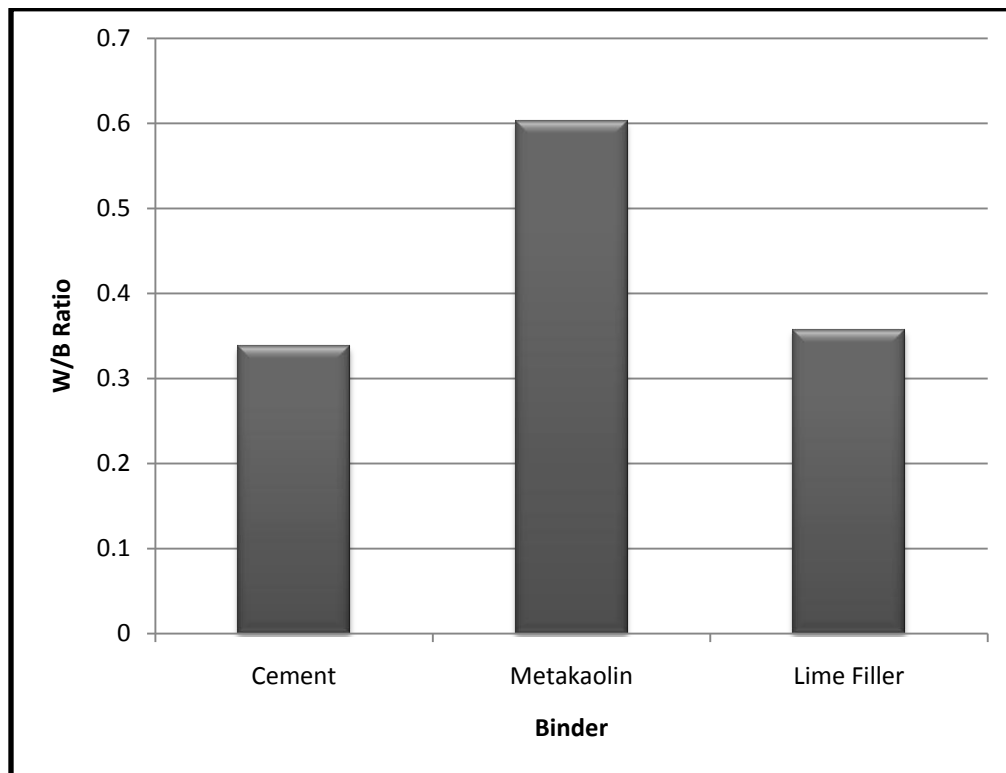


Figure 3.2 Water Demands of the Raw Materials.

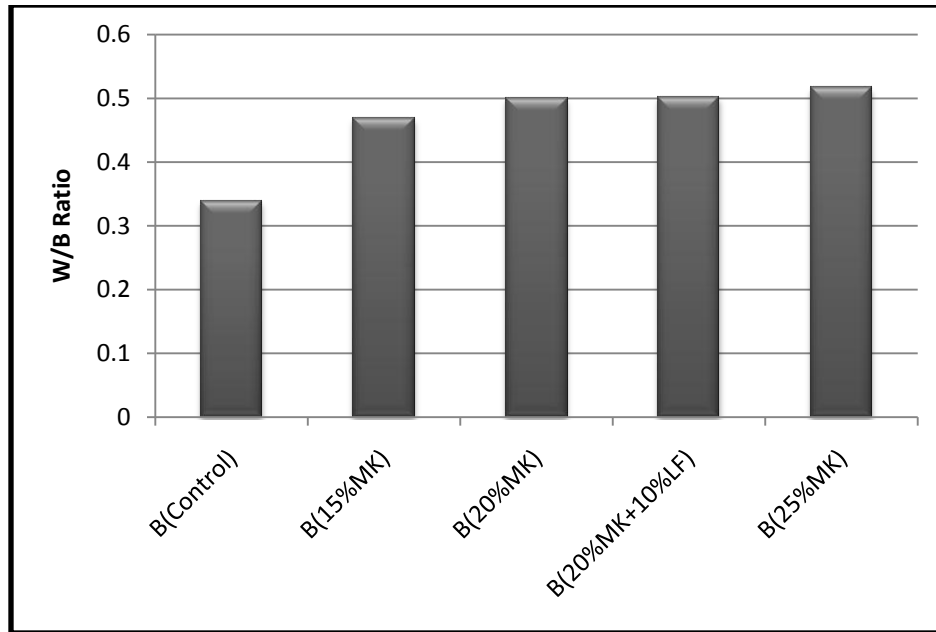


Figure 3.3 Water Demands of Binders with no SP.

The relationship between the SP/b and w/b ratios can be quite beneficial to recognize the optimum amount of SP to achieve the required fresh behaviour of the concrete mixes. This correlation is depicted for two different mixtures in Figures 3.4 and 3.5. The results of these two mixtures are considered to be sufficient enough to provide an idea of the consistency of the binders when the amount of SP varies.

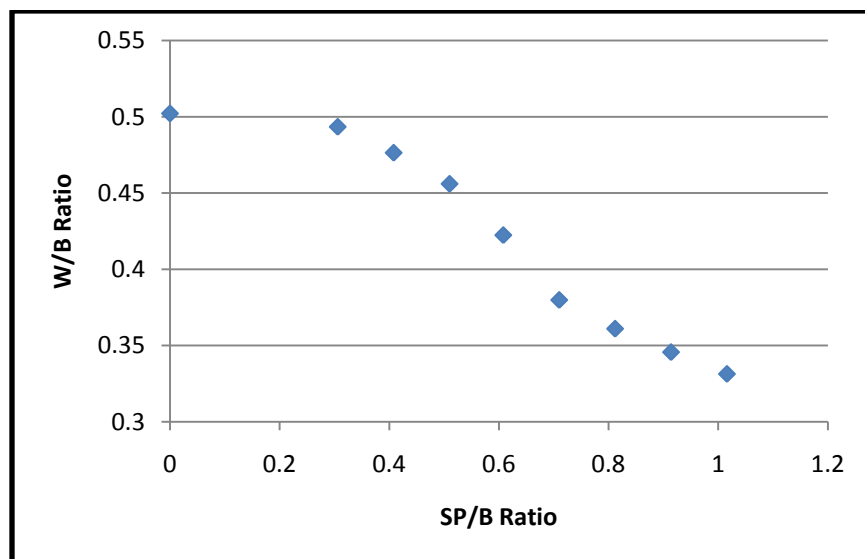


Figure 3.4 Correlation of w/b and SP/b ratios of a mixture with 10% LF and 20% MK.

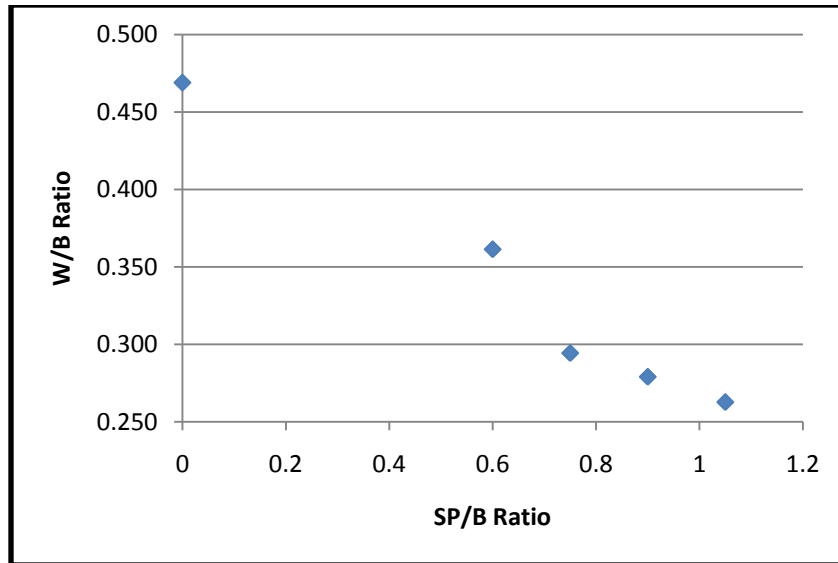


Figure 3.5 Correlation of the w/b and SP/b ratios of a mixture with 15% MK.

3.2.2 Introductory Studies on Sulfuric Acid Resistance of Concrete

A preliminary study has been conducted to evaluate the characteristics of different concrete mixtures subjected to a sulfuric acid solution with a specific concentration. Since there are no standard testing procedures to assess the performance of concrete with regards to resistance against sulfuric acid, this study will help to obtain a better understanding of the testing method and at the same time, the effects of different materials such as fly ash, latex polymer and Xypex can also be examined.

3.2.2.1 Mix, Design and Placing of Concrete Mixtures

Class F fly ash was used in all mixes at a replacement level of 20% in the total amount of binder. Latex 412 polymer was used in two mixes (SJ1 & SJ2) with polymer solids/total binder ratio of 7% and 12%, respectively. Two of the mixes (SJX5 & SJX7) contained Xypex in quantities of 5% and 7% of the total amount of binder.

Latex has the ability to increase the workability of fresh concrete and at the same time, incorporates a significant amount of air. Thus, AEA and SP were not needed in the two polymer

modified mixtures. In contrast, in the mixes with Xypex, a significant amount of SP was used to produce concrete with suitable workability. The control mix (SJCont) had 20% fly ash as the SCM and did not contain additional chemical or polymeric admixtures.

Table 3.5 Mix Proportions of Different Concrete Mixtures (Preliminary Studies)

Materials	Mixtures				
	SJCont	SJ1	SJ2	SJX5	SJX7
Coarse Aggregates (Kg/m ³)	1020	1020	1020	1020	1020
Sand (Kg/m ³)	694	702	621	721	748
GU 10 Cement (Kg/m ³)	357.5	357.5	357.5	357.5	357.5
Fly Ash (Kg/m ³)	89.4	89.4	89.4	89.4	89.4
Water (Kg/m ³)	156.4	125.1	102.8	156.4	156.4
Polymer/ Total Binder (%)	0	7	12	0	0
Latex 412 (Kg/m ³)	0	62.6	107.3	0	0
Xypex (Kg/m ³)	0	0	0	22.4	31.3
Xypex/Total Binder (%)	0	0	0	5	7
Water/Total Binder	0.35	0.35	0.35	0.35	0.35
Total Binder (Cement + Fly Ash) (Kg/m ³)	447	447	447	447	447

The concrete mixtures were produced by using a revolving drum mixer. The slump and air content of the fresh concrete was measured right after mixing. The fresh concrete was placed into plastic cylindrical moulds (100 mm x 200 mm) and covered with plastic sheets for 24 hours before demoulding. The polymer modified mixtures were moist cured for 14 days prior to air curing to strengthen the polymer films. All other mixtures were cured in a moist curing room. Due to time limitations and other reasons, the curing periods of the mixtures were different. The Sj1, Sj2 and SJX5 mixtures were tested after 28 days of curing, while SJCont and SJX7 mixtures were tested after 14 days of moist curing. It is important to note that the results of this preliminary study must be interpreted in consideration of the effects of the different curing periods. The mix proportions of the different concrete mixtures are illustrated in Table 3.5. It is important to note that all the procedures such as mixing, measuring the slump and air content were performed in accordance to ASTM standards that will be provided in the experimental program section 3.3.

3.2.2.2 Testing Method

The concrete specimens were subjected to a 3.5% sulfuric acid solution for two cycles of 14 days which makes it a total of 4 weeks. After every immersion cycle, the specimens were removed from the solution and their saturated surface dry weight was measured after smooth brushing by a nylon brush. The compressive strength of the specimens was measured after they were left for one day in 50% relative humidity. The weight and strength of the specimens were then compared to their initial values before the testing. The small size of the container and large number of concrete samples would result in an increase in the pH of the solution. Hence, at the end of every cycle, the solution was replaced with a new one to compensate for the change in pH. ASTM C267 was used as the basic standard for this testing procedure. A thorough description of the sulfuric acid degradation test and various factors involved in the final results and performance of the mixtures is provided in the following experimental program section of this study. It is important to note that in the experimental program (final investigation), no polymer latex, Xypex and fly ash were used in the concrete mixtures and instead MK and LF were used to modify the concrete durability properties and resistance against sulfuric acid attack. The low compressive strength of the LMC mixtures and unusual rheology properties of the mixtures that contained Xypex were the main reasons behind this decision that will be more discussed in chapter 4.

3.3 Experimental Program

The experimental program in this study primarily focuses on the resistance of different concrete specimens to sulfuric acid attacks. The pore structure and porosity of different concrete mixtures were also evaluated by performing a wide range of tests, such as water sorptivity, water porosity and rapid chloride permeability tests. In addition to these, experiments were conducted on degraded concrete specimens to assess their permeability characteristics. The freezing and thawing resistance of concrete prisms from different mixtures was examined as a part of the experimental program.

Several concrete specimens were made from five different concrete mixtures with each set associated with a specific test procedure.

3.3.1 Mix Designs, Placing and Curing

The concrete mixtures were designed with a low slump range of 25 mm to 45 mm. As previously stated, achieving a low slump with mixtures that contain various binders and admixtures is not a simple task, but fortunately, the results of the preliminary testing on the binders proved to be very useful in fulfilling this requirement. There are 5 concrete mixtures used in this study; each consists of 50 cylindrical specimens and 2 prisms for the rapid freezing and thawing testing for a total of 260 concrete samples. The water/total binder ratio of all the mixtures was fixed at 0.37 and the amount of SP was adjusted for every mix to achieve the desirable slump. AEA was used in all mixes for an air content of around 4%, which is appropriate for mild exposure to freezing/thawing temperatures. The total coarse to fine aggregate ratio was fixed at 0.83 and the total binder was 490 kg/m³ for the 5 mixes.

GU (Type 10) Portland cement was used as the only binder for the reference mix which is named as the control in this study. MK and LF were used to replace Portland cement in the other four mixes. In the M15 and M20 mixes, 15% and 20% MK were chosen as the appropriate amounts to replace cement. M15/L10 was made with a ternary binder of 15% MK and 10% LF and M20/L10 with 20% MK and 10% LF as the replacements for ordinary cement. The mix proportions of the 5 concrete mixtures are provided in the Table 3.6.

The concrete mixtures were mixed and cured in accordance to ASTM C192-02. A revolving drum mixer with a maximum capacity of 60 litres was used for the mixing process. The slump of the fresh concrete was measured based on ASTM C143. The air content of the freshly mixed concrete was also measured by using an air meter which conforms to the ASTM C231 standard test method for evaluating the air content of fresh concrete. Since the slump of the concrete was too low, using an external vibration (vibrating table) was considered to be a more suitable method to achieve a well consolidated concrete in different moulds. Subsequently, the moulds were placed in 50% relative humidity and covered with plastic sheets until the next day. The specimens were demoulded 24 hours after casting and placed in a moist curing room at a temperature of around 23°C until the day of their designated tests.

Table 3.6 Mix proportions of the concrete mixtures (experimental program)

Ingredients	Mixtures				
	Control	M 15	M20	M15/L10	M20/L10
GU 10 Cement (Kg/m ³)	490	416.5	392	367.5	343
Metakaolin (Kg/m ³)	0	73.5	98	73.5	98
Lime Filler (Kg/m ³)	0	0	0	49	49
Fine Aggregates (Kg/m ³)	978	971	968	966	961
Coarse Aggregates (Kg/m ³)	814	808	806	805	800
Water (Kg/m ³)	179.5	179.5	179.5	179.5	179.5
Air Admix (ml/m ³)	600	600	900	600	900
SP (ml/m ³)	1125	2444	2688	2200	2685
Total Binder (kg/m ³)	490	490	490	490	490
Water/Binder	0.37	0.37	0.37	0.37	0.37
Water/Cement	0.37	0.43	0.46	0.49	0.52
Coarse Aggregates/Sand	0.83	0.83	0.83	0.83	0.83
SP%	0.23	0.5	0.55	0.45	0.55
Air Admix%	0.12	0.12	0.18	0.12	0.18

3.3.2 Sulfuric Acid Test

There are no standards in the ASTM which is entirely dedicated to evaluate the resistance of concrete mixtures to the invasion of sulfuric acid. Thus, ASTM C267, which is the standard test method for the chemical resistance of mortars, grouts and polymer concrete, was used as the basis for this test procedure. The concrete specimens were immersed into sulfuric acid solutions with different concentrations after 28 days of moist curing in 98% relative humidity. The concrete samples were cylinders with a diameter of 100 mm and height of 200 mm. Each mixture consisted of 36 specimens for the sulfuric acid test. The initial weight of all the specimens was measured in accordance to ASTM C267 prior to the immersion. The average compressive strength of three concrete samples was also measured before the procedure.

Three containers which had a capacity each of around 700 litres were used to prepare the acidic solutions. Sulfuric acid with a 98% concentration was used to make the three solutions with concentrations of 3%, 5% and 7%. Every concrete mixture consisted of 12 specimens for each container which resulted in 60 specimens per container. The total number of specimens for this test was 180 and they were placed in two layers inside the containers with every layer consisting of 30 samples.

The immersion period of the specimens was divided into four cycles or phases. The length of each cycle was 2 weeks, thus the total length of the testing was 8 weeks. The solution was stirred once a week to provide a uniform distribution of sulfuric acid around the submerged specimens. The pH of the solutions was monitored biweekly after the 2 weeks period to see if the concrete samples had any significant effects on the acidity of the solutions.

As previously stated, the volume of the containers was quite large and the number of the specimens per container was limited. Aside from that, several specimens were also removed from the containers every two weeks, reducing the total number of the samples in every tank. Hence, it was considered prior to testing that the pH of the solutions would not undergo any considerable changes, especially after the removal of a specific amount of samples from the containers.

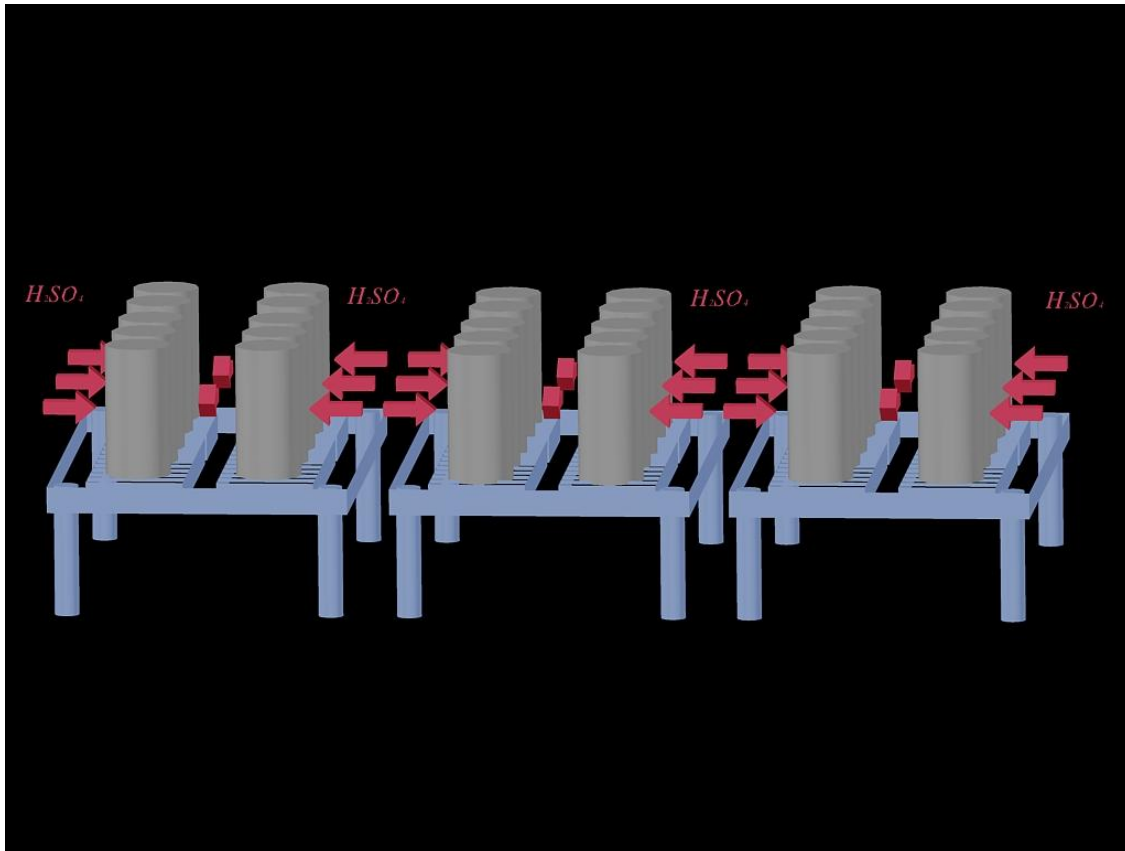


Figure 3.6 Sketch of the testing setup of one layer of concrete specimens inside the sulfuric acid tanks at the beginning of the testing period.

A special test setup (Figure 3.6 and 3.7) was designed to place the concrete specimens inside the tanks. The reason behind this decision was to avoid any issues which may cause inconsistent results in the testing. This issue was observed in the preliminary studies of concrete resistance to sulfuric acid attacks. It was observed that after a certain period of exposure to a sulfuric acid solution, the concrete cylinders would start to lose particles from their outside surface which would accumulate around the bottom of the samples. If the concentration of the solution is low and the total length of the testing is short, this would not cause any significant effects. However, if the concentration is high and the total period of the testing is quite considerable such as the case in this testing procedure, this can become an issue.

Here, the problem is that when there is a notable amount of discharged particles around the bottom of the concrete samples, they will provide some kind of protection layer for the concrete which will cause the ingress of sulfuric acid to be more difficult, while on the middle and top parts of the samples, the surface of the concrete is completely exposed to the sulfuric acid solution. This phenomenon will result in inconsistent behaviour of the specimens and examining the results of the testing will also become complex.

As illustrated in Figure 3.6, the concrete samples are sitting on tables in the containers. The table tops have openings and are designed and cut to fit the tanks. A photo of the tables and testing setup is also available in Figure 3.8. Figure 3.6 represents the concrete specimens inside the sulfuric acid tanks at the beginning of the exposure period.

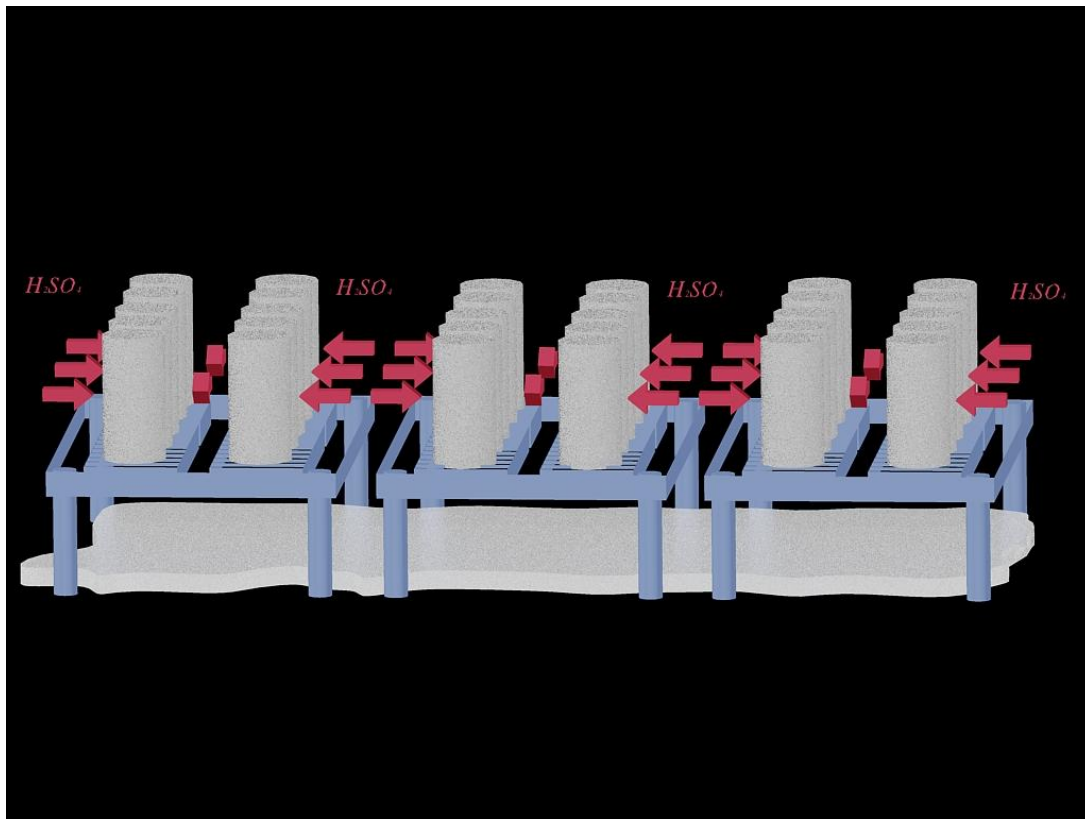


Figure 3.7 Sketch of the testing setup of the concrete specimens inside the sulfuric acid tanks after a certain time of immersion.

Figure 3.7 clearly shows the role of the tables in this testing procedure. As evident, the specimens are degraded and have lost a significant amount of particles after some period of exposure. These particles (white powders) have discharged from the surface of the concrete and

instead of piling up on the bottom of the concrete samples; they are deposited through the opening of the table to the bottom of the container.

Three concrete specimens from each mix were removed from each solution at the end of every cycle. Subsequently, they were washed smoothly with tap water to eliminate loose components on the surface. Afterwards, the specimens were placed in 50% relative humidity room for 24 hours to obtain the same condition when their initial weight was measured. The weight of the specimens was measured and recorded the next day. Two concrete samples from each mix and container were used to evaluate the average compressive strength following the exposure periods.



Figure 3.8 Concrete specimens in fresh sulfuric acid solution.

A visual inspection was conducted by taking high resolution pictures of the corroded specimens. According to previous studies, this is a useful method to compare the performance of the specimens and acquire a better understanding of the corrosion rate and resistance of the different samples exposed to sulfuric acid attack. The aforementioned process was repeated every two cycles until the end of the two month test period.

3.3.3 Water Sorptivity and Immersion Tests

Water sorptivity and water absorption by total immersion were employed to determine the absorption of water in concrete by different processes and subsequently, proper information could be obtained on the porous structure of the different concrete mixtures.

3.3.3.1 Water Sorptivity

One of the methods to examine the related permeability of concrete is sorptivity, which is measuring the rate of absorption of water into concrete. It should be noted that although absorption and permeability are related, they are not necessary correlated. Since it has been quite difficult to model the sorptivity in all directions, the test procedure has been configured to measure the process in one direction (Neville 1996). As described in ASTM C1585, the testing method is simple and economical, yet does not take a considerable amount of time.

For this testing method, the concrete cylinders were moist cured for a period of 56 days in 98% relative humidity. Afterwards, a concrete diamond saw was used to cut the cylinders into the desired size for the testing. Every mix consisted of 4 cut specimens with a diameter of 100 mm and height of 50 mm. The specimens went through consistent conditioning of 3 weeks in 35°C temperature prior to the testing. In order to avoid any absorption from the humidity of the surrounding environment, the concrete samples were covered with the required amount of adhesive aluminium foil.

Before the start of the testing, the weight of the specimens was measured by using a scale with a high accuracy of 0.001 g. The diameter of the specimens was also measured to the nearest 0.1 mm with a standard calliper.

The bottom of the two small containers were covered with washed coarse graded sand and filled with a specific level of water which covered the maximum 3 mm of the bottom of the specimen covered with aluminium foil. The test setup is illustrated in Figure 3.9.



Figure 3.9 Water sorptivity test setup

As demonstrated in the above figure, the specimens were placed in the containers on top of a low level of water. At specific time intervals indicated by the ASTM standard, they were removed from the water and their exposed surface was instantly wiped off with a paper towel and their weight was recorded. This process was repeated for several time intervals and subsequent days after the start of the testing until the end of the 8 days.

In addition to the sorptivity of the original sound specimens, the rate of water absorption of the degraded concrete samples after different periods of exposure to sulfuric acid solutions was also examined.

Two degraded concrete specimens, cut into an approximate thickness of 50 mm and diameter of 100 mm, were prepared from every mix after the end of every two weeks of exposure to different solutions. It should be noted that the initial diameter of the concrete samples was consecutively reduced throughout the testing period due to corrosion caused by sulphuric acid attacks. The degraded specimens were conditioned for a period of 3 weeks in a 35°C oven to achieve the required consistency. Afterwards, they were carefully covered with aluminium foil to limit absorption from the surrounding atmosphere. The changes in the rate of water absorption after acid corrosion could be evaluated by making comparisons to the values of the sound samples.

3.3.3.2 Water Absorption by Total Immersion

A wide range of techniques can be used to examine the absorption of concrete. One of the most popular methods to measure the rate of absorption by concrete is the ASTM C 642 standard test method for density, absorption and voids in hardened concrete. With the employment of this method, some useful knowledge of the pore space volume in the concrete can be achieved.

The test procedure is quite simple and does not need a thorough explanation. Similar to the sorptivity test, the concrete specimens were moist cured in a 98% relative humidity room for 56 days, followed by 1 day in a 40% relative humidity room prior to the immersion procedure. The specimens were cut into cylindrical samples which were 100 mm in diameter and approximately 50 mm in height. Three concrete specimens from every mixture were completely immersed into water and their saturated surface dry weight was measured every day following the 5 days of immersion until constant mass. Subsequently, the specimens were placed in an oven with a temperature of 105°C for a period of three weeks to reach a constant oven dry mass.

The water absorption percentage can be easily calculated by using the following equation in accordance to ASTM C 642:

$$\text{Absorption after immersion (\%)} = \{(W_a - W_b) / W_b\} \times 100 \quad (1)$$

where W_a represents the saturated mass after immersion and W_b represents the oven dry mass.

3.3.4 Rapid Chloride Permeability Test

Low permeability plays a critical role in protecting concrete from the ingress of harmful and aggressive substances, such as sulfates, chloride ions, etc. One of the most popular methods to examine the permeability of concrete is the RCPT. According to ASTM C1202-97, the task of this testing method is to measure the electrical conductivity of concrete to present a rapid indication of its resistance to the intrusion of chloride ions.

In this study, concrete specimens from the five mixtures were cut into the required sizes with a standard water cooled diamond saw. The diameter of the cut samples was 100 mm and the height was 51 ± 3 mm. Two specimens from each mix were tested after 56 days of moist curing in 98% relative humidity and 2 were examined following 95 days of the same curing method.

Special conditioning must be applied to the specimens before initiation of the testing. First, the concrete cylinders must be placed in a sealed dessicator and subsequently, the vacuum pump should run for a period of around 3 hours. With the vacuum pump still working, a sufficient amount of distilled water must be drained into the container to completely cover the samples. After the addition of water, the vacuum pump is required to continue operating for one more hour. Ultimately, the vacuum pump is turned off and the specimens are soaked in water for 18 ± 2 hours.

The two sides of the cell which contain the specimen must be filled with two different solutions. One is 3% NaCl which will be connected to the negative terminal of the power supply and the other one is 0.3 N of sodium hydroxide (NaOH) which will be connected to the positive terminal of the power supply. After attaching the lead wires to their specific locations, the power supply will be turned on. The rest of the process and adjustments must be done using the designated software. For example, the diameter of the samples must be entered correctly and the voltage should be maintained as 60 V.

One of the advantages of this type of testing is that it takes a short time to produce truly reliable results. If there are no problems, such as leakage of solution due to poor attachment of the cell parts, the test will be terminated after 6 hours and consequently, the software will represent the total charges passed in coulomb units.

3.3.5 Rapid Freezing and Thawing Test

Studying the durability of concrete in terms of resistance to freezing and thawing cycles is critical for concrete structures subjected to frost attack. A significant number of testing methods has been developed to examine this property of concrete. For example ASTM C 671 determines the magnitude of the critical dilation of continuously wet concrete during single freezing event. It should be noted that ASTM C 671 and C 682 (evaluation of coarse aggregates in air entrained concrete by critical dilation procedure) were withdrawn in 2003.

ASTM C 666 is the most common test procedure designed to evaluate concrete resistance to internal micro cracking following exposure to repeated freezing and thawing cycles. It is important to note that although this test generates worthy information on the frost resistance of concrete, the complex behaviour of the exposed concrete to severe cold climates cannot be entirely understood by only using this test.

Two concrete prisms sized 100 x 75 x 405 mm (4 x 3 x 16 inches) were made from each mix for a total of 10 prisms. The specimens were cured in 98% relative humidity for 14 days followed by 14 days of curing in air prior to the testing.

A standard apparatus which is commonly used to produce freezing and thawing cycles is employed for this test. The concrete prisms were placed in steel boxes after they were completely saturated in water. Wire hangers were used to make the lifting and placing of the samples more conveniently. Consequently, the steel containers were filled with water until the specimens were covered. The boxes sit on a steel plate which produces cool temperatures for freezing, while the thawing is provided by electrical elements in the middle of the containers. An image of the apparatus for this test is provided in Figure 3.10.

According to ASTM C 666, a nominal freezing and thawing cycle should consist of reducing the temperature of the samples from 4°C to -18°C and increasing it from -18°C to 4°C in not less than 2 hours and not more than 5 hours. The total maximum number of cycles must be set to 300.

The initial mass and pulse velocity of the samples were measured before turning on the machine. However, it should be noted that there were several problems with the ultrasonic tester in this study and it had to be repeatedly repaired throughout the total period of testing which ultimately produced some unreliable results. Therefore, only visual inspection and the mass change of the samples were used to compare the performance of the concrete prisms to each other.



Figure 3.10 Rapid freezing and thawing test setup

3.3.6 Water Porosity Test

As previously stated, there are several different kinds of tests to measure the volume of pores in concrete. In addition to the tests which were mentioned in the previous parts, the water porosity method was employed to measure the total volume of pores in concrete that can be penetrated by water. The AFPC-AFREM French standard was used as the reference for this method.

The concrete cylinders were moist cured for 56 days and afterwards cut by the water-cooled diamond saw to the desired size. The prepared specimens with a thickness of 51 ± 3 mm were cut again in the middle into two halves, so that there would be more exposed surface available for water ingress.

Prior to the weight measurements, the three concrete samples from each mix were placed in a sealed dessicator and positioned so that their faces would be uncovered. Afterwards, the vacuum pump was turned on for a period of about 4 hours. Then, while the specimens were in a vacuum condition, water was introduced into the dessicator. Again, the vacuum was turned on to run for at least 20 hours.

After the end of the conditioning, the immersed apparent mass of the specimens in water was measured by using a scale with an accuracy of 0.001 g and a steel wire for suspension. Afterwards, the surface of the specimens was wiped off by using a paper towel to measure their saturated surface-dry (SSD) weight. Eventually, the specimens were placed in an oven at 105°C for a period of three to four weeks until they reached a constant mass. The following is an equation to calculate the water porosity of the original concrete samples in this study.

$$P (\%) = (W_a - W_b) / (W_a - W_c) \times 100 \quad (2)$$

P: Water porosity (percentage)

W_a : Saturated surface dry weight (g)

W_b : Oven dry weight (g)

W_c : Immersed apparent weight (g)

The water porosity test was also performed on the deteriorated concrete specimens after exposure to three concentrations of sulfuric acid solutions for different periods of time.

Two degraded specimens that were cut into the same size and shape of the sound samples of the water porosity test were prepared after the specimens were exposed to sulphuric acid solutions at the end of each phase (two week exposure periods). It is important to state that the sample shapes were altered after the loss of surface materials due to the sulphuric acid attack. The water porosity test of each set of degraded samples started after they were left in a 50% relative humidity room for 3 days. The setup of the water porosity test method is provided in Figure 3.11.



Figure 3.11 The setup of the water porosity test.

3.3.7 Phenolphthalein Test

The phenolphthalein test was chosen to observe the changes in the alkalinity of the concrete after exposure to sulphuric acid solutions with different concentrations. According to New Shorter Oxford Dictionary, Phenolphthalein ($C_{20}H_{14}O_4$) is a whitish or yellowish crystalline solid which may be used to indicate the change of pH in the range of 8 (colourless) to 10 (red). Different preparation methods with regards to the quantities of distilled water, ethyl alcohol and phenolphthalein have been suggested in the literature, but here, the only concern is to employ phenolphthalein with the same strength in all the tests.

The cut degraded concrete specimens from different mixtures were placed alongside each other in an organized manner before lightly sprayed with the phenolphthalein solution. Note that this test does not measure the corrosion degree of the concrete samples, but only its pH. If the pH of the concrete surface is higher than 9, then it turns pink and if the pH is lower than 9, the solution will appear colourless, which may indicate the presence of sulfate components.

Chapter 4. Results and Discussion

Chapter 4 presents the various results from the experimental tests in this study and an in-depth analysis and discussion of the results. The results of the preliminary studies will also be presented and discussed.

4.1 Preliminary Studies

The results of the introductory studies on the sulfuric acid resistance of concrete specimens which contain different quantities of latex polymer and Xypex in addition to fly ash are presented in this section.

4.1.1 Fresh Properties

The fresh properties of the concrete mixtures are illustrated in Table 4.1. It can be observed that although no SP was employed in mixtures SJ1 and SJ2, they have a high slump and the air content is also satisfactory. It is notable that with an increase of polymer content, the slump and air content of the mixtures also increase.

Table 4.1 Fresh properties of concrete mixtures (introductory studies).

Mixes	Slump	Air Content
SJCont (Reference Mix)	40 mm	4%
SJ1 (7% Latex 412)	150 mm	5%
SJ2 (12% Latex 412)	210 mm	8%
SX5 (5% Xypex)	85 mm	3.5%
SX7 (7% Xypex)	70 mm	2.5%

4.1.2 Weight Loss

The result of the WL of concrete cylinders after the end of two consecutive periods of 14 days is illustrated in Table 4.2. The results of each mix is the average of the WL of the three specimens in an SSD condition after brushing with a nylon brush. At the end of the first phase of immersion in a 3.5% sulfuric acid solution, the mixture that contained 7% Xypex showed lower WL

(4.18%) than the other mixes and the mix with 5% Xypex had only lost 4.45% of its initial weight which was very close to the WL of SX7. These results are in agreement with the studies of Fattuhi and Hughes (1988) which suggested that the curing period does not have a significant effect on weight change behaviour of concrete subjected to sulfuric acid attacks. Obviously, the first 7 days of curing have the most crucial and highest impact on the development of concrete hydration and its resistance against sulfuric acid solutions. Another reason for these results is that in the first 14 days of the testing period, sulfuric acid is not able to reach deep into the concrete micro structure and hence, no critical damage or effect takes place in the ITZs between the aggregates and hydration products. Thus, concrete samples will resume their regular hydration process and consequently, their performance will reflect this phenomenon. It is curious that the mixtures with polymer modification did not show any improvements in comparison to the control mix after 14 days of immersion. However, there was a different scenario at the end of the testing. The WL results for the 28 days of immersion indicate that PMCs perform better than the control mix with approximately 25% reduction in WL, but there is only a slight difference between the two PMC mixtures which suggests that the increase in the quantity of polymer solids content from 7% to 12% does not improve the acid resistivity of concrete. Unlike the first phase of the testing, the average WL of the control specimens was the highest among all mixtures. The SJ2 mix had the best performance by losing 7.43% of its initial weight after brushing at the end of the testing period which can be the result of polymer films obstructing the moisture movement in the pores and subsequently, protecting the concrete from intrusion of acidic ions, and the bridging of microcracks which form due to expansions caused by reaction of sulfate ions with Ca(OH)_2 and sulphotoaluminate phases of hydration products.

Table 4.2 Weight loss results of the 3.5% sulfuric acid immersion test.

Mixes	Weight Change After 14 Days of Immersion (%)	Weight Change After 28 Days of Immersion (%)
Sj1	-5.80	-7.55
Sj2	-5.48	-7.43
Sj control	-5.67	-9.99
SX5	-4.45	-8.20
SX7	-4.18	-7.62

4.1.3 Strength Loss

The initial compressive strength and SL of concrete cylinders from different mixtures were measured to evaluate the performance of concrete specimens against sulfuric acid intrusion after 28 days of immersion. It can be seen from Table 4.3 that the concrete mixture with 7% Xypex behaves superior to other mixtures as not only its strength was not reduced but also it was increased around 18%. Surprisingly, the average strength of the specimens from the control mixture showed no loss of strength at the end of the second cycle of immersion. Moreover, contradictory to the results of the WL, the latex modified mixtures (SJ1 & SJ2) showed the worst performance in all the mixtures with regards to their strength characteristics as they have lost around 20% of their initial strength at the end of the four weeks of exposure. The increase in the strength of the SX7 mix can be the result of its undisturbed continuous hydration due to no damage to its inner core matrix after the end of the 28 days immersion period. It is important to note that this mix was subjected to sulfuric acid attack after 14 days of moist curing. Thus, it is probable that due to the inability of sulfuric acid to reach deeper into the concrete structure, the concrete specimens of this mixture carried on with their strength development which is also justified from the result of the SX5 mixtures as they had already gone through the 28 days of moist curing. Hence, due to a smaller quantity of Xypex and more cement content, SX5 had lost around 5% of its strength, but was still considerably less than the LMC mixtures. The behaviour of the control samples may be also due to their continuous hydration and strength gain in the solution, as their average strength at the end of the 28 day immersion period showed no sign of decrease.

Table 4.3 Compressive strength results of concrete specimens before and after 28 days of exposure to a 3.5% sulfuric acid solution.

Mixes	Initial strength (MPa)	Strength after 28 days of immersion (MPa)	Change in strength after 28 days of immersion (%)
SJ1	34.7	26.9	-22.30
SJ2	37.2	29.8	-19.91
Sjcontrol	36.6	36.9	0.73
SX5	48.9	46.0	-5.83
SX7	41.3	48.9	18.38

This preliminary study has been done to evaluate the effects of different kinds of polymer and mineral admixtures on the performance of concrete in terms of battling against the intrusion of sulfuric acid ions. The other important aim of this brief study was to gain familiarity with the sulfuric acid test method and the effects of different parameters, such as brushing, refreshing the solution and the concentration of acid on concrete performance subjected to a severe acidic solution. Performing this study can be very helpful to avoid any mistakes and achieve more accurate results in subsequent experimental program. The results of this study were used to evaluate the efficiency and effects of Latex 412 and Xypex on modifying the properties of concrete.

The compressive strength of the latex modified mixes after 28 days of combined moist and air curing did not satisfy the specific requirements of this research. Hence, although these mixes showed acceptable performances in terms of WL after exposure to sulfuric acid, they are not able to fulfill the requirements of projects with high strength demands.

Both the compressive strength and WL results suggest that Xypex can be a worthy substitute for Portland cement at replacement levels that are below 10%. The improved resistance of Xypex concrete can be attributed to the property of this product which reacts with water and hydration products of cement as soon as it is mixed in fresh concrete. Consequently, a catalytic reaction takes place which results in non-soluble crystalline formation in the capillaries and other pores of concrete. The only disadvantage of Xypex was its unusual rheology properties when it was incorporated into concrete. The problem was observed while making the trial mixtures with Xypex and also noticed in water demand tests on mortars. The strange and complex fresh properties of concrete that contains Xypex made it difficult to achieve a consistent concrete with a desired slump.

It can also be concluded from the results of this introductory study that the characteristics of concrete with regards to resistance against sulfuric acid attack can be better judged by measuring the weight change of concrete specimens as their results are more consistent than the SL results. It is also important to keep in mind that this preliminary study is a brief introduction to the main experimental procedures of the research. Hence, the results of this section can be justified and explained by focusing on the results of the subsequent experimental program on the resistance of different concrete mixtures to sulfuric acid.

4.2 Experimental Program

The results of the usage of MK and LF and their effects on concrete performance with regards to sulfuric acid resistance, pore structure, permeability properties, and freezing and thawing durability are presented in this section. An in-depth analysis and discussion about the results of the various experiments are provided in the following sections of Chapter Four.

4.2.1 Fresh Properties

The slump of the freshly mixed concrete was measured by using a slump cone in accordance to ASTM C143. It can be observed from Table 4.4 that all mixtures have a slump of less than 40 mm. Note that the control and M15 mixtures possess the highest slump values.

As described in Chapter Three, the air content of fresh concrete was measured by using an air meter. Table 4.4 represents the air content of different mixes which are in the range of 3.5% to 4.5%. In consideration of the w/c ratio and the low slump of the mixes, these values will satisfy the requirements of CSA A23.1.

Table 4.4 Slump and air content of different mixtures

Fresh Properties	Mixtures				
	Control	M 15	M20	M15/L10	M20/L10
Slump (mm)	38	38	32	25	35
Air Content (%)	3.5	3.5	4.5	4.5	3.5

4.2.2 Hardened Properties

The compressive strength of the concrete specimens was measured after 7 and 28 days of moist curing in 98% relative humidity. The average strength of the three concrete cylinders from every mix is given in Table 4.5. It is illustrated that the M15/L10 mix has less compressive strength than the M15 mix and similar behaviour can be observed for the M20 and M20/L10 mixes. These outcomes are the result of the addition of LF as a replacement of Portland cement, as it does not significantly contribute to the development of strength. It is also apparent that the use of MK in concrete has resulted in an increase of compressive strength in comparison to the control mixture which contains no SCMs.

Table 4.5 Strength results of the concrete mixtures.

Compressive Strength	Mixtures				
	Control	M 15	M20	M15/L10	M20/L10
Strength (7 days) MPa	36.13	40.69	41.19	39.38	41.92
Strength (28 days) MPa	41.17	45.12	47.26	43.56	44.83

4.2.3 Sulphuric Acid Test

The performance of the concrete specimens which were immersed into the sulphuric acid solutions was evaluated by three different methods. As stated in Chapter 3, the weight of the concrete samples was monitored biweekly through the entire testing period, the compressive strength of two samples was measured and the average was recorded at the end of every two weeks of exposure. In addition to these parameters, the appearance of the degraded samples was compared to each other by visual inspection.

4.2.3.1 Weight Loss

Measuring the change in mass of concrete specimens after a certain time of exposure to a sulphuric acid solution is the most widely accepted method to evaluate the resistance of concrete subjected to this aggressive conditions. Bassuoni and Nehdi (2007) stated in their studies that WL measurements are more efficient than other methods for the understanding and comparison of the performance of different mixtures while Chang et al. (2005) believed that monitoring the strength of degraded concrete samples is a more reliable method than examining the mass loss throughout the period of the experiment.



Figure 4.1 Specimens inside the tanks which contain sulfuric acid solutions.

As mentioned in Chapter 3, concrete cylinders from each mix were placed simultaneously in sulphuric acid solutions with concentrations of 3%, 5% and 7%. The specimens were placed on special plastic tables to avoid the settlement of particles around the surface of the samples.

The total period of the testing was 8 weeks which was divided into 4 phases that consisted of 2 week periods. The condition of the two tanks with different acid concentrations can be observed in Figure 4.1. A higher rate of corrosion can be seen from the condition of the solution in the container with 7% sulphuric acid than the one with 5% as the specimens and the tables are more visible in the one with higher pH after only one week of immersion. This observation indicates that the reaction of the 7% solution with the specimens is more severe, which in return, has already resulted in more removal of particles from the surface of the concrete samples and subsequent turbidness of the solution. The pH of the 3%, 5% and 7% sulfuric acid solutions were around 1.3, 1.2 and 1.15, respectively. These values were recorded after three weeks of exposure and the continuous monitoring of the pH in the following weeks did not show any significant changes. It should be noted that although immersed concrete samples will increase the pH of the solutions (caused by dissolution of hydration products), due to the removal of these specimens every two weeks and the large volume of the solutions, the effects of the remaining samples on the pH of the solutions became insignificant.

The changes in the mass of the concrete specimens after different periods of exposure to a 3% sulphuric acid solution are represented in Figure 4.2. The concrete specimens from the control mixture have undergone more WL than the specimens from the other mixtures at the end of all the phases except for the first two weeks. The concrete samples from the M15/L10 mixture have performed the best among all mixtures in terms of WL. For instance, the control specimens have lost 7.09%, 12.58%, 17.16% and 22% of their initial weight after the end of the four phases of immersion in a 3% sulfuric acid solution which are 10.44%, 25.55%, 18.51% and 33.6% more than the WL of the M15/L10 specimens, respectively. The same trend was also observed for other mixtures that contained MK and LF.

For the M15/L10 specimens, the addition of 10% LF had positive effect on their performance as they had lost less weight than the concrete samples from the M15 mixture without LF, but it was limited to only around 10% reduction at the end of the eight weeks of immersion. This effect was not observed for the M20 and M20/L10 mixtures.

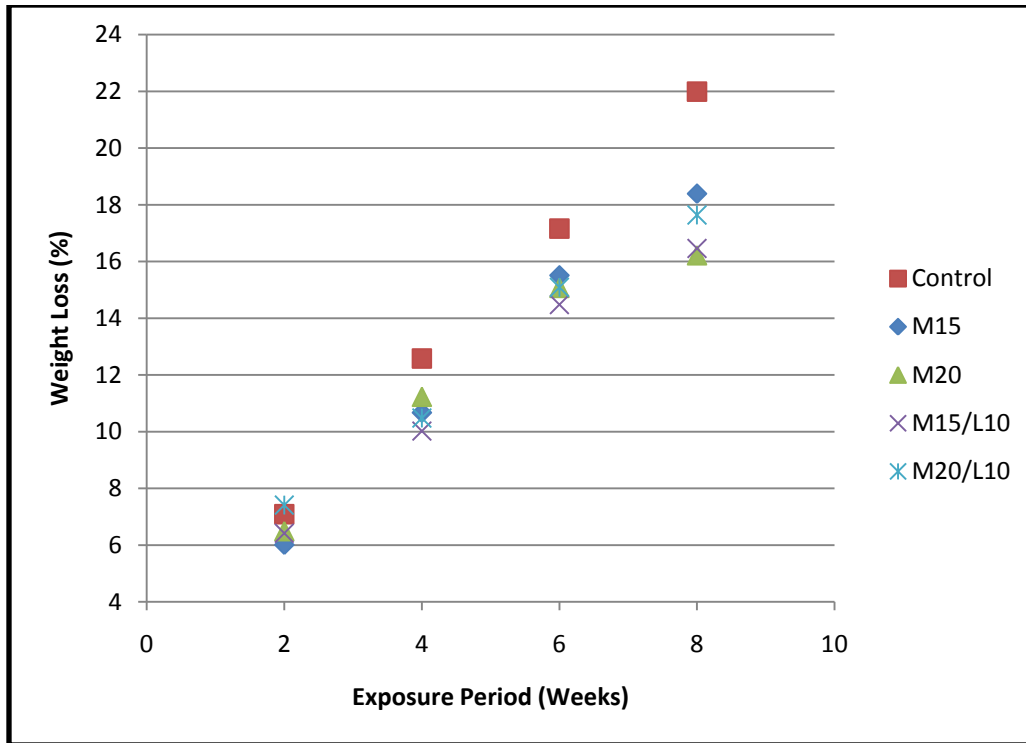


Figure 4.2 Weight loss vs. exposure periods of the specimens subjected to a sulfuric acid solution with 3% concentration.

As the concentration of the sulphuric acid increased, the rate of the WL also increased for all the specimens. It is shown in Figure 4.3 that the WL of the specimens ranges from 12.9% for the M15/10 mixture at the end of two weeks to 39.4% for the control mixture at the end of eight weeks of exposure to a 5% sulfuric acid solution. The control mixture also experiences the highest WL of 15.5%, 24.3% and 33% at the end of 2, 4 and 6 weeks. The high amount of cement hydration products in the reference mixture will result in a higher WL, as the sulfuric acid will react with these constituents to form soluble reaction products which subsequently will be removed from the concrete surface. Also, the $\text{Ca}(\text{OH})_2$ phase that is more abundant in the control mixture is most susceptible to the sulfate ions of sulfuric acid, which will consequently lead to the production of white expansive gypsum components that can be noticed on the surface of concrete cylinders.

The replacement of Portland cement with 10% LF in the M15 mixture has shown positive results as the WL of the M15/L10 mixture has been reduced by 8.43%, 12.85%, 8.12% and 15.86% with referenced to the M15 mix at the end of the four phases of exposure to a 5% sulfuric acid solution. While similar to the WL results of the 3% sulfuric acid solution, this difference is not as significant for the M20 and M20/L10 mixtures.

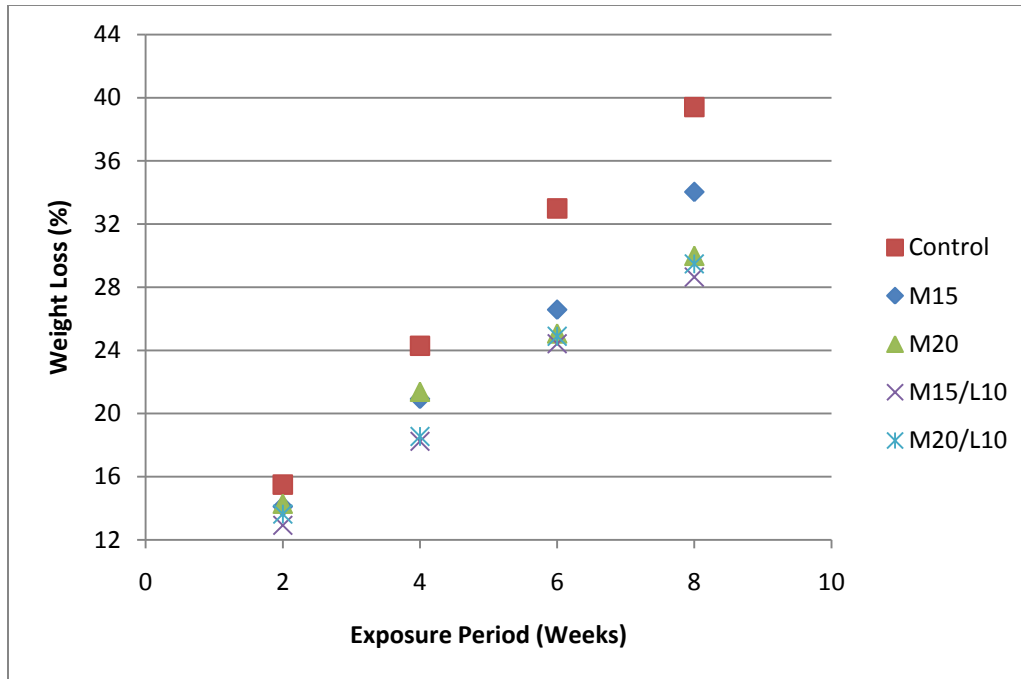


Figure 4.3 Weight loss vs. exposure periods of the specimens subjected to a sulfuric acid solution with 5% concentration.

The 7% sulphuric acid solution had a severe detrimental effect on the concrete specimens which was the result of its high H^+ concentration and hence, very low pH, which subsequently, will make it more chemically reactive. It is shown in Figure 4.4 that the WL ranges from 15.6% for the M15/L10 mixture at the end of two weeks to 53.3% for the control mixture at the end of the immersion period. The figure indicates that by increasing the replacement level of ordinary cement with MK and LF, the WL percentages of the specimens will decrease. For example, the M20/L10 mixture has experienced WL of 16.2%, 25.04%, 30.2% and 36.3% at the end of the four phases of exposure to 7% sulfuric acid, which are 10.79%, 21.53%, 29.47% and 31.87% reduction with reference to the WL of the control specimens, respectively. It should be noted that the effect of the incorporation of LF in MK concrete is more pronounced here than the specimens subjected to less aggressive solutions as the M20 mixture has lost 12.65%, 5.95%, 12.64% and 7.63% more weight in the four phases than the M20/L10 mixture which contains 10% LF. In addition to a pore reducing effect and densification of the concrete micro structure, LF also has the ability to react with the acid solution around the concrete and increase the surrounding pH, hence, making it less aggressive which will result in improved resistance of concrete to sulfuric acid attacks.

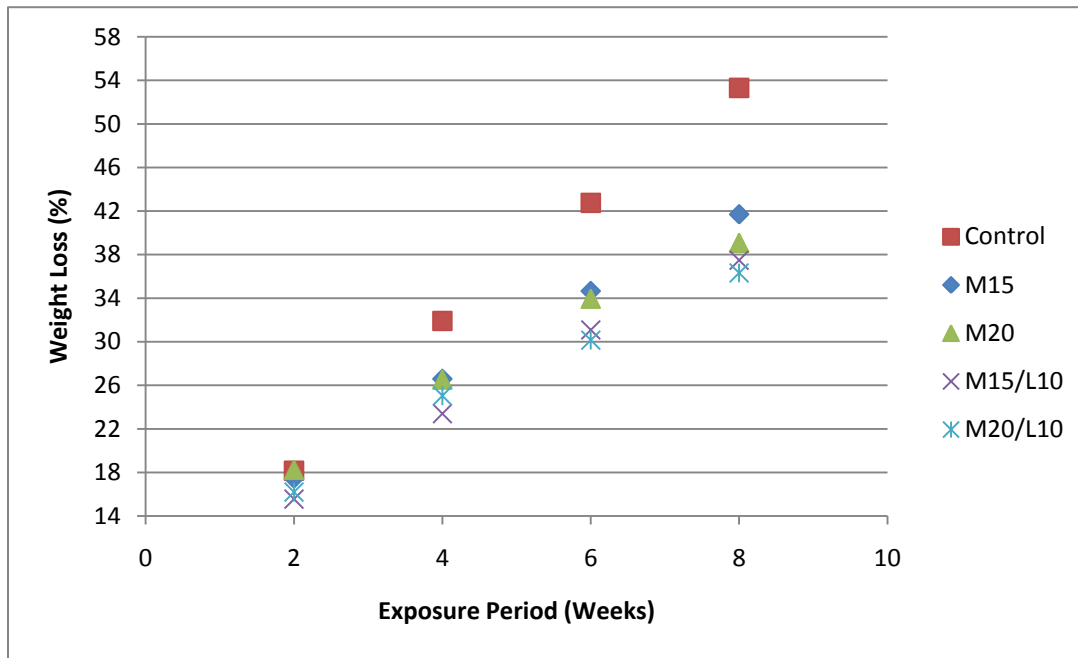


Figure 4.4 Weight loss vs. exposure periods of the specimens subjected to a sulfuric acid solution with 7% concentration.

Table 4.6 The ratio of the weight loss of the modified mixtures to the control mixture.

Mixes	3% Sulfuric Acid Solution				5% Sulfuric Acid Solution				7% Sulfuric Acid Solution			
	Immersion Period (Weeks)				Immersion Period (Weeks)				Immersion Period (Weeks)			
	2	4	6	8	2	4	6	8	2	4	6	8
M15 (%)	85	85	90	84	91	86	81	86	96	83	81	78
M20 (%)	92	89	88	74	92	88	76	76	100	83	79	73
M15/L10 (%)	91	80	84	75	83	75	74	73	86	73	73	70
M20/L10 (%)	100	83	88	80	88	76	76	75	89	79	71	68

The contribution of MK in improving the resistance of concrete specimens to the invasion of sulfuric acid can be clearly noticed from the results of Figures 4.4 to 4.6 and Table 4.6 which depicts the ratios of the WL of modified mixtures with MK and LF to the control mixture. For instance, after eight weeks of immersion in 3%, 5% and 7% sulfuric acid solutions, the mixture that contained 20% MK experienced a 74%, 76% and 73% WL to the control mixture, respectively. While, the mixture with 15% MK experienced an 84%, 86% and 78% WL to the

reference mixture with no supplementary materials. Hence, increasing the quantity of MK in lieu of Portland cement has been beneficial with regards to the WL of concrete specimens subjected to severe sulfuric acid solutions. MK has different means to reduce the deterioration of concrete immersed in sulfuric acid. The C_3A of Portland cement, which is the most vulnerable to the intrusion of sulfate ions and responsible for secondary ettringite formation, is reduced by the incorporation of MK. The amount of $Ca(OH)_2$ content is also decreased by the pozzolanic reaction of MK. Last but not least, the reduction of the large capillary pores to small ones and somehow blocking of these pores which is caused by the formation of secondary C-S-H through a pozzolanic reaction that refines the pore structure, plays a critical role in protecting concrete against ingress of harmful chemicals (Al-Akhras 2006).

Another interesting observation which can be made from Table 4.6 is that the role of MK and LF becomes more pronounced in the final weeks of the exposure period which indicates the critical effect of the immersion time. For example at the end of the 6 weeks of immersion in 3%, 5% and 7% solutions, the M20/L10 mixture experienced a 87.9%, 75.5% and 70.5% WL to the control mixture, respectively, which indicates a significant benefit of replacing cement with MK and LF in concrete mixtures subjected to higher concentrations of sulfuric acid for longer periods of time.

4.2.3.2 Strength Loss

The results of the change in mass depend on the size of the samples and cement type (such as Portland cement, sulfate resistance cement and use of SCMs), while it can also be significantly affected by the process of treating the reaction products, and disintegrated cement paste on the samples in an experiment (Chang et al. 2005). Thus, the average compressive strength of the degraded samples was evaluated at the end of every phase of exposure to the sulphuric acid solutions and compared with the initial 28 day compressive strength. Note that due to the loss of materials and surface irregularities, determining the accurate value of the strength becomes a difficult task.

Hence, to avoid measuring the varying areas of the cylindrical specimens to determine the strength, it was considered more appropriate to record the maximum load that each sample could take after degradation and compare it to the initial load, and ultimately report it as the SL of the concrete samples after exposure to sulfuric acid solutions.

Figure 4.5 illustrates the concrete cylinders that are immersed in a 3% sulphuric acid solution which have undergone some considerable SL after different periods of exposure. The trend of SL for the control and M15 samples is rather unusual as both have lost high strength at the end of the two weeks, but these values significantly decrease at the end of the 4 weeks. This trend was not observed for the other samples in the first 4 weeks of the testing and may have occurred for the following reasons.

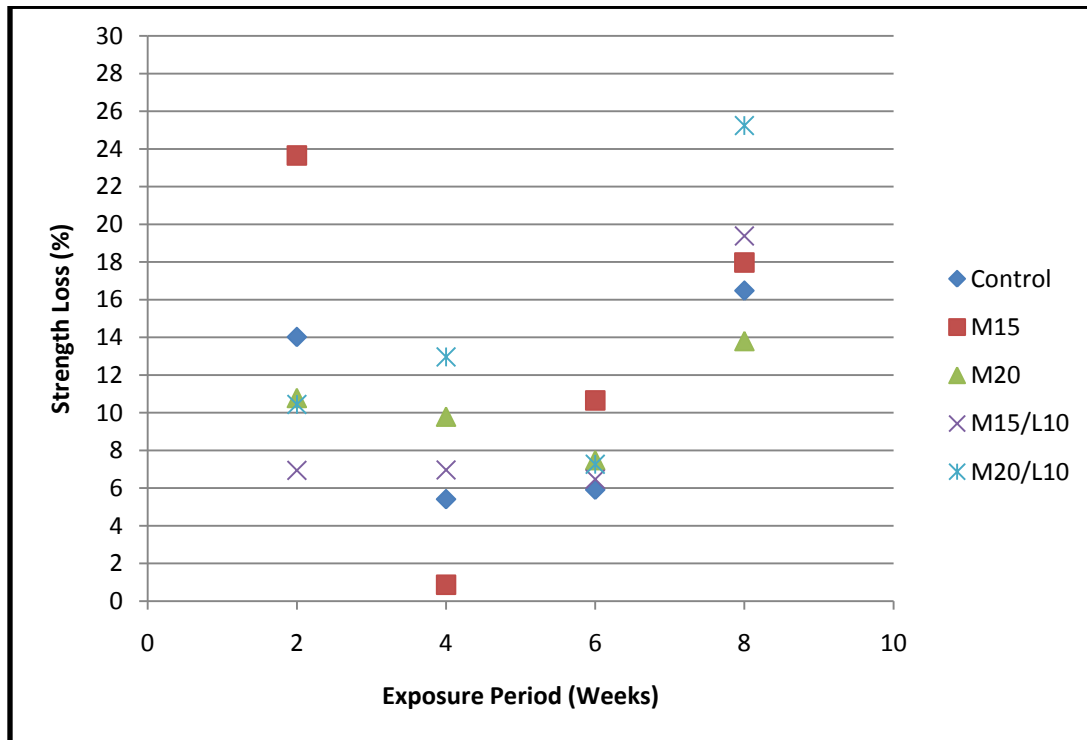


Figure 4.5 Strength loss of concrete samples from different mixtures after exposure to a 3% sulphuric acid solution.

After immersion in a sulfuric acid solution, due to the chemical reaction between the hydration products of concrete and the surrounding acid, a calcium sulfate hydrate or a protective layer forms on the sound inner part of the concrete that has not experienced an acid attack yet. The limestone aggregates of the concrete specimens also play a part in the formation of this layer by reacting with sulfuric acid. Although the protective layer, which consists of loose particles and

reaction products, is thoroughly washed after each exposure period, a visual inspection of the specimens and crushed pieces of the concrete cylinders after the compression test indicates that the protective layer still exists and its effects on the load bearing capacity and other properties of the specimens cannot be neglected.

It is suspected that the protective layer has a weaker structure and lower adhesion to the sound part of the concrete with less or no supplementary materials in comparison to the other mixtures with higher replacement levels of MK and LF. Therefore, due to the low strength of this layer and its partial attachment to the undamaged part of the concrete, the application of the compressive load will subsequently result in a quicker failure of the concrete which may explain the higher SL of these mixes for the first 2 weeks. The unusual behaviour of specimens in terms of SL has also been observed in the studies of Chang et al. (2005), and Bassuoni and Nehdi (2007).

Another debatable observation can be made from Figure 4.5. Most of the mixtures that contain different quantities of MK and LF have lost more of their strength than the control samples following four weeks of exposure to 3% sulphuric acid. It is suspected that, the protective layer on the modified concretes which was stronger and had better adhesion to the surface of the specimens at the initial stages of exposure, had become softer with time. Thus, this can be the reason behind the better performance of the control samples in terms of SL, as it is suspected that after two weeks, the white gypsum layer on the surface of these specimens is too weak to play any role in the load bearing capacity of the concrete and hence, the sound part of the specimens is responsible for their strength while this may not be the case for samples from the modified mixtures.



Figure 4.6 Crushed degraded concrete sample under compressive load.

Bassuoni and Nehdi (2007) stated that the compressive strength of concrete specimens is affected by the properties of the concrete matrix (binder type, aggregates, w/c ratio, etc.), consolidation and curing methods, geometry and aspect ratio. The irregularities in geometry across the height of the degraded concrete cylinders can result in non-uniform distribution of stresses while applying the compressive load and subsequent inconsistent results. The effects of the continuous hydration of the sound parts of the specimens and formation of a gypsum layer on the load bearing capacity of concrete samples should also not be neglected.

As expected, the specimens immersed in a 5% sulphuric acid solution have suffered higher SL than the ones in the solution with 3% concentration. For example, at the end of the 8 weeks exposure period, the M15/L10 samples had an SL of 19.4% and 30.5% in the 3% and 5% sulphuric acid solutions, respectively.

The major difference between Figures 4.7 and 4.5 is that the SL of the concrete samples in the 5% solution has an almost consistent increasing trend which can be the result of a higher concentration of sulfuric acid which results in the significant removal of the surface layer. Hence, the undisturbed sound inner core of the concrete will play a major part in its strength.

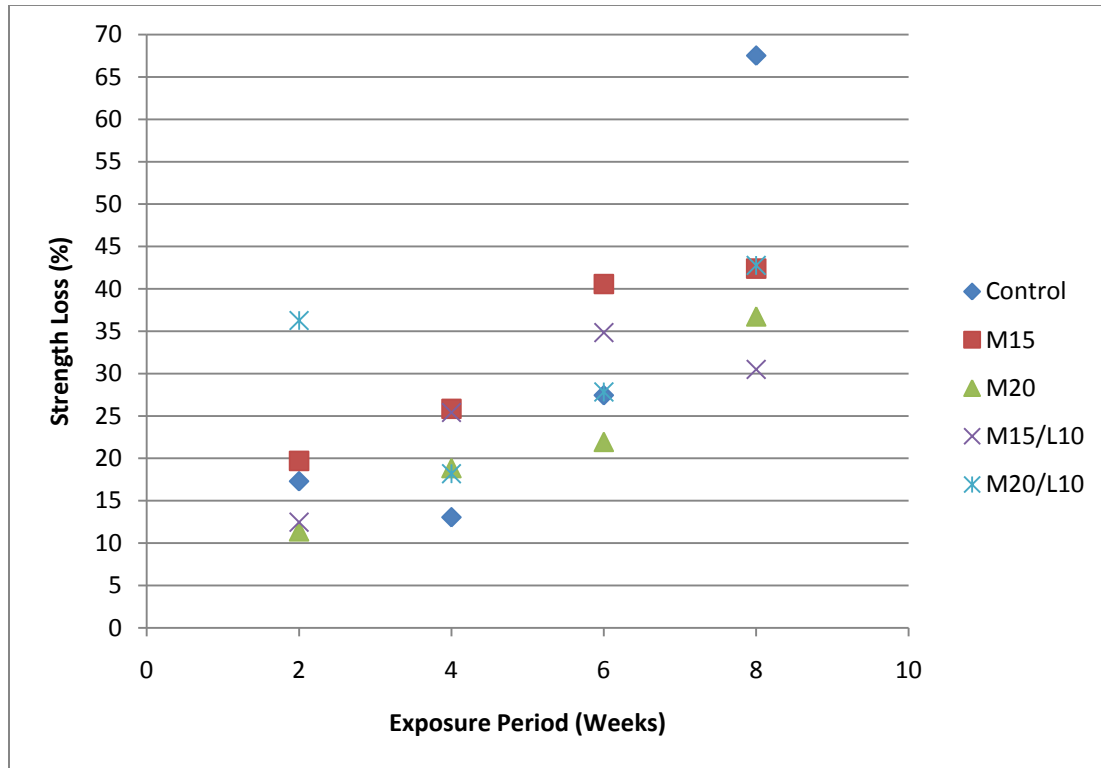


Figure 4.7 Strength loss of concrete samples from different mixtures after exposure to a 5% sulphuric acid solution.

The behaviour of the specimens from the control mix in Figure 4.7 is interesting to observe. They have experienced 17.3%, 13%, 27.4% and 67.5% in SL after 2, 4, 6 and 8 weeks of immersion in a 5% solution, respectively. The reason behind the significant loss of strength of the control samples at the end of the 8 weeks period can be the result of nearly complete destruction of the concrete structure as will be shown in the visual inspection section of this chapter.

The severity of the attack and its detrimental effect on the control samples becomes more significant after 6 weeks of exposure where a considerable amount of their strength is lost while the other mixtures have not experienced such a significant SL at the end of the experiment. The M15/L10 mixture has shown better performance than the other mixtures as its SL was reduced by 54.83%, 28.05%, 17% and 28.69% with reference to the control, M15, M20 and M20/L10 mixtures after 8 weeks of exposure to 5% sulfuric acid.

Figure 4.8 represents the results of the strength measurements of concrete specimens subjected to the most severe condition with a 7% sulphuric acid solution. Here, the deterioration rate of the samples is much higher than the other solutions. As observed, most of the specimens have lost more than 50% of their strength after 6 weeks in the solution.

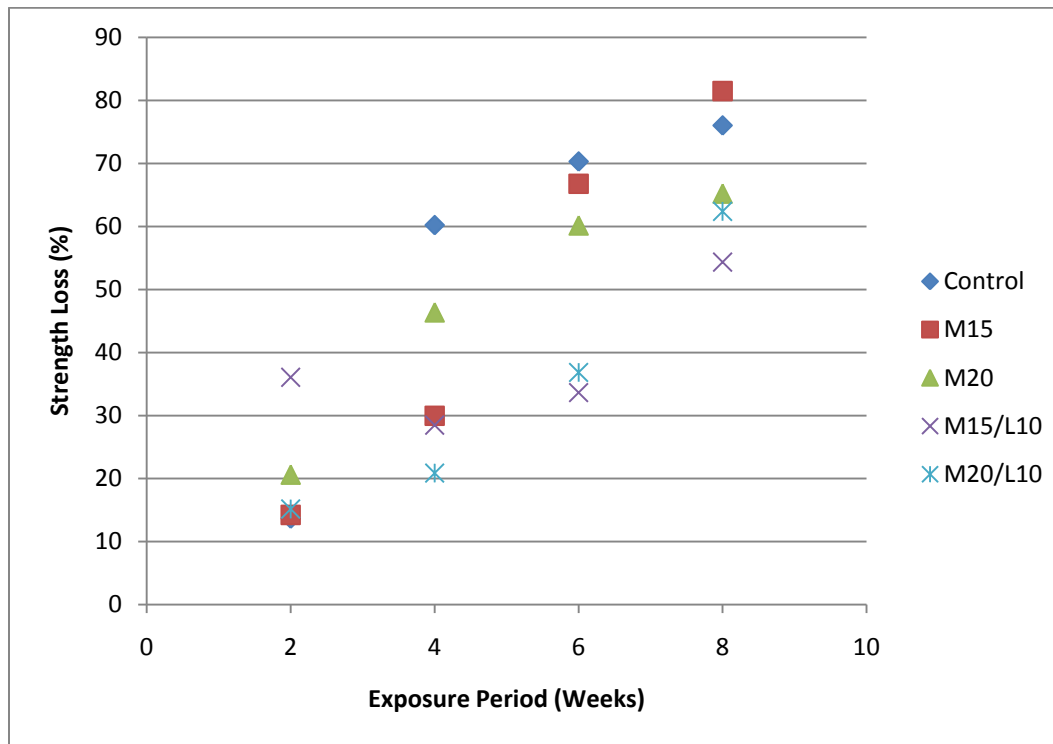


Figure 4.8 Strength loss of concrete samples from different mixtures after exposure to a 7% sulphuric acid solution.

Due to the very low pH of the acidic solution and higher rate of corrosion, almost all the samples have the same increasing SL trend. For example, the M20/L10 mix has lost 15.2%, 20.9%, 36.8% and 62.4% of its strength after 2, 4, 6 and 8 weeks of immersion, respectively. It is important to note that for the M15/L10 and M20/L10 mixtures, high SLs (more than 50%) were recorded at the end of 8 weeks while the M15 and M20 mixes had started to lose more than 50% of their strength at the end of 6 weeks. This result suggests that at the higher concentrations of sulfuric acid, the incorporation of 10% LF results in improved resistance of concrete against the invasion of sulfuric acid. These results can be both the effect of using less cement in concrete and also the physical effect of LF, which causes a better packing of the cement granular skeleton (Bonavetti et al. 2003) and also chemically contributes to reducing the pH of the areas close to the concrete samples.

It should be noted that the uniform degradation of limestone aggregates and LF will produce a continuous ITZ (Chang et al. 2005) which can provide additional strength to the concrete specimens that contain LF after exposure to sulfuric acid.

The inconsistency of the SL results of the concrete specimens subjected to sulfuric acid attacks means that the WL measurements are a more reliable method to compare the performance of the concrete samples.

It should be noted that the major parameter that can affect the WL results is the washing and brushing of the samples, which in this study, comprise consistent washing and no brushing. While as discussed before, the compressive strength can be affected by many factors, such as the sulfuric acid reaction products, geometry and aspect ratio of specimens.

4.2.3.3 Visual Inspection

The performance of the concrete specimens with regards to resistance against severe sulfuric attacks can be compared and examined by visual assessment. The specimens were removed from the solutions and carefully washed every two weeks before they were placed alongside each other for the performance evaluations.

As previously stated, the pH and concentration of the sulfuric acid plays a major role in the corrosion process and severity of the degradation of the concrete samples. The sulfuric acid solutions are at their highest pH level before the immersion of the concrete samples. Hence, the specimens will be subjected to most aggressive conditions right after they are placed in the solution tanks. If significant numbers of concrete specimens are placed in a small volume of acid, the leaching out of the alkalies and disintegration of the concrete sample will result in a continuous increase of pH in the sulfuric acid solutions. However, in this study, due to the removal of a considerable amount of samples from the solutions at the end of every two weeks to perform testing and also due to the large size of the tanks in comparison to the specimens, the pH monitoring showed a constant pH after the first two weeks of the experiment for all the solutions.

It can be observed from Figure 4.9 that the specimens in a 7% sulphuric acid solution has already lost some of their surface particles and the exposure of the aggregates have already started after only two weeks into the total testing period. The specimens in a 5% sulfuric acid solution have also undergone some deterioration, but it is obviously milder than the 7% solution. The

acceleration of the attack is significantly lower for specimens subjected to a 3% sulphuric acid solution as the formation of a white gypsum layer on the outer surface is the only apparent corrosion feature.

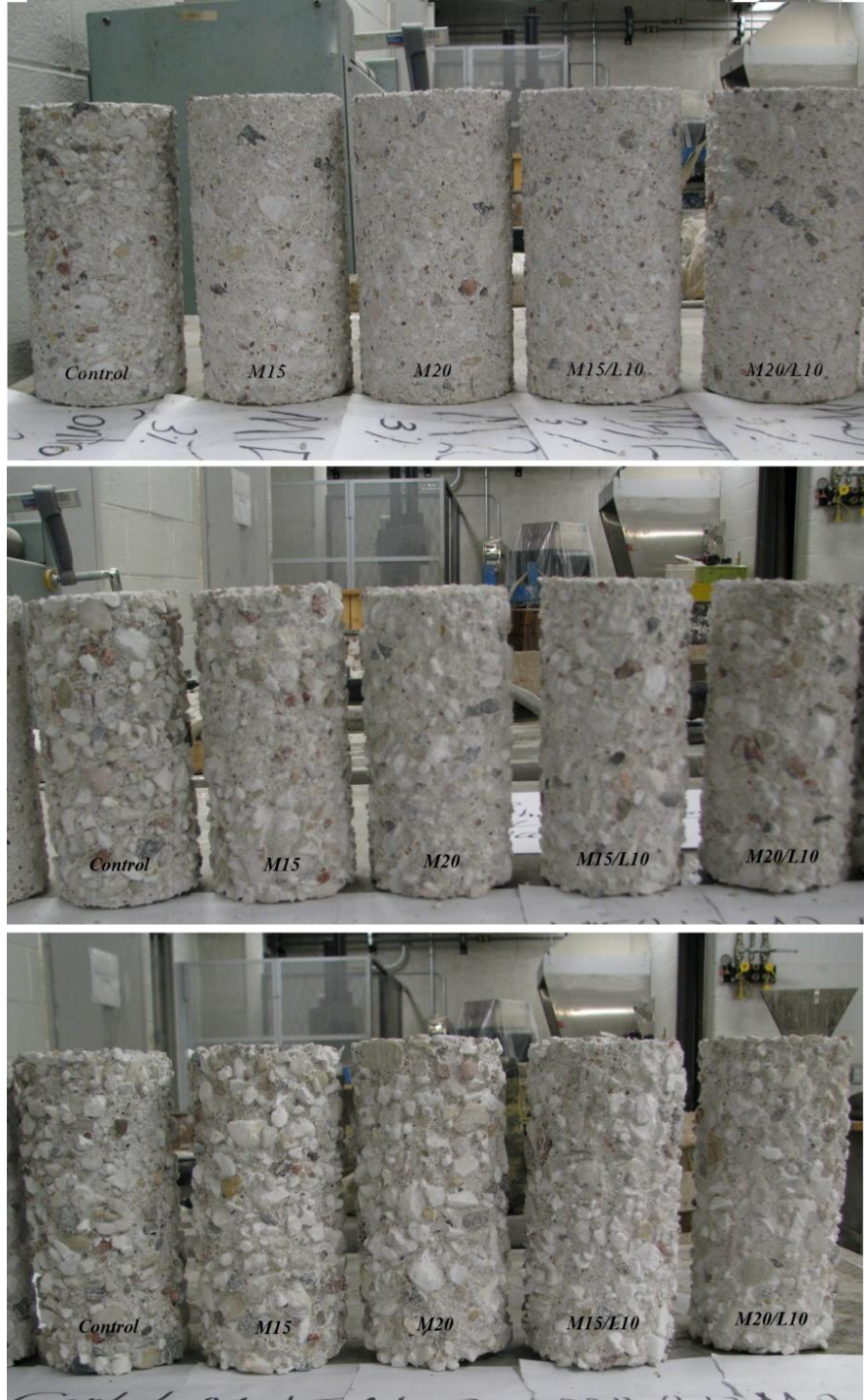


Figure 4.9 Degraded specimens after two weeks of immersion in sulfuric acid solutions with concentrations of 3% (top), 5% (middle), and 7% (bottom).

Figure 4.10 represents the condition of concrete specimens from the five mixtures in this study after 8 weeks of exposure to a 3% sulphuric acid solution. Upon close examination of the degraded samples, it is noticed that the control sample clearly has the lowest resistance to the sulphuric acid attack in comparison to the specimens from the rest of the mixtures. Although the difference among the other mixtures is not as clear as their difference to the control sample, it is obvious that the specimen from the M15 mix has lost more surface compounds than the other modified mixtures. The appearances of the M15/L10 and M20/L10 specimens are considered to be the best among all the samples as they have a smoother surface with less exposed components.

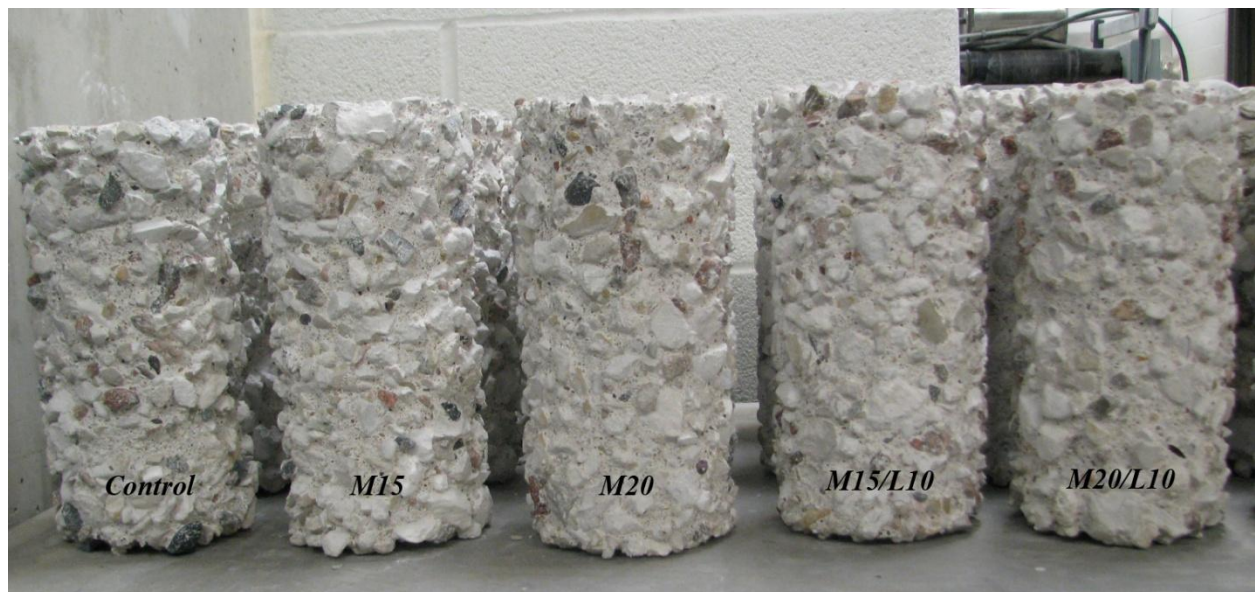


Figure 4.10 Visual assessment of degraded concrete samples after 8 weeks of exposure to a 3% sulfuric acid solution.

One of the primary reasons behind the improved resistance of the concrete samples that contain MK could be the production of C-S-H with a lower C/S ratio of around 1. In low pH acidic environments, the C-S-H releases most of its lime while a layer that consists of silica and alumina silicate gels remains and protects the cement paste from further corrosion (Shi and Stegemann 2000).

In concrete with 100% Portland cement, due to a high C/S ratio (about 3), the dissolution of $\text{Ca}(\text{OH})_2$ and calcium sulphoaluminates, and the decalcification of C-S-H, will result in formation of a porous degraded layer vulnerable to more acid attacks, while in concrete that

contains supplementary cementing materials, such as MK, due to lower C/S ratio, a dense silica gel layer will form, which subsequently, protects the cement paste from more deterioration.

As also observed in the results of the SL and WL measurements, the difference between the performance of the samples and effects of incorporation of MK and LF becomes more pronounced with an increase in concentration of sulphuric acid and subsequently, reduction of pH. From Figure 4.11, the inferior performance of the control sample with Portland cement as the only binder is obvious, while M15 with 15% MK is in a better condition, but has more exposed aggregates and a rougher surface in comparison to the specimens from other mixtures. It can be seen that the aggregates are completely exposed in all the specimens, but there are some significant differences between the mixtures in this regard.



Figure 4.11 Visual assessment of degraded concrete samples after 8 weeks of exposure to a 5% sulfuric acid solution.

Figure 4.12 presents the conditions of the deteriorated specimens after 4 weeks of immersion in a 7% sulphuric acid solution. It is interesting to observe that the severity of degradation is so high that they have lost slightly less material than the specimens immersed into a 5% sulphuric acid solution for the entire 8 weeks of the testing period. More images of the degraded specimens from different solutions and periods of exposure are provided in Appendix A.



Figure 4.12 Visual assessment of degraded concrete samples after 4 weeks of exposure to a 7% sulphuric acid solution.

4.2.4 Phenolphthalein Test

The phenolphthalein colour test has been used in this study to determine the depth of the penetration of sulphuric acid ions into the concrete samples. As previously stated, a pink colour indicates a high pH (around 9) and alkalinity of the concrete. The colourless areas normally signify a lower pH of less than 8 and the presence of products formed from reaction with chemical solutions.

After exposure to sulphuric acid solutions with different concentrations, the concrete specimens were cut and placed on a white plastic sheet and the prepared phenolphthalein solution was sprayed on the surface of the cut degraded samples. In Figure 4.13, the name of the mixtures and concentrations of the sulphuric acid solutions are shown. It can be observed that no colourless zones can be spotted on any of the corroded samples and only a bright pink colour is noticed. The same results were observed for all phases of the sulphuric acid experiment.

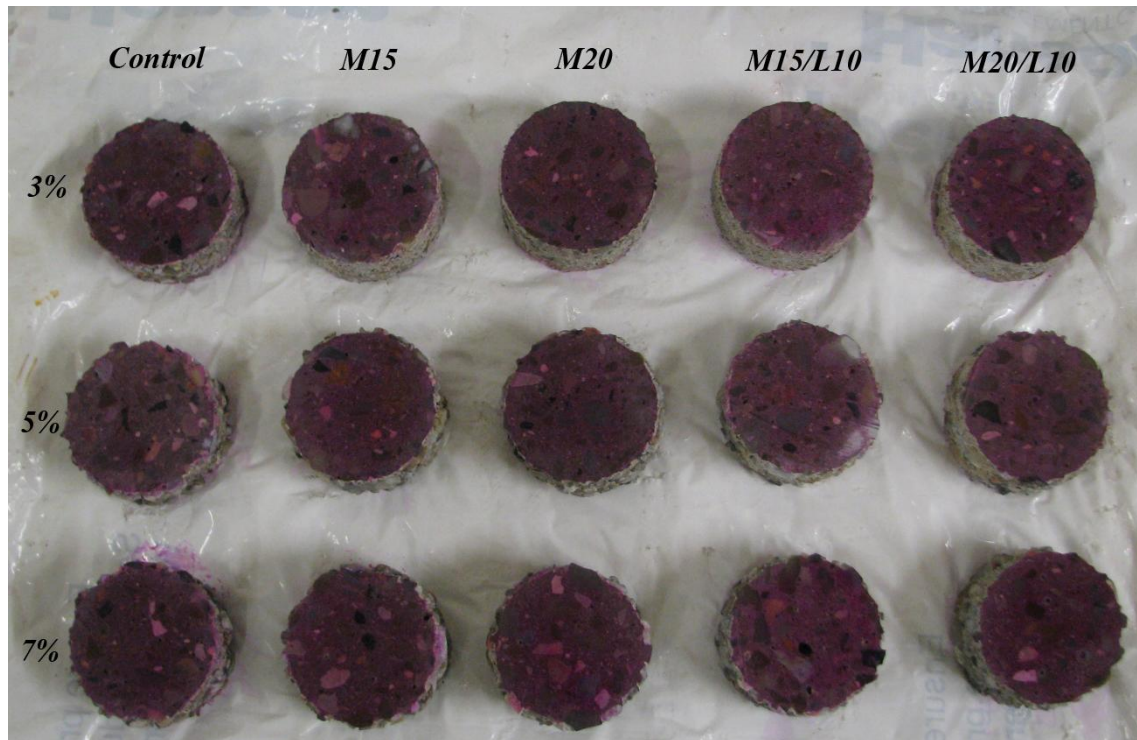


Figure 4.13 Degraded concrete samples covered with phenolphthalein solution.

As previously mentioned, the concrete specimens were thoroughly washed at the end of every period of exposure to the sulphuric acid solutions. This washing procedure plus the low pH of the sulphuric acid solutions have resulted in a significant removal of loose particles from the surface of the degraded concrete specimens. Thus, after the application of the phenolphthalein solution, no distinction of colour can be noted on the surface of the specimens, which indicates a significantly thin layer of reaction products (between sulfuric acid and concrete hydration components) that could not be detected by the phenolphthalein solution.

4.2.5 Rapid Chloride Permeability Test

RCPT is the electrical indication of a concrete's ability to resist chloride ion penetration and has been used to provide some useful information on the permeability characteristics of the concrete specimens from various mixtures in this study. This test is widely regarded as one of the most efficient and quickest way to evaluate concrete resistance to chloride ion ingress. Table 4.7 can be used to evaluate the penetrability of the specimens by using the coulomb charge information obtained from the RCPT.

Table 4.7 Chloride ion penetrability based on charge passed (ASTM C1202)

Charge Passed (Coulombs)	Chloride Ion Penetrability
≥ 4000	High
2000 - 4000	Moderate
1000 - 2000	Low
100 - 1000	Very Low
≤ 100	Negligible

The specimens were tested for rapid chloride penetration after being cured in a 98% relative humidity room for 56 and 95 days. The results of these experiments are displayed in Figure 4.14. It is shown that the specimens from the control mixture have the highest amount of average coulomb charges (2049 and 1478) than any of the other samples. These results are in total agreement with previous research, such as Poon et al. (2006) who reported that the use of MK in concrete at replacement levels that range from 5% to 20% will result in lower chloride penetrability than concrete with only Portland cement at all ages. The permeability of the control samples can be classified as moderate and low for the 56 and 95 days of curing, respectively. The increase in the replacement level of MK from 15% to 20% for the M15 and M20 mixtures has resulted in a decrease of the total coulomb charges from 395 to 336 for 56 days and from 342 to 294 for 95 days of curing.

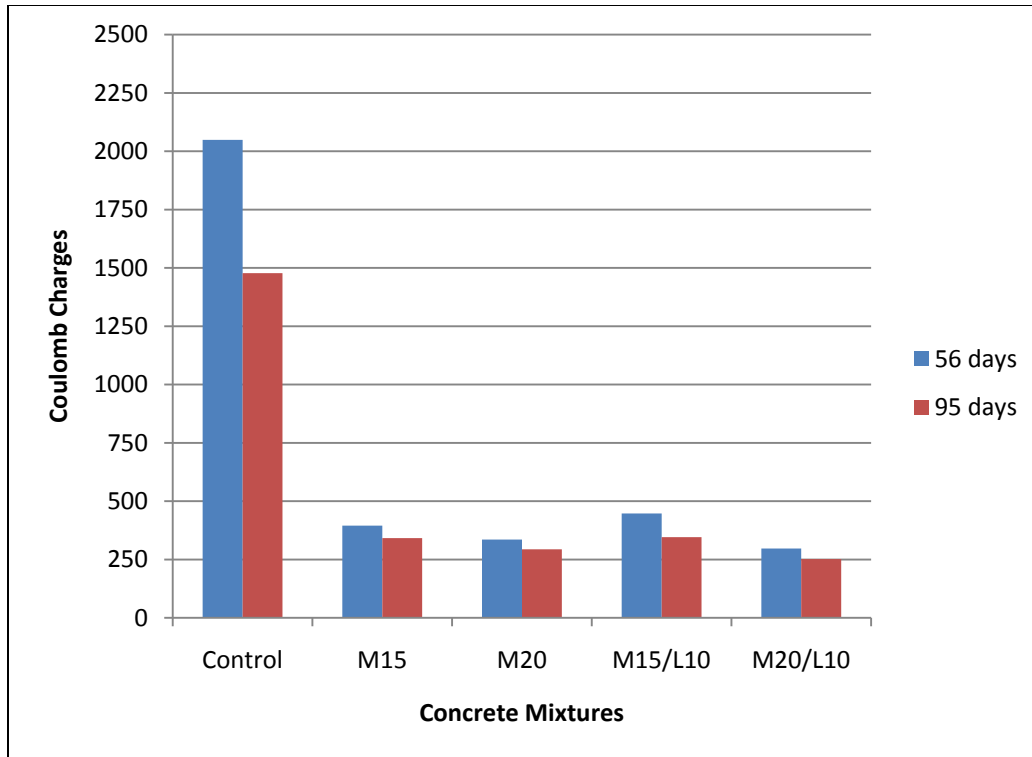


Figure 4.14 Rapid chloride permeability of concrete specimens at different ages.

It can also be noticed from Figure 4.14 that the difference between the two average coulomb charges of the mixtures with only MK at the two ages is not significant. This result is due to the higher hydration rate and pozzolanic reaction of MK at early ages and much slower rate at older ages of over 28 days. The faster rate of hydration at initial ages for concrete with MK can be attributed to its Al_2O_3 phases which are responsible for the formation of C_2ASH_8 and a small amount of crystalline C_4AH_{13} phase (Poon et al. 2001). The addition of 10% LF to the M15 mix has resulted in a slight decrease in resistance to chloride ion ingress, but the overall difference is not considerably significant. The M20/L10 mix exhibited the best performance among all of the mixtures with very low average coulomb charges of 297 and 252 for 56 and 95 days of moist curing, respectively. These results indicate that the incorporation of 10% LF to concrete with 15% and 20% MK will not cause any considerable effects on the performance of the concrete samples with regards to their resistivity to chloride ion penetration. The values of the coulomb charges of the specimens from different mixtures can be found in Appendix B.

4.2.6 Rapid Freezing and Thawing Test

It is generally known that concrete is vulnerable to continuous drastic changes of temperatures. Entraining a specific amount of air into concrete by using AEA is the most common way to deal with this issue and in most cases, has been successful. It is important to note that several parameters are involved in the durability of air entrained concrete in terms of resistance to freezing and thawing. The w/c ratio, SCM, curing method, pore system, saturation degree and temperature are factors that can have significant effects on the performance of concrete in terms of freezing and thawing durability.

The incorporation of MK results in the superior improvement of the pore structure and penetrability of the concrete. Hence, a well designed MK concrete will have satisfactory resistance against damages from repeated freezing and thawing cycles (Newman and Choo 2003). In this study, the effect of MK alone and also in combination with LF on the durability of concrete against rapid freezing and thawing cycles was examined.

As mentioned in Chapter Three of this study, the equipment and testing procedure to evaluate the frost resistance of the different mixtures follow ASTM C666. The ultrasonic tester is normally used to measure the pulse velocity and subsequently, durability factor of the concrete prisms subjected to a specific amount of freezing and thawing cycles. Unfortunately, the values which were recorded from this machine were found somewhat unreliable due to several problems of the equipment. Therefore, visual inspection and weight change of the prisms were used to compare their resistance against repeated cycles of freezing and thawing.

Two samples from each mix were subjected to 300 cycles of rapid freezing and thawing. The changes in mass of the prisms were recorded every 30 cycles. The control specimens which contained only Portland cement as its binder lost an average of 0.22% of their weight at the end of the testing period which was the highest among all the mixtures. The average WL of the concrete prisms from other mixtures was very close to each other in which M15, M20, M15/L10 and M20/L10 lost 0.064%, 0.084%, 0.073% and 0.072% of their weight, respectively, at the end of the 300 cycles.

Figure 4.15 shows the two prisms from the M15 and control mixes placed next to each other. It can be seen that the surface of the control specimen is more scaled than that of M15. This difference is not very noticeable in Figure 4.16 as the specimens have not suffered any significant damage or scaling. These outcomes indicate the advantage of employing MK and LF as replacements for Portland cement with regards to resistance of concrete to freezing and thawing cycles. The reader can refer to Appendix D for complete information on the mass changes of the concrete prisms at the end of every 30 cycles of freezing and thawing.

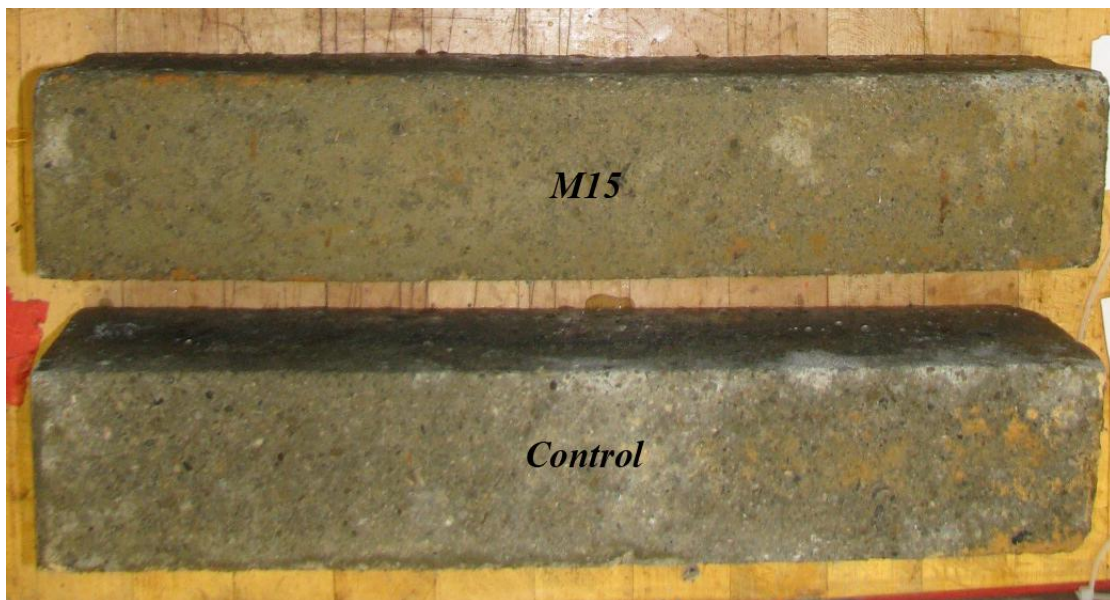


Figure 4.15 Concrete prisms from the control and M15 mixes after 300 repeated cycles of freezing and thawing.



Figure 4.16 Concrete prisms from the M20, M15/L10 and M20/L10 mixes after 300 repeated cycles of freezing and thawing.

4.2.7 Water Sorptivity

Various studies have been done on the water sorptivity of different types of concrete which is the measurement of the rate of water absorption by one side of the concrete surface through capillary suction. Several parameters, such as w/c, curing method and use of different types of SCMs, can alter the outcomes of this test. In this part of the study, the results of the water sorptivity of the sound and degraded specimens are presented and analyzed.

4.2.7.1 Water Sorptivity of the Sound Specimens

The initial sorptivity rate of the concrete samples, which is the average of four values from each mix after 6 hours of test, is depicted in Figure 4.17. It is clear that the control sample with only Portland cement and no SCM has the highest absorption rate in comparison to the samples from the other mixtures. It can also be seen that with an increase in MK from 15% to 20% in the M15 and M20 mixes, the sorptivity drops from 0.328 mm/ \sqrt{h} to 0.234 mm/ \sqrt{h} . The addition of 10% LF to the M15 and M20 mixtures has some effects on the sorptivity of the concrete samples as illustrated in Figure 4.17, in which the difference between the initial water sorptivity of these mixtures is not significant.

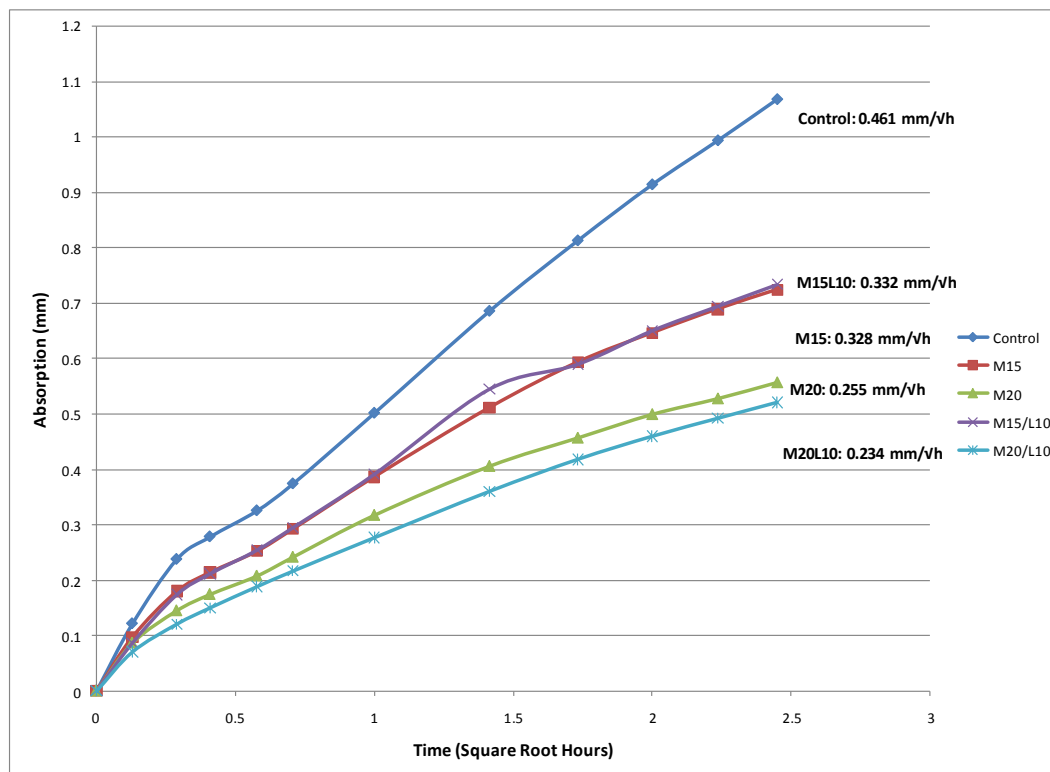


Figure 4.17 Initial absorption rates of the concrete specimens from different mixtures.

The outcomes of this experiment are in agreement with the results of the study done by Bai et al. (2002). They used different quantities of pulverized fuel ash (PFA) and MK to replace Portland cement in their concrete mixtures. MK and PFA were used in different proportions as the maximum replacement level of these two SCMS was set to 10% and 30%, respectively. The final

results showed that the 28 day water cured mixtures that contained the highest amount of MK (10%) had the lowest sorptivity of all the mixtures while the mixtures with only PFA had a higher sorptivity. Bai et al. (2002) employed two curing methods (air curing and water curing) in their studies and the incorporation of MK in concrete had shown positive results in both cases. The reduced sorptivity in the PC-PFA-MK mixtures was attributed to the finer pore structure which will inhibit the penetration of aggressive elements into the pore system.

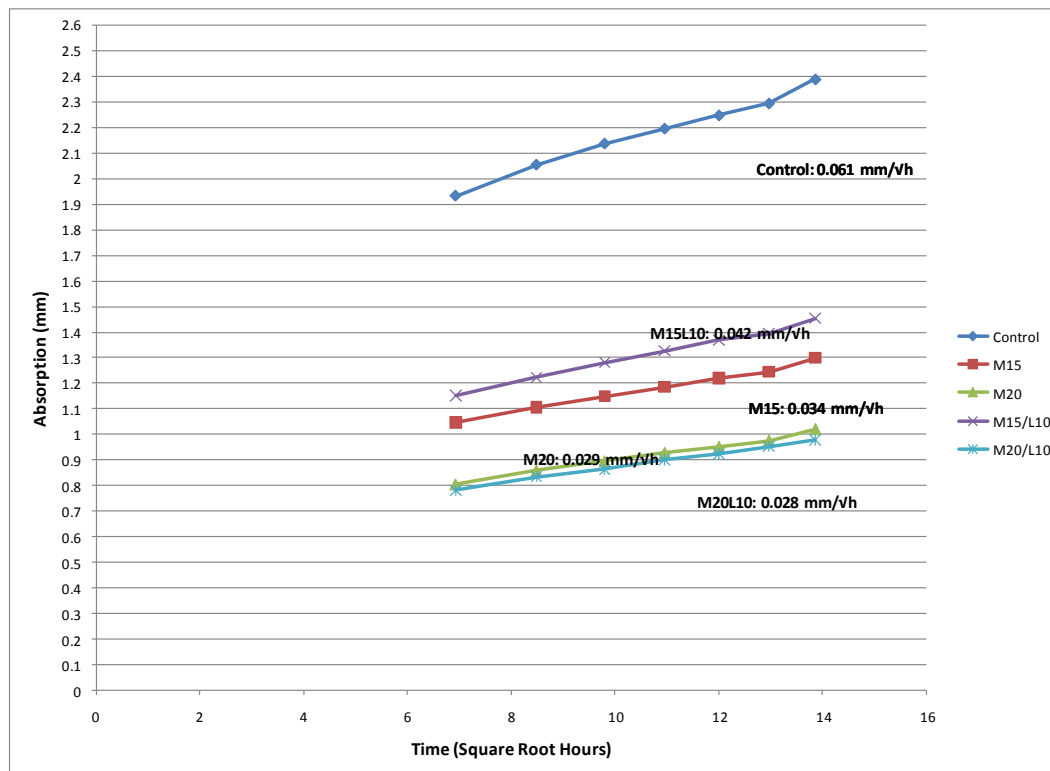


Figure 4.18 Secondary absorption rate of specimens from different concrete mixtures.

The secondary absorption rates of the concrete specimens which are the results of the measurements after 24 hours can be observed in Figure 4.18. It is shown that the sorptivity trend of all specimens is the same as the initial sorptivity. Upon a closer examination of the sorptivity values which are shown for every mixture, it is apparent that the control and M20/L10 mixtures have the highest (0.061 mm/√hour) and lowest (0.028 mm/√hour) sorptivities, respectively. The lower capillary suction of mixtures that contain MK is the result of both reduction of pore size distribution and obstruction of capillary pores caused by inclusion of MK, while the addition of 10% LF in these mixtures has not resulted in any significant changes in sorptivity which makes it a suitable economical and green (environmentally friendly) substitute for OPC.

4.2.7.2 Water Sorptivity of the Degraded Specimens

The water sorptivity test was also performed on the degraded concrete specimens subjected to sulfuric acid attack. After every phase of immersion in different concentrations of sulphuric acid, the degraded concrete specimens were cut and prepared to examine the rate of water absorption. The testing follows the same original procedure which has been done for the sound specimens. The only difference here is that the sorptivity test of the degraded samples was terminated after 24 hours. Hence, only the initial absorption rate was measured.

As previously stated, a white layer, which is suspected to comprise calcium sulfate components, was formed around the specimens after exposure to a sulphuric acid attack. It was observed that this so called protective layer would lose its adhesion and is subsequently removed from the surface of the concrete after a certain period of immersion into water. The measurements of the absorption of the degraded concrete specimens after 24 hours showed reduction instead of an increase in mass for some of the specimens and for almost all of them after 48 hours, which confirms this phenomenon. Therefore, the secondary absorption rate could not be measured and the test was discontinued to avoid any irregularities in the results.

Figure 4.19 represents the sorptivity coefficients of the degraded concrete specimens after different periods of immersion in a 3% sulphuric acid solution. It is shown that the control specimens always demonstrate a higher sorptivity rate of all the specimens before and after exposure. For instance, the sorptivity coefficient of the control sample at the end of the sulfuric acid test period is 0.17, 0.18, 0.19 and 0.21- mm/ $\sqrt{\text{hour}}$ more than the coefficients of M15, M20, M15/L10 and M15/L10 mixtures, respectively. It is also noticed that the sorptivity of all the samples have increased after 2 weeks of immersion in 3% sulphuric acid. This could be the result of different factors, such as the existence of a calcium sulfate layer around the specimens which may absorb the water and also continuous increase in diameter of the specimens due to loss of surface compounds. Thus, the absorption rate will be increased in comparison to the original sound samples. After the first 2 weeks, the sorptivity coefficients of almost all the mixtures have a tendency to increase, but at a much more reduced rate after 4 weeks. The sorptivity coefficient of the control mix shows a decrease (0.062 mm/ $\sqrt{\text{hour}}$) from 2 to 4 weeks, but it is clearly not significant and following this period, becomes steady. The M20/L10 mix shows an unusually

high increasing rate of coefficient (0.20 mm/ $\sqrt{\text{hour}}$) in the 2 to 4 week period, but afterwards, similar to the sound samples, behaves very similar to the M20 mix.

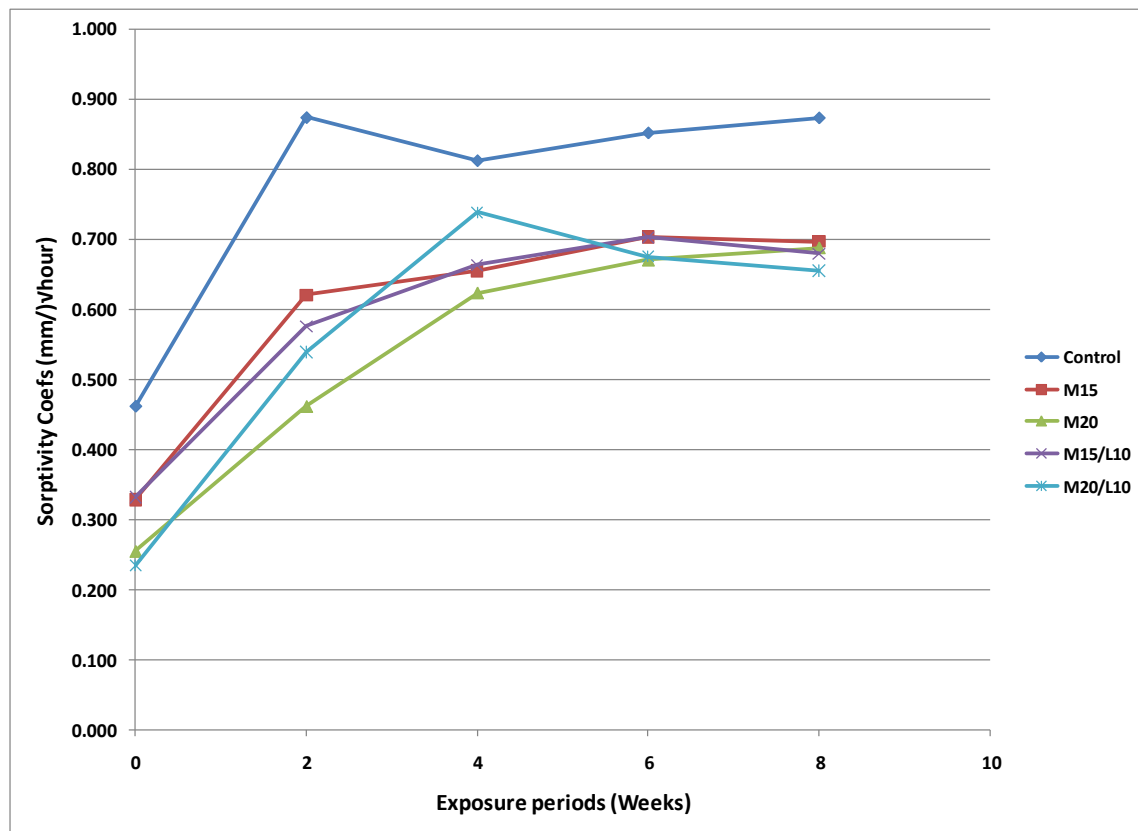


Figure 4.19 Sorptivity coefficients of the degraded specimens after different periods of immersion in a 3% sulphuric acid solution.

It is important to note that the clear distinction which exists between the sorptivity rates of the original sound specimens cannot be observed here. This could be due to the existence of the protective layer around the samples which can produce some unexpected results. However, keeping that in mind, it can be seen from Figure 4.19 that except some few exceptions, the overall trend of the sorptivity coefficients follows the previous results of the sound samples. Sorptivity coefficients of concrete mixtures after exposure to 5% and 7% sulphuric acid solutions are represented in Figures 4.20 and 4.21, respectively. The control mixture has the highest sorptivity coefficients among all of the mixtures in both concentrations. For example, the sorptivities of the control samples after eight weeks immersion in 5% and 7% solutions are 1.02 and 1.19 mm/ $\sqrt{\text{hour}}$ which are 0.34 and 0.52 mm/ $\sqrt{\text{hour}}$ higher than the M20 mixture with the lowest sorptivity. It is important to note that in the calculations of the sorptivity values, the

diameter change of the specimens was taken into account which can be quite responsible for the fluctuations of sorptivities of the degraded specimens. For instance, the sorptivity of the control sample has increased 0.25 mm/ $\sqrt{\text{hour}}$ from 6 to 8 weeks of immersion in 7% sulfuric acid which is most likely due to its significant loss of diameter.

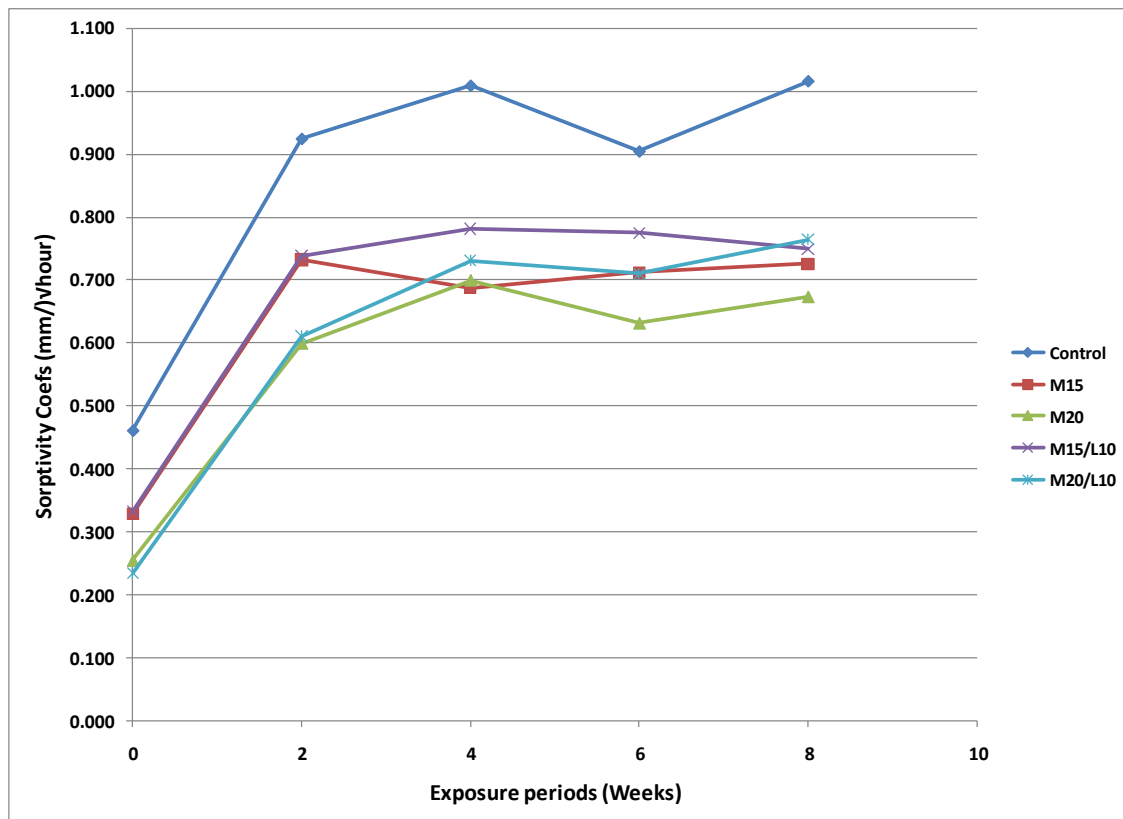


Figure 4.20 Sorptivity coefficients of the degraded specimens after different periods of immersion in a 5% sulphuric acid solution.

The high increase in the sorptivity coefficients (mm/ $\sqrt{\text{hour}}$) is completely evident in the results of both the 5% and 7% concentrations at the end of the 2 week immersion period, this increasing trend continues after two weeks with a reduced rate and in some cases it does not change significantly. For 5% solution, the sorptivities of the original sound control, M15, M20, M15/L10 and M20/L10 specimens have increased 0.46, 0.40, 0.35, 0.40 and 0.38 mm/ $\sqrt{\text{hour}}$ and for the 7% solution, they have increased 0.47, 0.36, 0.32, 0.32 and 0.38 mm/ $\sqrt{\text{hour}}$ after 2 weeks exposure, respectively.

It is shown in Figure 4.21 that except for one unusual case in which there is a high decrease (0.20 mm/ $\sqrt{\text{hour}}$) of absorption rate for the M15 mixture at 6 weeks in 7% sulphuric acid, all other

mixtures exhibit consistent behaviour as they have not experienced any considerable fluctuations in their sorptivity coefficients after 2 weeks of exposure. This suggests that the gypsum layer may be responsible for the sorptivity rate of the degraded samples; however more investigation in this regard is needed. Reviewing and analyzing the results of the water porosity testing on degraded concrete samples are necessary to reach a more comprehensive understanding of the pore structure of the concrete mixtures after immersion into sulfuric acid. The complete data for the absorption rate of the degraded concrete specimens are available in Appendix F.

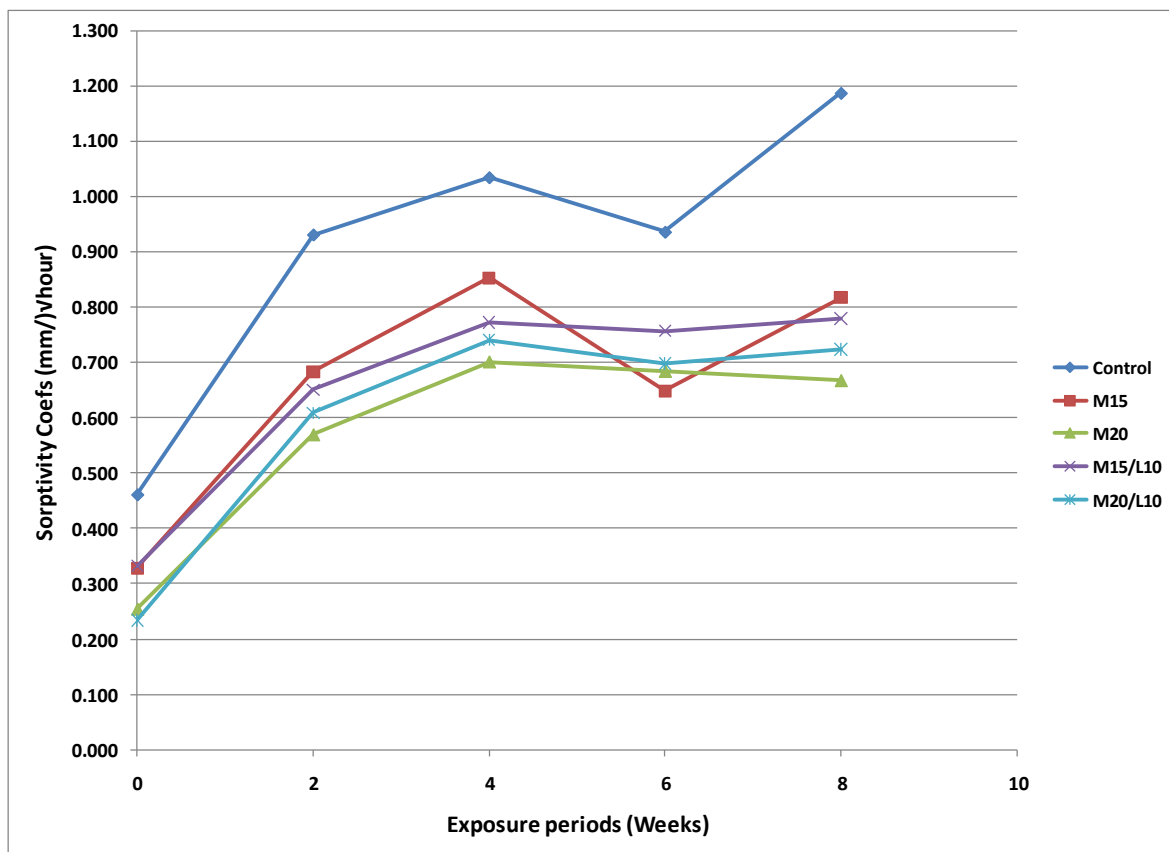


Figure 4.21 Sorptivity coefficients of the degraded specimens after different periods of immersion in the 7% sulphuric acid solution.

4.2.8 Water Porosity

Water porosity test was performed on the sound and degraded concrete specimens. The results of these tests are as follows.

4.2.8.1 Water Porosity of the Sound Specimens

As described in Chapter Three, three specimens were prepared from every mix to determine the percentages of water porosity. The specimens were conditioned in accordance to AFPC-AFREM and their required weights were measured. Figure 4.22 displays the average water porosity of the concrete samples from the five different mixtures.

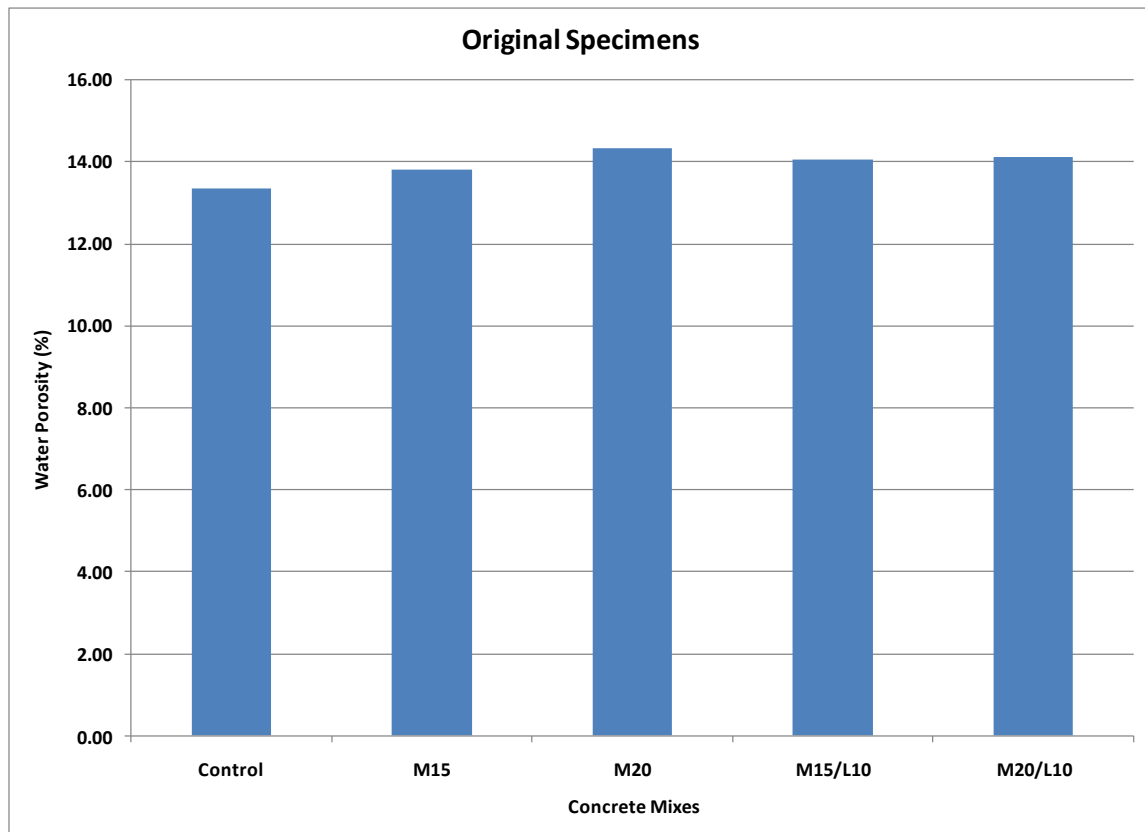


Figure 4.22 Water porosity of sound specimens from different concrete mixtures.

It can be seen that the control mixture has a lower total porosity (13.34%) than the mixtures that contain MK. Moreover, raising the replacement level of MK from 15% to 20% has resulted in a very slight increase (3.69%) in the total average porosity that can be reached by water. These results are in agreement with the previous studies of Khatib and Wild (1996) which discussed the pore size distribution of four different pastes, in which one was made with 100% Portland cement and the other three contained 5%, 10% and 15% MK.

The studies of Khatib and Wild (1996) showed that pastes that contained MK had a higher total pore volume than the control mix, but it was also observed that an increase in the amount of MK would lead to the refinement of the pore structure. It is important to note that the standard deviation of the average water porosities of the sound concrete mixtures is only 0.34, which shows very little difference between the data of the test. An addition of 10% LF affects the MK mixtures differently. For the M15 mix, LF increased the water porosity by 1.81% and for the M20 mix, reduced it by 1.54%. For complete information on the measurements of this experiment, please refer to Appendix E.

4.2.8.2 Water Porosity of the Degraded Specimens

The water porosity of the deteriorated concrete samples after different periods of immersion into the three concentrations of sulfuric acid solution was evaluated by using the same standard procedure described in Chapter Three.

Figure 4.23 illustrates the results of the average water porosity of concrete mixtures subjected to a 3% sulphuric acid solution. It can be observed that the water porosity of the concrete specimens from different mixtures does not undergo any significant changes throughout the testing periods. This may be caused by the high degree of acid concentration which will result in production of very loose reaction particles on the surface of concrete specimens which can be easily removed by washing the samples.

It should be noted that in order to clean the dust off the specimens that were produced by the sawing, the samples were washed again after cutting. Thus, more particles have been removed

from the specimen surface for water porosity test. According to the geometry of the water porosity samples, the area of the surface covered with gypsum compounds is smaller than other areas. Hence, significant removal of the gypsum layer by washing and small area of this surface in comparison to other sound areas of concrete samples will diminish the effect of the gypsum layer on the results of the water porosity test.

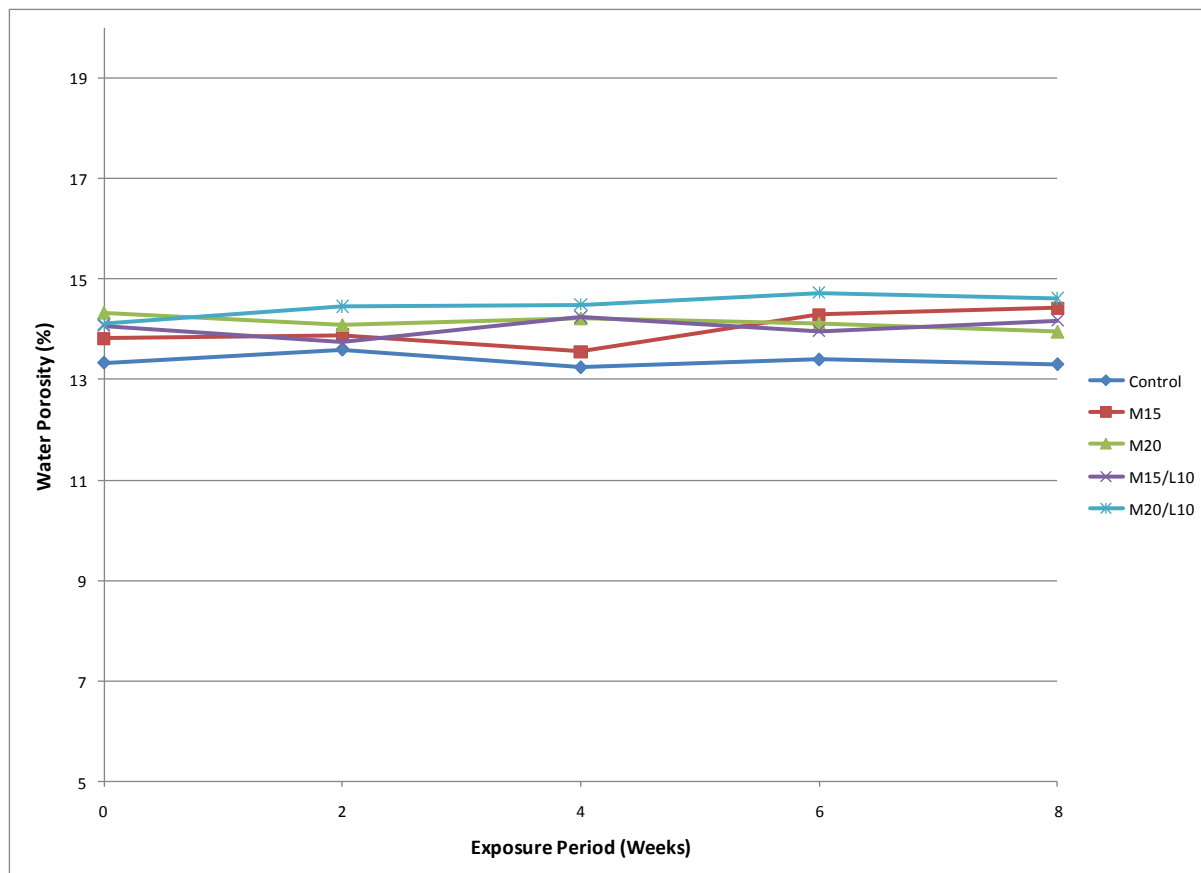


Figure 4.23 Water porosity of degraded concrete samples after different periods of exposure to a 3% sulphuric acid solution.

Tables 4.8 and 4.9 show the values of the water porosity test for concrete mixtures after exposure to 5% and 7% sulphuric acid solutions. In Table 4.8, the maximum change in the water porosity percentage is around only 1% and in most cases, less than that, which is insignificant. In Table 4.9, it can be observed in the final four weeks of the exposure period that all the mixtures have experienced a slight increase in their water porosity after 6 weeks of exposure to the most aggressive sulphuric acid solution. Although the values are not significantly higher than the

previous ones, they refer to the severely porous structure of the calcium sulfate components on the surface of the specimens which may have resulted in higher volume of the reachable pores for water. The highest increase in water porosity was observed for the control specimen (15.3% water porosity) at 8 weeks of immersion in 7% sulphuric acid. It should be noted that some increases were also observed for the M15 and M15/L10 mixtures after 6 weeks of exposure to the solution with highest concentration.

Table 4.8 Water porosity (%) of deteriorated specimens after different exposure periods to a 5% sulphuric acid solution.

Mixes	Period of exposure to 5% sulphuric acid (weeks)				
	0	2	4	6	8
Control	13.34	12.63	12.99	13.65	14.26
M15	13.82	14.11	13.76	14.1	13.6
M20	14.33	13.65	13.64	13.95	13.4
M15/L10	14.07	13.86	13.86	14.38	13.72
M20/L10	14.11	13.55	13.81	14.87	14.46

Table 4.9 Water porosity (%) of deteriorated specimens after different exposure periods to a 7% sulphuric acid solution.

Mixes	Period of exposure to 7% sulfuric acid (weeks)				
	0	2	4	6	8
Control	13.34	13.53	13.61	13.96	15.29
M15	13.82	13.54	13.83	14.82	14.19
M20	14.33	13.54	13.83	14.77	15.14
M15/L10	14.07	14.1	13.94	15.01	14.58
M20/L10	14.11	14.07	14.32	14.93	14.62

Note the results of the two previous experiments (Water sorptivity and porosity) on degraded samples show that the sorptivity of the specimens has undergone some significant changes while the water porosity was not changed considerably after the sulphuric acid invasion.

By taking into account the results of the phenolphthalein test in addition to the outcomes of these experiments, it can be concluded that the significant increase in the sorptivity of the deteriorated samples, which was most notable at the end of the two weeks of immersion, is more likely due to the presence of the white reaction products of sulphuric acid and concrete around the outside

surface areas of the specimens and it does not indicate that the capillary pores at the sound areas of the samples have undergone serious changes, as the results of the water porosity also suggest that the pore structure of the inner parts of the concrete samples has not been influenced by the intrusion of sulfuric acid.

4.2.9 Water Absorption by Total Immersion

Figure 4.24 represents the percentages of water absorption by total immersion for all mixtures. The standard deviation of the data is only 0.12 which shows a very small and marginal difference between the results. However, it is apparent that the incorporation of MK and LF in concrete has not reduced the water absorption by total immersion.

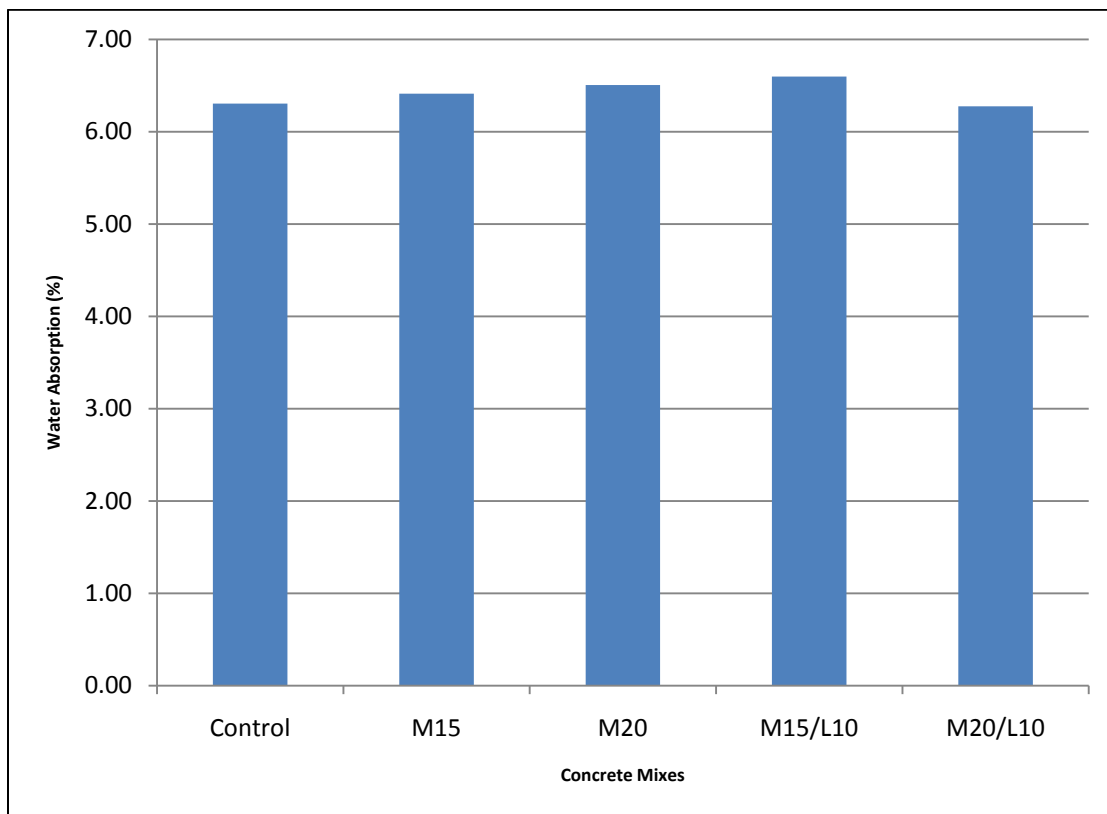


Figure 4.24 Average water absorption by complete immersion of the specimens from the different concrete mixtures.

It is important to note that the values here are less than the water porosity percentages of the samples due to the absence of the vacuuming process which makes more pores available for the water to enter into the concrete and subsequently, the porosity percentage will be higher. However, the overall results of this test agrees with the water porosity test, as the control and M20/L10 mixtures have the lowest absorption of 6.31% and 6.28% of all the samples, respectively.

The results of water absorption by total immersion and the water porosity test do not follow the results of the sorptivity test. In the water sorptivity test, the reduction in capillary suction of water caused by incorporation of MK is apparent. This could be due to the densification and refinement of the pore structure by MK and also the discontinuation and blocking of the pores which resulted from replacement of Portland cement with this type of SCM. On the other hand, the effect of MK on the water penetration by total immersion and water porosity is not that significant at all, which can be due to higher total volume of pores in the MK concrete than the PC concrete and the addition of LF also does not considerably help this behaviour.

Chapter 5. Conclusions and Recommendations

5.1 Summary

A comprehensive study was performed on concrete durability in terms of resistance to sulfuric acid attack. In the preliminary studies, the effect of the incorporation of fly ash, acrylic latex polymer and Xypex admixtures on concrete resistance to a 3.5% sulfuric acid solution was evaluated. Also, the preliminary studies provided the basis for familiarity with the sulfuric acid testing method, and the role of different factors, such as brushing, refreshing the solution and concentration of acid on concrete performance in this aggressive condition, was examined.

In the experimental program of this investigation, five different concrete mixtures that contained metakaolin (MK) and limestone filler (LF) as replacements for Portland cement were prepared. The resistance of the specimens from these mixtures were examined by exposure to sulfuric acid solutions with three different concentrations of 3%, 5% and 7%. Mass loss, visual inspection and strength loss were used to evaluate the inclusion of different quantities of MK and LF on the concrete resistance to sulfuric acid attack. It is important to note that immersing specimens into sulfuric acid solutions for specified time periods may not represent the real condition of the sewer pipes where bacteria corrosion is involved. Nevertheless, the testing takes into account the low pH that concrete substructures face in the harsh environments of sewage systems. Moreover, as mentioned in Chapter 2, concrete structures that come into contact with groundwater and acidic rain, and industrial floors of chemical and food processing plants are also vulnerable to sulfuric acid attacks. By performing immersion tests (chemical resistance method), the durability of these structures can be evaluated.

In order to acquire a better understanding of the pore structure of concrete after sulfuric acid attack, water sorptivity, water porosity and phenolphthalein colour tests were performed on degraded concrete samples. It should be noted that the permeability characteristics of the original sound specimens were also investigated by using water porosity, sorptivity and rapid chloride penetration tests. In addition to all these tests, the durability of concretes to rapid freezing and thawing cycles was also examined. The results of these tests were thoroughly analyzed and discussed in Chapter 4 and the following conclusions are drawn.

5.2 Conclusions

1. The results of the preliminary studies on the resistance of different concrete mixtures to sulfuric acid intrusion indicates that, in terms of weight loss (WL), specimens that contain acrylic latex polymer perform better than other mixtures, which could have resulted from the obstruction by the polymer film on water transport which subsequently slows the ingress of sulfuric acid in concrete. An increase in Xypex content has resulted in the reduction of the WL of concrete samples, which can be attributed to the pore filling effects of Xypex.

2. The WL results of the concrete specimens that contain MK with different replacement levels have shown an improved resistance of these mixtures in comparison to the reference mix against sulfuric acid invasions. For instance the incorporation of 20% MK has resulted in 26.24%, 23.90% and 26.67% reduction of WL with reference to the control mixture after 8 weeks of exposure to 3%, 5% and 7% sulfuric acid solutions, respectively. The pozzolanic reaction, formation of secondary C-S-H, refinement of concrete pore structure and consumption of vulnerable $\text{Ca}(\text{OH})_2$ phases of hydration products are considered to be the reasons behind the enhanced resistance of MK concretes that are subjected to sulfuric acid solutions with three different concentrations.

3. Aside from the economic and environmental advantages of replacing ordinary cement with LF, this mineral additive has the ability to neutralize and reduce the pH of acidic areas close to the surface of concrete samples. Thus, as the results of the WL and SL show, in most cases, the concrete mixtures that contained 10% LF in addition to MK have shown improved resistance against aggressive sulfuric acid solutions. For instance, the incorporation of 10% LF to the M15 mixture has resulted in 10.49%, 15.86% and 10.12% reduction of its WL after 8 weeks of exposure to 3%, 5% and 7% sulfuric acid solutions, respectively.

4. An increase in the MK content and the addition of LF to concrete have resulted in a reduction of SL after 8 weeks of exposure to high concentrations (5% and 7%) of sulfuric acid. In the case of M15/L10 mixture, the SL was reduced by 54.83% and 28.52% with reference to the control mixture after 8 weeks of exposure to 5% and 7% sulfuric acid solutions, respectively. The concrete mixtures with limestone aggregates and LF will experience uniform degradation due to their high acid solubility which will result in the formation of a continuous ITZ that will help to

increase the strength of these samples. The results of the SL have shown some fluctuations (especially in the 3% solution) which can be attributed to several reasons, such as the change in geometry of the specimens after an attack and the formation of a layer of gypsum on the outer surface of the cylinders.

5. The critical effects of acid concentration and the immersion periods are completely obvious by observing the results of visual inspection of the degraded samples. It can be seen that the difference between the behaviour of the specimens and the inferiority of the control mixture is more evident for higher sulfuric acid concentrations of 5% and 7%. As the exposure period increases, the concrete specimens would lose more surface particles and the aggregates become more visible due to the high penetration depth of the sulfuric acid into the concrete matrix. The M15/L10 and M20/L10 mixtures are considered to have the best performance of all the mixtures through a comparison of high resolution images of the degraded samples.

6. The results of the RCPT indicate that the mixtures with MK and LF have significantly less permeability in comparison to the reference mixture. The increase in MK from 15% to 20% has resulted in less chloride penetrability for both 56 and 95 days of curing. Moreover, the addition of LF did not have any considerable effects on the performance of the MK mixtures as only resulted in slight changes in their chloride permeability.

7. According to the visual inspections and weight change measurements, the freezing and thawing resistance of the modified concrete mixtures with MK and LF was better than the control mix. These results can be attributed to sufficient air content and reduced pore size distribution of these concrete mixtures in comparison to the reference mixture.

8. The water sorptivity rate of concrete mixtures that contained supplementary cementing materials was lower than the reference mixture (0.461 mm/ \sqrt{h}). It was found that an increase in the MK content from 15% to 20% would result in reduction of sorptivity rate (from 0.328 mm/ \sqrt{h} to 0.255 mm/ \sqrt{h}). The absorption rate of the M20/L10 mixture was slightly lower than the mixture with only 20% MK as the SCM. However, in general, the addition of 10% LF did not create any particular changes in the behaviours of the MK concretes in this regard.

9. The water porosity results demonstrated that the reference mixture had the lowest average total porosity of all mixes. This result agrees with previous studies on the effects of MK on pore

structure. Even though the incorporation of MK in concrete would result in finer pore size distribution, at the same time, there will be some increase in the total pore volume which is reflected in the results here. It is important to note that the major difference in water porosity percentages was detected between M20 and control mixtures with 14.33% and 13.34% of water porosity, respectively. The little difference between the results indicates that MK and LF are worthy substitutes for Portland cement.

10. The results of the water absorption by total immersion of the conditioned concrete samples followed the results of the water porosity test with less absorption being the main difference between the two tests. The smaller amount of absorption was the consequence of vacuuming in the water porosity test, which in return, would open more pores for water to ingress. It should be noted that there are only marginal differences in the percentage of water absorption of the concrete specimens in this test.

11. The phenolphthalein colour test on degraded samples showed no signs of colourless zones on the surface of the cut samples which indicates no changes in pH of the sound areas. The washing and cleaning of the specimens will result in high removal of loose calcium sulfate components from the surface of the samples. Hence, the thickness of the remaining white layers was not significant enough for detection by the phenolphthalein solution.

12. The water sorptivity on degraded samples showed that the control mixture had the highest sorptivity coefficient of all the degraded specimens, regardless of the exposure periods and concentration of sulfuric acid. It was also noticed that the sorptivity coefficients of the specimens significantly increased at the end of the two weeks of exposure and became more consistent afterwards. This behaviour and other unusual observations in the sorptivity test of the deteriorated concrete samples was most likely due to the diameter change and existence of the gypsum layer on the outer surface of the concrete specimens which can result in some radical changes in the water absorption of the corroded samples.

13. A water porosity test was also performed on the concrete specimens subjected to sulfuric acid solutions with different concentrations. The results of this test did not show any considerable changes in the porosity percentages of the specimens except for slight increases in the final

weeks when exposed to a 7% sulfuric acid solution that could be due to the high loss of materials and severe deterioration of the concrete samples, especially in the case of the control specimens.

14. The results of the water porosity and phenolphthalein tests on degraded samples imply that sulfuric acid penetrates the concrete from the outer surfaces and moves towards the inside by reacting with cement hydration products. Thus, although the concrete is continuously losing its surface particles, as long as the acid has not reached into the deeper areas, the interior remains sound and the concrete maintains its original pore structure.

5.3 Recommendations

Concrete structures of sewage systems are constantly subjected to aggressive environmental conditions and the corrosion of concrete in these environments is caused by a complex process which is a more biological than chemical type of attack. However, in both types of attacks, sulfuric acid is the ultimate responsible element for the deterioration of these types of structures. Hence, in order to gain a more comprehensive understanding of the behaviour of concrete mixtures in terms of resistance to these severe conditions, it is recommended that both chemical and biological sulfuric acid tests are performed.

Various types of SCM, mineral additives and chemical and polymeric admixtures have been used in this study to improve the chemical resistance of concrete against sulfuric acid attack. The incorporation of MK has resulted in significant improvement and its combination with LF also has shown positive results in terms of resistance against different concentrations of sulfuric acids. It is important to note that, the requirement of the Ontario Concrete Pipe Association was that the modified concrete mixes have the maximum of 70% WL of the reference mixture (after exposure to 3%, 5% and 7% solutions) which could not be satisfied. It is recommended to investigate the effect of using MK and LF at higher replacement levels on the performance of concrete exposed to sulfuric acid attack. It is also suggested to study the effect of other kinds of SCMs such as silica fume and fly ash on the concrete performance in these aggressive conditions.

Latex polymer has enhanced the resistance of concrete specimens but due to the low compressive strength of these mixtures, it is not recommended for projects with high strength demands. According to the results of the preliminary studies, Xypex can also be a suitable substitute for Portland cement. However, more investigation in this regard is necessary.

It is generally known that sulfuric acid attacks are most probable in concrete sewer pipes rather than other structures. Thus, it is recommended that for future studies, concrete specimens in the shape of actual sewer pipes, but preferably a smaller size, be produced in the lab. Subsequently, these specimens can be introduced to sulfuric acid solutions with required concentrations. In this way, the final results of the study will better represent actual real life conditions of concrete sanitary infrastructures. Nevertheless, it is clear that more investigation and study of details will be required in this regard.

The chemical sulfuric acid tests in this study have been quite accelerated by using acidic solutions with high concentrations. If time is not a concern, it is recommended that the concentration levels of the sulfuric acid are lowered to around 0.5% or a maximum of 1% to better observe the formation of the white calcium sulfate layer around the samples and monitor the reaction of sulfuric acid and concrete specimens with more precision.

According to the limited number of previous studies, the concrete specimens in sulfuric acids with low concentrations will undergo some initial expansion and also gain weight due to ettringite formation and acid absorption, respectively. It has been observed in this study that the low pH of the sulfuric acid solutions completely governs the attack process and does not allow other reactions to take place. Therefore, in this research, a sulfuric acid invasion has been more of an acid attack than a sulfate attack.

As stated in the literature review and experimental program of this study, there is no standard available for performing the sulfuric acid test and different methods have been used by various researchers to determine the sulfuric acid resistance of concrete, while parameters such as concentration and pH of the acid, washing method and total period of the test can have significant effect on the final results. Hence, a standard guideline specifically dedicated to evaluating the durability of concrete in terms of resistance to sulfuric acid is highly needed and the results of this research and previous studies can be quite helpful to develop it.

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Appendix A

The Results of the Sulfuric Acid Test

1. Weight Loss

Weights Before Immersion (2 weeks)			
Mixes	Sample 1 (kg)	Sample 2 (kg)	Sample 3 (kg)
Control	3.922	3.892	3.913
M 15	3.952	3.914	3.944
M 20	3.978	3.981	3.966
M15/L10	3.922	3.89	3.925
M20/L10	3.94	3.914	3.931

Weights Before Immersion (2 weeks)			
Mixes	Sample 1 (kg)	Sample 2 (kg)	Sample 3 (kg)
Control	3.927	3.903	3.941
M 15	3.982	3.929	3.976
M 20	3.966	3.973	3.963
M15/L10	3.932	3.971	3.919
M20/L10	3.94	3.918	3.922

Weights Before Immersion (2 weeks)			
Mixes	Sample 1 (kg)	Sample 2 (kg)	Sample 3 (kg)
Control	3.931	3.897	3.886
M 15	3.911	3.977	3.954
M 20	3.973	3.961	3.909
M15/L10	3.923	3.947	3.931
M20/L10	3.964	3.915	3.891

Weights after 2 weeks immersion (3% Solution)			
Mixes	Sample 1 (kg)	Sample 2 (kg)	Sample 3 (kg)
Control	3.643	3.614	3.638
M 15	3.714	3.678	3.708
M 20	3.722	3.744	3.685
M15/L10	3.657	3.661	3.665
M20/L10	3.644	3.648	3.62

Weights after 2 weeks immersion (5% Solution)			
Mixes	Sample 1 (kg)	Sample 2 (kg)	Sample 3 (kg)
Control	3.324	3.285	3.338
M 15	3.419	3.37	3.421
M 20	3.447	3.345	3.409
M15/L10	3.439	3.468	3.388
M20/L10	3.43	3.358	3.387

Weights after 2 weeks immersion (7% Solution)			
Mixes	Sample 1 (kg)	Sample 2 (kg)	Sample 3 (kg)
Control	3.222	3.184	3.181
M 15	3.182	3.319	3.276
M 20	3.232	3.267	3.183
M15/L10	3.322	3.305	3.339
M20/L10	3.313	3.334	3.216

Weights Before Immersion (4 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.935	3.902	3.885
M 15	3.977	3.982	3.961
M 20	3.962	3.973	3.944
M15/L10	3.917	3.936	3.912
M20/L10	3.928	3.911	3.904

Weights after 4 weeks immersion (3% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.442	3.454	3.352
M 15	3.508	3.552	3.588
M 20	3.552	3.499	3.494
M15/L10	3.535	3.561	3.49
M20/L10	3.479	3.504	3.529

Weights Before Immersion (4 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.919	3.939	3.932
M 15	3.925	3.968	3.93
M 20	3.957	3.975	3.922
M15/L10	3.981	3.926	3.934
M20/L10	3.931	3.915	3.924

Weights after 4 weeks immersion (5% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	2.955	2.989	2.982
M 15	3.111	3.176	3.062
M 20	3.069	3.1	3.15
M15/L10	3.24	3.29	3.151
M20/L10	3.145	3.182	3.26

Weights Before Immersion (4 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.937	3.932	3.913
M 15	3.963	3.948	3.921
M 20	3.973	3.961	3.959
M15/L10	3.942	3.925	3.923
M20/L10	3.902	3.952	3.927

Weights after 4 weeks immersion (7% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	2.644	2.744	2.635
M 15	2.942	2.882	2.862
M 20	2.902	2.988	2.848
M15/L10	3.035	2.94	3.056
M20/L10	2.981	2.943	2.906

Weights Before Immersion (6 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.943	3.922	3.921
M 15	3.955	3.972	3.916
M 20	3.979	3.988	3.961
M15/L10	3.895	3.951	3.922
M20/L10	3.924	3.928	3.939

Weights after 6 weeks immersion (3% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.298	3.229	3.237
M 15	3.274	3.401	3.331
M 20	3.367	3.373	3.39
M15/L10	3.402	3.334	3.327
M20/L10	3.333	3.379	3.3

Weights Before Immersion (6 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.981	3.917	3.931
M 15	3.938	3.948	3.93
M 20	3.948	3.931	3.974
M15/L10	3.948	3.888	3.925
M20/L10	3.915	3.954	3.937

Weights after 6 weeks immersion (5% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	2.59	2.684	2.652
M 15	2.808	2.986	2.882
M 20	2.856	3.019	3.006
M15/L10	2.929	3.005	2.954
M20/L10	2.951	2.968	2.948

Weights Before Immersion (6 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.936	3.899	3.912
M 15	3.964	3.92	3.947
M 20	3.902	3.982	3.904
M15/L10	3.966	3.914	3.926
M20/L10	3.928	3.912	3.969

Weights after 6 weeks immersion (7% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	2.25	2.267	2.208
M 15	2.71	2.627	2.393
M 20	2.52	2.56	2.703
M15/L10	2.763	2.612	2.761
M20/L10	2.729	2.749	2.77

Weights Before Immersion (8 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.929	3.933	3.938
M 15	3.903	3.946	3.961
M 20	3.922	3.937	3.951
M15/L10	3.91	3.893	3.927
M20/L10	3.936	3.922	3.916

Weights after 8 weeks immersion (3% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.035	3.076	3.094
M 15	3.164	3.226	3.248
M 20	3.276	3.292	3.327
M15/L10	3.274	3.258	3.267
M20/L10	3.265	3.204	3.228

Weights Before Immersion (8 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.924	3.948	3.943
M 15	3.961	3.972	3.952
M 20	3.937	3.939	3.946
M15/L10	3.91	3.923	3.954
M20/L10	3.941	3.942	3.918

Weights after 8 weeks immersion (5% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	2.398	2.318	2.442
M 15	2.643	2.57	2.626
M 20	2.789	2.79	2.697
M15/L10	2.78	2.779	2.852
M20/L10	2.776	2.772	2.774

Weights Before Immersion (8 weeks)			
Mixes	Sample 1	Sample 2	Sample 3
Control	3.955	3.951	3.9
M 15	3.928	3.937	3.919
M 20	3.951	3.914	3.925
M15/L10	3.924	3.92	3.898
M20/L10	3.943	3.954	3.923

Weights after 8 weeks immersion (7% Solution)			
Mixes	Sample 1	Sample 2	Sample 3
Control	1.932	1.851	1.73
M 15	2.328	2.336	2.205
M 20	2.524	2.313	2.345
M15/L10	2.5	2.349	2.491
M20/L10	2.489	2.587	2.451

2. Strength Loss

Strengths after 2 weeks immersion (3% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	35.398	-	278.03	-
M 15	34.44	-	270.51	-
M 20	36.883	47.45	289.7	372.67
M15/L10	43.844	37.232	344.32	292.43
M20/L10	41.203	39.094	323.61	307.01

Strengths after 2 weeks immersion (5% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	34.053	31.585	267.43	248.09
M 15	39.762	33.074	312.27	256.76
M 20	44.168	39.604	346.9	311.02
M15/L10	38.556	37.708	302.79	296.17
M20/L10	30.089	27.055	236.34	212.47

Strengths after 2 weeks immersion (7% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	36.053	35.06	283.15	275.36
M 15	38.797	38.57	304.71	302.93
M 20	35.476	39.535	278.627	310.52
M15/L10	27.503	28.186	216.03	221.38
M20/L10	38.659	37.384	303.64	293.63

Strengths after 4 weeks immersion (3% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	38.576	39.307	302.97	308.74
M 15	46.747	42.686	367.14	335.27
M 20	43.658	41.61	342.87	326.82
M15/L10	44.906	36.149	352.71	283.91
M20/L10	37.846	40.197	297.23	315.7

Strengths after 4 weeks immersion (5% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	34.722	30.516	272.69	289.65
M 15	32.399	34.515	254.44	271.06
M 20	37.88	38.826	297.51	304.93
M15/L10	30.62	34.364	240.5	269.9
M20/L10	39.218	34.129	308	268.05

Strengths after 4 weeks immersion (7% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	16.127	16.637	126.66	130.64
M 15	29.765	33.426	233.75	262.53
M 20	25.814	24.87	202.72	195.33
M15/L10	29.44	33.178	228.84	260.59
M20/L10	34.46	36.48	270.66	286.54

Strengths after 6 weeks immersion (3% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	41.817	35.66	328.44	280.04
M 15	39.631	40.983	311.24	321.86
M 20	45.244	42.211	355.37	331.524
M15/L10	39.935	41.548	313.64	326.33
M20/L10	41.1	42.051	322.82	330.25

Strengths after 8 weeks immersion (3% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	33.316	35.453	261.67	278.46
M 15	38.17	35.832	299.79	281.43
M 20	41.258	40.217	324.04	315.88
M15/L10	29.317	40.914	230.28	321.36
M20/L10	36.915	30.11	289.93	236.48

Strengths after 6 weeks immersion (5% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	29.489	30.261	231.62	237.65
M 15	25.669	27.945	201.63	219.48
M 20	26.462	29.622	346.9	232.65
M15/L10	26.414	30.358	207.44	238.44
M20/L10	33.226	31.48	260.97	247.243

Strengths after 8 weeks immersion (5% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	15.817	10.921	124.24	85.77
M 15	26.428	25.545	207.56	200.64
M 20	30.151	29.634	236.81	232.75
M15/L10	30.468	30.082	239.29	236.27
M20/L10	25.759	25.545	202.35	200.65

Strengths after 6 weeks immersion (7% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	12.19	12.273	95.73	96.37
M 15	14.377	15.603	112.916	122.56
M 20	21.277	16.375	167.09	128.59
M15/L10	32.116	25.691	252.24	201.823
M20/L10	26.504	28.847	218.17	226.563

Strengths after 8 weeks immersion (7% Solution)				
Mixes	Sample 1 Mpa	Sample 2 Mpa	Sample 1 KN	Sample 2 KN
Control	10.825	8.262	85.02	70.05
M 15	6.86	9.839	53.86	77.29
M 20	17.582	15.293	138.07	120.12
M15/L10	19.381	20.402	152.21	160.23
M20/L10	14.851	18.861	116.62	148.15

3. Diameter Change

Diameter of the Specimens after 2 Weeks Immersion in 3% Sulfuric Acid (mm)							Diameter of the Specimens after 4 Weeks Immersion in 3% Sulfuric Acid (mm)					
Mixes	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %
Control	100.86	98.63	100.10	99.40	99.75	-2.21	99.43	99.89	100.09	98.90	99.58	-2.38
M 15	100.90	99.52	99.92	100.09	100.11	-1.86	100.84	99.67	100.03	99.35	99.97	-1.99
M 20	100.09	99.55	100.57	100.37	100.15	-1.82	100.14	100.19	99.78	99.13	99.81	-2.15
M15/L10	100.46	100.51	100.90	100.02	100.47	-1.50	99.49	97.76	100.97	99.81	99.51	-2.44
M20/L10	99.02	100.82	100.80	99.55	100.05	-1.91	99.96	98.27	101.40	98.95	99.65	-2.31

Diameter of the Specimens after 2 Weeks Immersion in 5% Sulfuric Acid (mm)							Diameter of the Specimens after 4 Weeks Immersion in 5% Sulfuric Acid (mm)					
Mixes	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %
Control	95.85	100.80	94.44	89.67	95.19	-6.68	91.88	90.01	94.98	100.05	94.23	-7.62
M 15	98.72	100.59	96.35	98.49	98.54	-3.39	98.68	97.81	89.01	90.46	93.99	-7.85
M 20	93.44	98.79	97.21	100.56	97.50	-4.41	89.01	89.44	98.17	99.92	94.14	-7.71
M15/L10	97.30	98.31	96.22	99.05	97.72	-4.20	99.64	92.28	89.40	98.64	94.99	-6.87
M20/L10	98.28	98.63	95.41	96.21	97.13	-4.77	97.23	91.42	92.15	99.36	95.04	-6.82

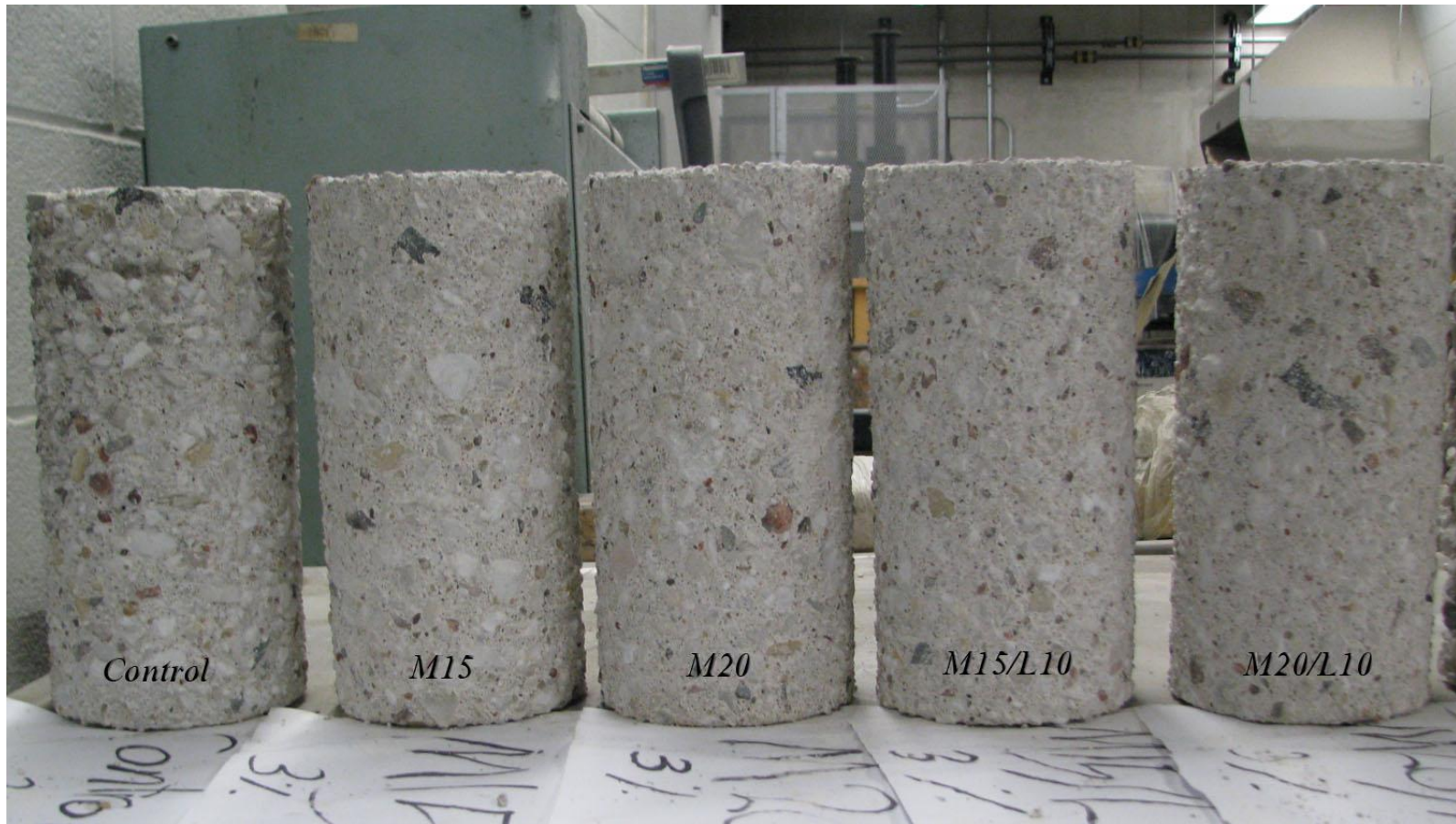
Diameter of the Specimens after 2 Weeks Immersion in 7% Sulfuric Acid (mm)							Diameter of the Specimens after 4 Weeks Immersion in 7% Sulfuric Acid (mm)					
Mixes	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %
Control	92.53	97.59	95.35	95.21	95.17	-6.70	82.76	85.71	95.31	95.91	89.92	-11.84
M 15	98.07	97.92	96.32	100.34	98.16	-3.76	89.48	86.50	98.06	95.29	92.33	-9.48
M 20	98.81	94.26	99.61	96.83	97.38	-4.53	84.76	82.58	98.09	99.97	91.35	-10.44
M15/L10	97.54	97.27	100.09	95.40	97.58	-4.34	86.77	87.76	97.60	97.71	92.46	-9.35
M20/L10	98.46	95.38	94.67	99.02	96.88	-5.02	87.84	86.06	99.98	97.47	92.84	-8.98

Diameter of the Specimens after 6 Weeks Immersion in 3% Sulfuric Acid (mm)							Diameter of the Specimens after 8 Weeks Immersion in 3% Sulfuric Acid (mm)					
Mixes	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %
Control	97.16	90.17	100.04	89.74	94.28	-7.57	100.36	88.95	98.82	87.85	94.00	-7.85
M 15	100.36	92.55	101.15	91.70	96.44	-5.45	100.09	92.25	100.88	91.84	96.27	-5.62
M 20	101.01	94.69	101.49	93.88	97.77	-4.15	101.58	93.54	100.26	92.50	96.97	-4.93
M15/L10	101.33	95.05	101.11	92.99	97.62	-4.29	100.04	92.13	100.53	96.65	97.34	-4.57
M20/L10	100.01	94.40	101.27	94.37	97.51	-4.40	101.70	91.55	101.40	92.04	96.67	-5.22

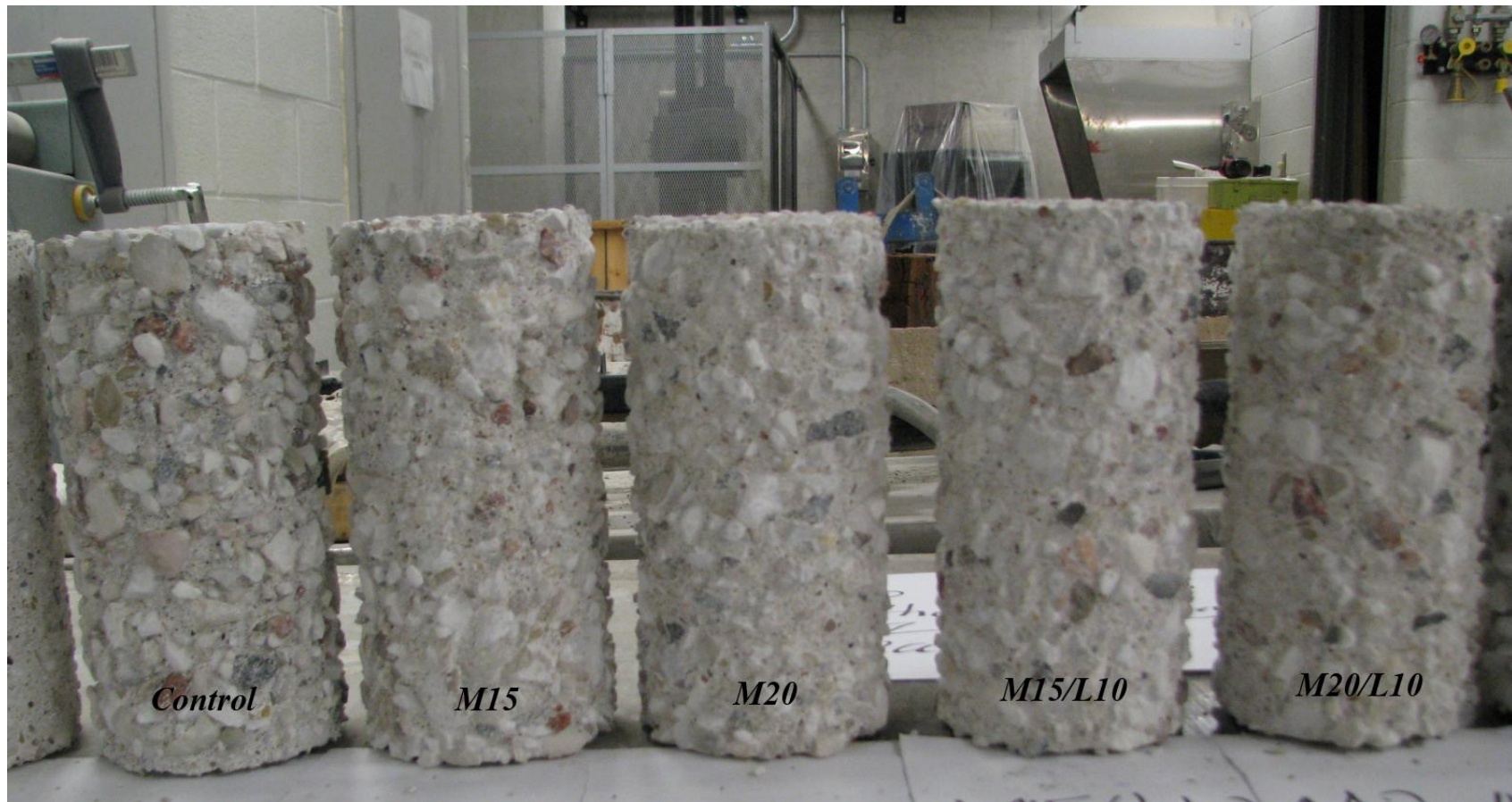
Diameter of the Specimens after 6 Weeks Immersion in 5% Sulfuric Acid (mm)							Diameter of the Specimens after 8 Weeks Immersion in 5% Sulfuric Acid (mm)					
Mixes	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %
Control	99.33	81.30	101.71	79.83	90.54	-11.23	99.13	71.09	95.49	72.68	84.60	-17.06
M 15	101.75	85.43	100.68	82.55	92.60	-9.21	100.24	80.02	96.33	82.78	89.84	-11.92
M 20	100.25	84.49	101.55	87.07	93.34	-8.49	101.90	82.81	98.66	79.47	90.71	-11.07
M15/L10	100.01	84.46	98.82	87.04	92.58	-9.23	95.20	82.83	99.61	84.03	90.42	-11.36
M20/L10	99.04	84.36	100.44	84.33	92.04	-9.76	98.43	82.36	98.03	85.96	91.20	-10.59

Diameter of the Specimens after 6 Weeks Immersion in 7% Sulfuric Acid (mm)							Diameter of the Specimens after 8 Weeks Immersion in 7% Sulfuric Acid (mm)					
Mixes	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %	Diameter 1	Diameter 2	Diameter 3	Diameter 4	Average	Change %
Control	98.48	74.44	93.13	77.87	85.98	-15.71	84.80	71.13	84.05	63.15	75.78	-25.70
M 15	100.62	79.77	97.69	83.58	90.42	-11.36	93.38	74.15	92.43	73.76	83.43	-18.21
M 20	98.97	79.41	97.90	80.96	89.31	-12.44	95.34	77.82	98.07	73.90	86.28	-15.41
M15/L10	100.54	82.42	97.07	84.43	91.12	-10.67	96.15	75.85	73.10	95.93	85.26	-16.41
M20/L10	98.76	83.33	99.69	80.01	90.45	-11.33	96.19	79.19	93.07	76.20	86.16	-15.53

4. Visual Inspection



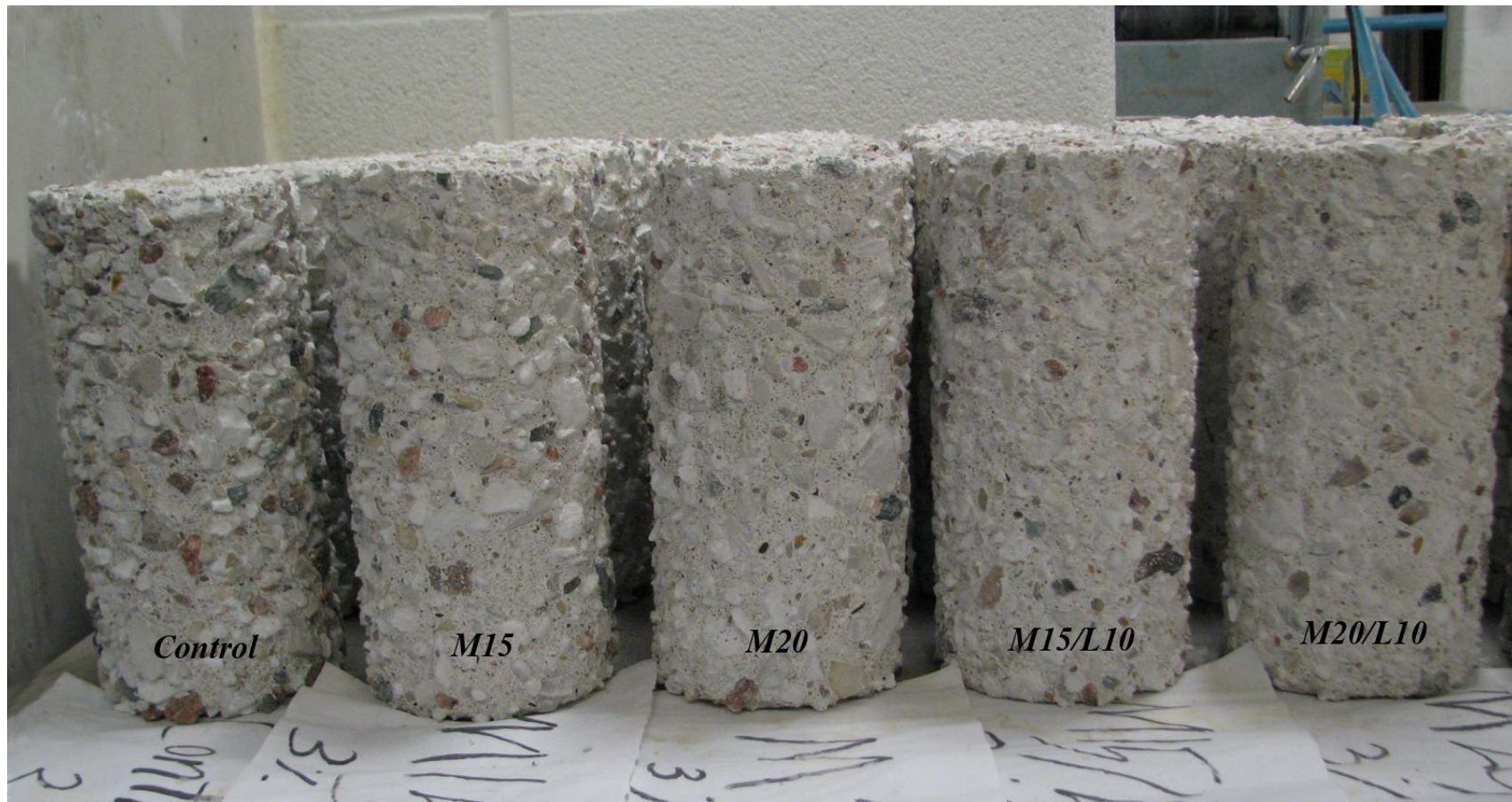
Concrete specimens immersed in 3% sulfuric acid solution for the period of 2 weeks



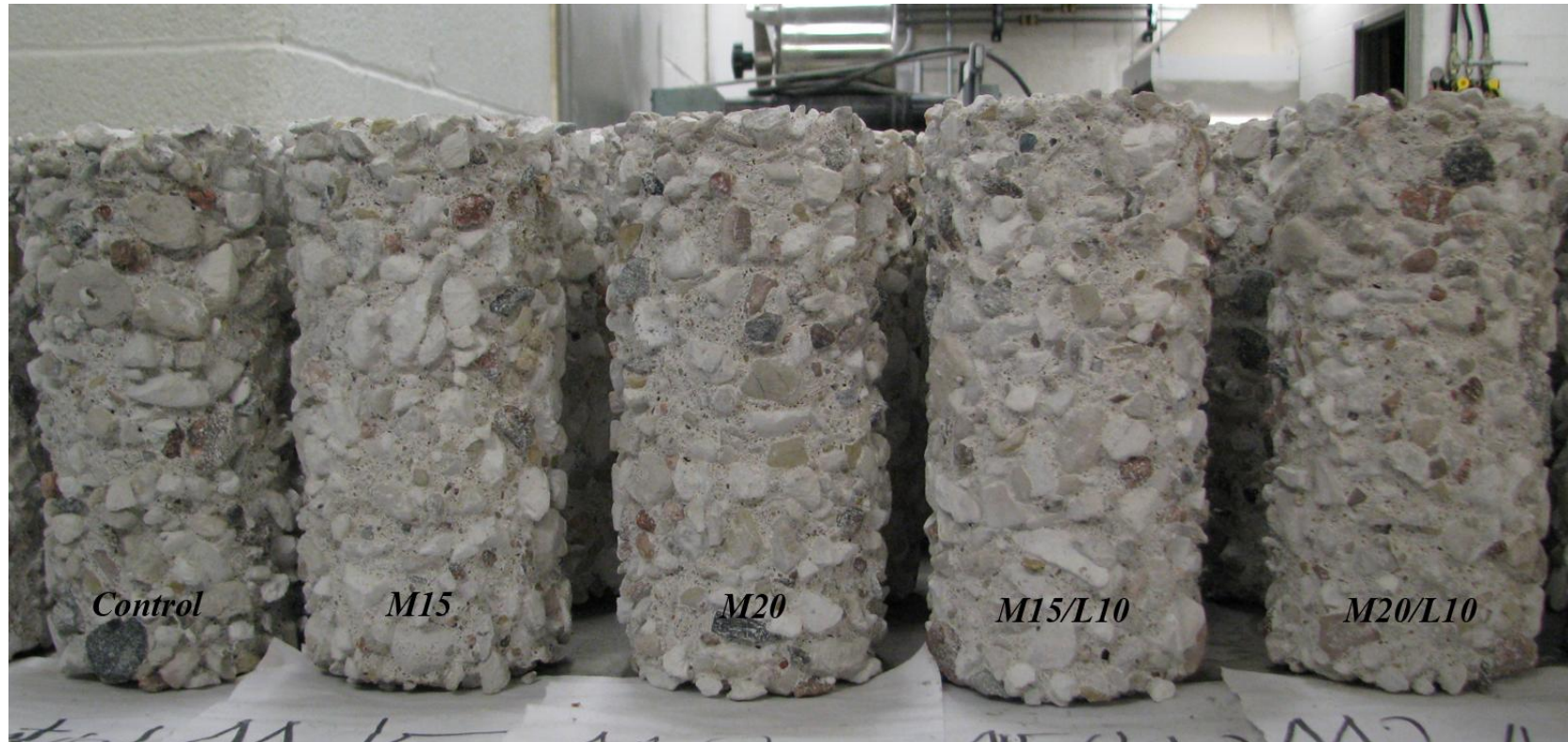
Concrete specimens immersed in 5% sulfuric acid solution for the period of 2 weeks



Concrete specimens immersed in 7% sulfuric acid solution for the period of 2 weeks



Concrete specimens immersed in 3% sulfuric acid solution for the period of 4 weeks



Concrete specimens immersed in 5% sulfuric acid solution for the period of 4 weeks



Concrete specimens immersed in 7% sulfuric acid solution for the period of 4 weeks



Concrete specimens immersed in 3% sulfuric acid solution for the period of 6 weeks



Concrete specimens immersed in 5% sulfuric acid solution for the period of 6 weeks



Concrete specimens immersed in 7% sulfuric acid solution for the period of 6 weeks



Concrete specimens immersed in 3% sulfuric acid solution for the period of 8 weeks



Concrete specimens immersed in 5% sulfuric acid solution for the period of 8 weeks



Concrete specimens immersed in 7% sulfuric acid solution for the period of 8 weeks

Appendix B

RCPT & Water Immersion Tests Results

1. RCPT

RCPT After 56 Days of 100% Humidity Curing			
Mix	C Charges 1	C Charges 2	Average
Control	1949	2148	2049
M15	394	396	395
M20	336	335	336
M15/L10	401	493	447
M20/L10	320	274	297

RCPT After 95 Days of 100% Humidity Curing			
Mix	C Charges 1	C Charges 2	Average
Control	1453	1502	1478
M15	342	341	342
M20	290	297	294
M15/L10	344	348	346
M20/L10	273	231	252

2. Water Absorption by Total Immersion

Weights after Immersion in Water (g)			
Mixes	Sample 1	Sample 2	Sample 3
Control	1011.33	1009.6	1008.44
M15	1020.12	974.3	987.49
M20	985.9	1007.32	1026.45
M15/L10	1005.01	995.92	1007.11
M20/L10	953.57	970.25	960.93

Weights after drying in oven (105c)			
Mixes	Sample 1	Sample 2	Sample 3
Control	951.77	950.79	947.14
M15	958.27	913.83	930.14
M20	926.4	945.1	963.7
M15/L10	942.81	934.49	944.54
M20/L10	893.94	909.25	898.89

Absorption After Immersion in Water (%)				
Mixes	A1	A2	A3	Average
Control	6.26	6.19	6.47	6.31
M15	6.45	6.62	6.17	6.41
M20	6.42	6.58	6.51	6.51
M15/L10	6.60	6.57	6.62	6.60
M20/L10	6.25	6.29	6.29	6.28

Appendix C

Water Sorptivity Measurements of the Original Samples

Mixes	Time	0 min	1 min	5 min	10 min	20 min	30 min	60 min	2 hours	3 hours	4 hours	5 hours	6 hours	1 day	2 days	3 days	4 days	5 days
	hour	0	0.017	0.083	0.167	0.333	0.5	1	2	3	4	5	6	24	48	72	96	120
	√hour	0	0.129	0.289	0.408	0.577	0.707	1	1.414	1.732	2	2.236	2.449	4.899	6.928	8.485	9.798	10.954
	√second	0	7.7	17.3	24.5	34.6	42.4	60	84.9	103.9	120	134.2	147	293.9	415.7	509.1	587.9	657.3
Control	I* Control 1	0	0.122	0.235	0.268	0.318	0.355	0.470	0.647	0.772	0.873	0.956	1.028	1.716	1.912	2.044	2.129	2.192
	I Control 2	0	0.132	0.280	0.313	0.354	0.408	0.547	0.743	0.887	0.993	1.071	1.150	1.813	1.999	2.123	2.203	2.271
	I Control 3	0	0.132	0.225	0.263	0.310	0.359	0.475	0.640	0.750	0.838	0.920	0.991	1.647	1.817	1.926	2.007	2.045
	I Control 4	0	0.099	0.211	0.269	0.321	0.376	0.515	0.713	0.843	0.955	1.029	1.104	1.809	2.006	2.127	2.213	2.279
M15	I M15 1	0	0.089	0.184	0.218	0.255	0.297	0.397	0.520	0.601	0.654	0.694	0.725	0.967	1.010	1.064	1.094	1.120
	I M15 2	0	0.102	0.186	0.220	0.255	0.296	0.388	0.521	0.619	0.668	0.712	0.747	1.021	1.072	1.136	1.180	1.220
	I M15 3	0	0.115	0.202	0.239	0.284	0.330	0.427	0.556	0.634	0.691	0.738	0.778	1.040	1.109	1.174	1.225	1.274
	I M15 4	0	0.084	0.148	0.180	0.217	0.246	0.335	0.449	0.520	0.573	0.614	0.649	0.933	0.999	1.053	1.095	1.130
M20	I M20 1	0	0.082	0.143	0.171	0.198	0.234	0.299	0.379	0.432	0.472	0.503	0.532	0.755	0.810	0.877	0.909	0.955
	I M20 2	0	0.114	0.160	0.193	0.225	0.261	0.343	0.430	0.485	0.523	0.551	0.584	0.778	0.819	0.870	0.908	0.937
	I M20 3	0	0.076	0.127	0.157	0.190	0.224	0.295	0.381	0.430	0.472	0.510	0.535	0.743	0.788	0.840	0.875	0.904
	I M20 4	0	0.075	0.149	0.176	0.218	0.248	0.333	0.433	0.481	0.530	0.547	0.576	0.769	0.805	0.844	0.886	0.911

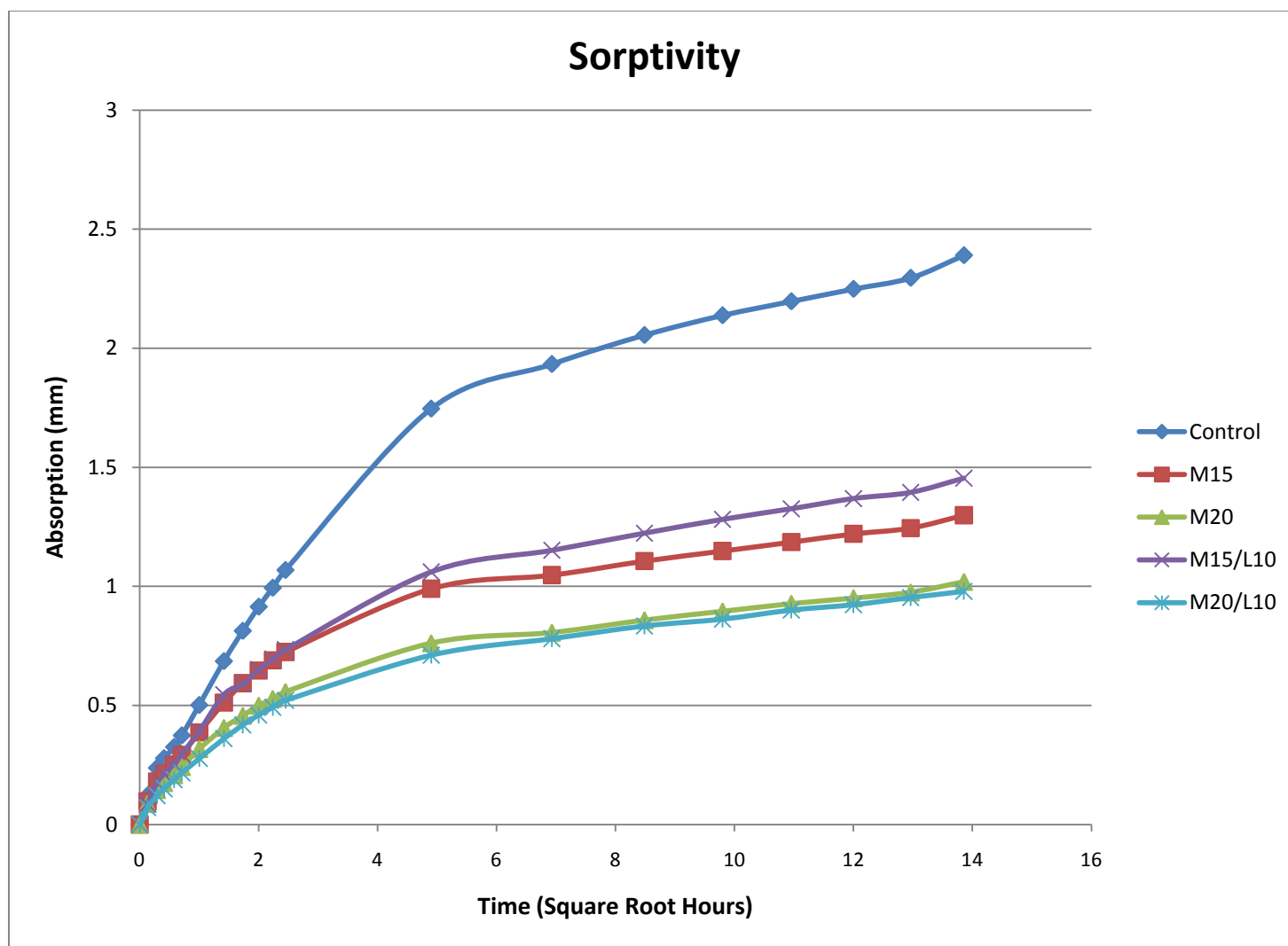
*Letter I represents the Absorption calculated by the following formula: $I = \frac{m_t}{a/d}$ (ASTM C1585)

*I: Absorption, m_t : The change in mass in grams at the time t, a: Exposed area of the specimens (mm^2), d: The density of water in g/mm^3

Mixes	Time	6 days	7 days	7-9 days
	hour	144	168	192
	√hour	12	12.961	13.856
	√second	720	777.7	831.4
Control	I Control 1	2.242	2.300	2.373
	I Control 2	2.322	2.368	2.442
	I Control 3	2.100	2.136	2.290
	I Control 4	2.331	2.378	2.456
M15	I M15 1	1.146	1.165	1.204
	I M15 2	1.256	1.280	1.334
	I M15 3	1.322	1.351	1.417
	I M15 4	1.159	1.183	1.240
M20	I M20 1	0.982	1.006	1.051
	I M20 2	0.962	0.984	1.027
	I M20 3	0.924	0.951	0.993
	I M20 4	0.933	0.957	1.005

Mixes	Time	0 min	1 min	5 min	10 min	20 min	30 min	60 min	2 hours	3 hours	4 hours	5 hours	6 hours	1 day	2 days	3 days	4 days	5 days
	hour	0	0.017	0.083	0.167	0.333	0.5	1	2	3	4	5	6	24	48	72	96	120
	√hour	0	0.129	0.289	0.408	0.577	0.707	1	1.414	1.732	2	2.236	2.449	4.899	6.928	8.485	9.798	10.954
	√second	0	7.7	17.3	24.5	34.6	42.4	60	84.9	103.9	120	134.2	147	293.9	415.7	509.1	587.9	657.3
M15/L10	I M15/L10 1	0	0.081	0.153	0.176	0.213	0.246	0.318	0.423	0.487	0.542	0.584	0.613	0.901	0.977	1.039	1.082	1.119
	I M15/L10 2	0	0.088	0.207	0.247	0.294	0.343	0.455	0.594	0.674	0.734	0.783	0.818	1.095	1.170	1.234	1.280	1.323
	I M15/L10 3	0	0.098	0.191	0.239	0.288	0.332	0.439	0.696	0.657	0.728	0.771	0.824	1.197	1.298	1.383	1.470	1.525
	I M15/L10 4	0	0.081	0.146	0.185	0.224	0.261	0.354	0.468	0.542	0.598	0.641	0.682	1.049	1.160	1.237	1.294	1.338
M20/L10	I M20/L10 1	0	0.078	0.133	0.152	0.190	0.215	0.273	0.356	0.410	0.454	0.485	0.519	0.723	0.795	0.849	0.885	0.918
	I M20/L10 2	0	0.065	0.119	0.141	0.177	0.202	0.261	0.340	0.400	0.438	0.472	0.503	0.689	0.762	0.815	0.841	0.887
	I M20/L10 3	0	0.066	0.115	0.147	0.185	0.214	0.278	0.359	0.415	0.456	0.492	0.508	0.715	0.784	0.846	0.874	0.908
	I M20/L10 4	0	0.073	0.116	0.162	0.202	0.235	0.296	0.387	0.448	0.491	0.520	0.554	0.717	0.780	0.825	0.851	0.889

Mixes	Time	6 days	7 days	7-9 days
	hour	144	168	192
	√hour	12	12.961	13.856
	√second	720	777.7	831.4
M15/L10	I M15/L10 1	1.148	1.170	1.221
	I M15/L10 2	1.354	1.379	1.422
	I M15/L10 3	1.603	1.622	1.693
	I M15/L10 4	1.371	1.407	1.481
M20/L10	I M20/L10 1	0.926	0.971	0.991
	I M20/L10 2	0.909	0.946	0.973
	I M20/L10 3	0.944	0.962	0.989
	I M20/L10 4	0.913	0.934	0.963



Appendix D

Rapid Freezing & Thawing

- **Weight Change**

Control Prisms (kg)			M15 Prisms (kg)		M20 Prisms (kg)		M15/L10 Prisms (kg)		M20/L10 Prisms (kg)	
Cycles	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II	Sample I	Sample II
0	7.637	7.723	7.920	7.643	7.766	7.696	7.517	7.490	7.613	7.640
30	7.639	7.727	7.926	7.644	7.773	7.698	7.519	7.494	7.616	7.645
60	7.644	7.734	7.927	7.647	7.772	7.698	7.521	7.489	7.620	7.645
90	7.650	7.739	7.930	7.650	7.775	7.701	7.526	7.494	7.620	7.644
120	7.659	7.748	7.936	7.657	7.778	7.705	7.532	7.500	7.620	7.641
150	7.660	7.745	7.940	7.658	7.774	7.705	7.531	7.500	7.619	7.641
180	7.662	7.745	7.940	7.657	7.772	7.703	7.530	7.499	7.620	7.642
210	7.663	7.741	7.939	7.657	7.772	7.703	7.529	7.499	7.619	7.639
240	7.663	7.743	7.939	7.655	7.774	7.702	7.529	7.497	7.618	7.637
270	7.656	7.735	7.938	7.654	7.774	7.702	7.527	7.494	7.617	7.637
300	7.649	7.725	7.935	7.653	7.770	7.700	7.527	7.494	7.617	7.637

Appendix E

Water Porosity Test Results

Weights of the Original Cut Cylinders after Conditioning (g)						
Mixes	W Mass	SSD Mass	Dry Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	267.78	464.30	438.60	439.14	13.08	13.34
Control 2	270.66	471.74	444.74	445.42	13.43	
Control 3	236.71	413.44	389.54	390.19	13.52	
M15 1	299.92	517.99	488.24	488.76	13.64	13.82
M15 2	220.55	382.41	359.41	359.87	14.21	
M15 3	298.86	516.80	487.16	487.77	13.60	
M20 1	267.77	461.07	433.96	434.47	14.02	14.33
M20 2	240.02	415.51	390.10	390.62	14.48	
M20 3	247.76	431.66	405.00	405.59	14.50	
M15/L10 1	274.03	476.30	447.27	447.88	14.35	14.07
M15/L10 2	301.92	523.19	492.29	492.97	13.96	
M15/L10 3	288.08	499.10	469.78	470.46	13.89	
M20/L10 1	266.00	464.14	436.30	436.89	14.05	14.11
M20/L10 2	272.73	476.31	447.28	447.96	14.26	
M20/L10 3	269.17	472.79	444.22	444.77	14.03	

Appendix F

Degradation Test Results

1. Water Sorptivity

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 2 Weeks														
Group	vHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
1	I Control 3%	0	0.2367	0.4197	0.5374	0.7217	0.8586	1.1133	1.4997	1.6942	1.8235	1.9297	1.9949	2.4364
	I M15 3%	0	0.1664	0.2871	0.3735	0.4790	0.5590	0.7191	0.9693	1.0913	1.1739	1.2234	1.2679	1.6147
	I M20 3%	0	0.1993	0.3491	0.4443	0.5370	0.6017	0.7236	0.9026	0.9902	1.0866	1.1450	1.1869	1.5398
	I M15/L10 3%	0	0.2220	0.3532	0.4604	0.5500	0.6105	0.7455	0.9473	1.0368	1.1529	1.1983	1.2614	1.6751
	I M20/L10 3%	0	0.1297	0.2188	0.2887	0.3485	0.4147	0.5775	0.8039	0.9196	0.9947	1.0685	1.1193	1.5658
	I Control 5%	0	0.2192	0.3836	0.5241	0.6646	0.8009	1.1354	1.5288	1.7284	1.8042	1.9644	2.0094	2.5012
	I M15 5%	0	0.2426	0.3986	0.5075	0.6242	0.7291	0.9048	1.1264	1.2352	1.2942	1.3585	1.3716	1.6705
	I M20 5%	0	0.2317	0.3764	0.5036	0.6108	0.6844	0.8505	1.0206	1.1398	1.1894	1.2523	1.2670	1.5604
	I M15/L10 5%	0	0.2373	0.4440	0.5653	0.7000	0.7787	0.9587	1.1813	1.2920	1.3800	1.4467	1.5013	1.9934
	I M20/L10 5%	0	0.2456	0.4022	0.4697	0.5938	0.7058	0.9596	1.2092	1.3725	1.4778	1.5966	1.6317	2.1418
	I Control 7%	0	0.2882	0.4976	0.6031	0.7999	0.9053	1.2033	1.6040	1.8387	1.9526	2.0932	2.1410	2.7736
	I M15 7%	0	0.2762	0.4440	0.5352	0.6673	0.7585	0.9435	1.2567	1.3531	1.5619	1.6108	1.6438	2.7327
	I M20 7%	0	0.2697	0.4118	0.4762	0.6130	0.6906	0.8209	0.9774	1.1669	1.2182	1.2826	1.3050	1.5878
	I M15/L10 7%	0	0.2193	0.3717	0.4573	0.5736	0.6739	0.8237	1.0483	1.2155	1.2877	1.3385	1.3960	1.7236
	I M20/L10 7%	0	0.2048	0.3541	0.4110	0.5196	0.6132	0.7800	0.9822	1.0866	1.1382	1.2399	1.2901	1.6862

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 2 Weeks														
Group	vHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
2	I Control 3%	0	0.1740	0.3276	0.4415	0.6104	0.7767	1.0864	1.4741	1.7672	1.9476	2.1267	2.3008	2.9495
	I M15 3%	0	0.1639	0.3024	0.3926	0.5133	0.6009	0.8144	1.1421	1.3784	1.5410	1.7049	1.8167	2.4672
	I M20 3%	0	0.2526	0.3910	0.4722	0.5662	0.6144	0.7528	0.9241	1.0600	1.1590	1.2593	1.3380	1.7645
	I M15/L10 3%	0	0.3368	0.4881	0.6193	0.7064	0.7606	0.9536	1.2336	1.4531	1.5969	1.7533	1.8466	2.4332
	I M20/L10 3%	0	0.1132	0.2035	0.2824	0.4096	0.4884	0.6907	0.9451	1.1397	1.2809	1.3953	1.5442	2.0326
	I Control 5%	0	0.2052	0.3667	0.4890	0.6534	0.7939	1.1101	1.5401	1.8604	2.0909	2.3270	2.5307	3.4413
	I M15 5%	0	0.2032	0.3580	0.4681	0.6451	0.7854	1.0752	1.4909	1.7636	1.9747	2.1295	2.3275	2.9490
	I M20 5%	0	0.2746	0.4474	0.5357	0.7018	0.8197	1.0969	1.3554	1.5202	1.6555	1.7599	1.8818	2.3935
	I M15/L10 5%	0	0.2067	0.3280	0.4253	0.5680	0.6760	0.9587	1.3440	1.6454	1.8894	2.0894	2.2707	2.9387
	I M20/L10 5%	0	0.2132	0.3603	0.4710	0.6316	0.7261	0.8880	1.0797	1.2214	1.3482	1.4184	1.5372	1.9745
	I Control 7%	0	0.2179	0.3739	0.4850	0.6958	0.8322	1.1344	1.5688	1.8345	2.1185	2.3012	2.4840	3.2079
	I M15 7%	0	0.2603	0.4030	0.5035	0.6422	0.7783	1.0149	1.3095	1.5011	1.6333	1.7509	1.8711	2.4460
	I M20 7%	0	0.1921	0.3105	0.3947	0.5038	0.6170	0.8301	1.1366	1.3050	1.4273	1.5378	1.6220	2.1443
	I M15/L10 7%	0	0.2006	0.3330	0.4399	0.5656	0.7020	0.9320	1.2556	1.5057	1.6528	1.7691	1.8975	2.5085
	I M20/L10 7%	0	0.2008	0.3378	0.4436	0.5806	0.7231	0.9550	1.2562	1.4624	1.5845	1.7147	1.8178	2.4106

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 4 Weeks														
Group	VHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
1	I Control 3%	0	0.2042	0.3672	0.4635	0.6292	0.8064	1.0015	1.3289	1.6243	1.8104	1.9350	1.9607	2.5282
	I M15 3%	0	0.2319	0.3924	0.4905	0.6230	0.7122	0.9198	1.3428	1.5186	1.6027	1.7543	1.8180	2.2575
	I M20 3%	0	0.2825	0.4256	0.5253	0.6748	0.7771	0.9816	1.3228	1.5030	1.6283	1.7408	1.8111	2.2699
	I M15/L10 3%	0	0.3137	0.4642	0.5696	0.7111	0.8216	1.0402	1.3861	1.4915	1.6600	1.8117	1.9133	2.2425
	I M20/L10 3%	0	0.1834	0.2988	0.3795	0.4988	0.6270	0.8514	1.2271	1.5297	1.7399	1.8656	1.9566	2.5503
	I Control 5%	0	0.2538	0.4230	0.5549	0.6983	0.8389	1.1414	1.5544	1.9659	2.1710	2.3703	2.4692	3.1504
	I M15 5%	0	0.4338	0.5679	0.6716	0.8331	0.9426	1.1977	1.4629	1.7166	1.8117	1.8765	1.9414	2.4271
	I M20 5%	0	0.3520	0.5215	0.6839	0.8405	0.9884	1.2600	1.5071	1.7398	1.8619	1.9941	2.0415	2.4955
	I M15/L10 5%	0	0.2159	0.3796	0.4812	0.6096	0.7408	0.9906	1.4069	1.6848	1.8711	1.9431	1.9925	2.5654
	I M20/L10 5%	0	0.2481	0.3792	0.4722	0.6118	0.7231	0.9614	1.3997	1.6253	1.7691	1.8085	1.8931	2.4513
	I Control 7%	0	0.2598	0.4315	0.5354	0.6866	0.8173	1.1007	1.5873	1.9652	2.2203	2.3778	2.5006	3.2439
	I M15 7%	0	0.3734	0.5452	0.6736	0.8424	0.9828	1.2367	1.7355	1.9864	2.1373	2.2448	2.3374	2.9125
	I M20 7%	0	0.2289	0.3433	0.4211	0.5523	0.6546	0.8758	1.2756	1.4800	1.6051	1.6128	1.7058	2.1681
	I M15/L10 7%	0	0.2830	0.4185	0.4721	0.6300	0.7760	1.0396	1.4521	1.7604	1.9153	1.9585	2.0806	2.6749
	I M20/L10 7%	0	0.2689	0.3870	0.4373	0.5953	0.7194	1.0001	1.4255	1.6072	1.7712	1.7800	1.9100	2.4049

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 4 Weeks														
Group	VHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
2	I Control 3%	0	0.2042	0.3672	0.4635	0.6292	0.8064	1.0015	1.3289	1.6243	1.8104	1.9350	1.9607	2.5282
	I M15 3%	0	0.2306	0.4013	0.5262	0.6829	0.7083	1.0281	1.1581	1.2218	1.3874	1.4995	1.5314	2.0817
	I M20 3%	0	0.2326	0.3745	0.4985	0.6608	0.7387	0.9522	1.0889	1.2104	1.2794	1.3752	1.4557	1.8136
	I M15/L10 3%	0	0.2893	0.4243	0.5542	0.6686	0.7483	0.9862	1.1187	1.3257	1.4041	1.5275	1.6536	2.3106
	I M20/L10 3%	0	0.3770	0.5488	0.6603	0.7629	0.8770	1.1963	1.3514	1.5002	1.6194	1.7028	1.8361	2.3900
	I Control 5%	0	0.2782	0.4546	0.5764	0.7485	0.8948	1.3422	1.7222	1.9788	2.1681	2.3560	2.4922	3.2565
	I M15 5%	0	0.2724	0.4454	0.5592	0.7235	0.8230	1.1256	1.3101	1.4254	1.4759	1.6517	1.7151	2.2599
	I M20 5%	0	0.3003	0.4870	0.5977	0.7298	0.8318	1.0775	1.2715	1.3979	1.4870	1.5674	1.6939	2.1392
	I M15/L10 5%	0	0.3344	0.4967	0.5856	0.7422	0.8608	1.2389	1.4097	1.6397	1.6961	1.7314	1.9769	2.4242
	I M20/L10 5%	0	0.2918	0.4708	0.5737	0.7161	0.8599	1.1390	1.3264	1.5322	1.5943	1.7676	1.7493	2.3498
	I Control 7%	0	0.3134	0.5433	0.6724	0.8724	1.0488	1.5385	1.8392	2.1274	2.3148	2.5368	2.5809	3.4517
	I M15 7%	0	0.3420	0.5661	0.7109	0.8902	0.9902	1.2860	1.5085	1.7370	1.8431	2.0193	2.0731	2.5674
	I M20 7%	0	0.3875	0.5447	0.6271	0.7843	0.9063	1.2267	1.4449	1.5517	1.6555	1.8157	1.9057	2.4123
	I M15/L10 7%	0	0.3143	0.4989	0.5987	0.7670	0.8623	1.1706	1.2928	1.4953	1.6592	1.7813	1.8572	2.4098
	I M20/L10 7%	0	0.3412	0.4978	0.5983	0.7652	0.8819	1.2024	1.3561	1.5274	1.6766	1.7830	1.8834	2.3561

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 6 Weeks														
Group	VHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
1	I Control 3%	0	0.2349	0.4555	0.6016	0.7492	0.8781	1.2247	1.5843	1.8192	1.8722	1.9424	2.0598	2.7345
	I M15 3%	0	0.2259	0.3819	0.4983	0.6420	0.7420	0.9843	1.1937	1.3567	1.4155	1.4539	1.5086	1.9754
	I M20 3%	0	0.2144	0.4222	0.5275	0.6913	0.7686	0.9670	1.2054	1.3120	1.3666	1.4199	1.5225	1.9900
	I M15/L10 3%	0	0.2378	0.4690	0.5692	0.6974	0.7656	1.0475	1.2265	1.3855	1.4336	1.4764	1.5792	2.0616
	I M20/L10 3%	0	0.2317	0.3602	0.4540	0.5517	0.6387	0.8892	1.0753	1.2012	1.2333	1.2949	1.3699	1.8828
	I Control 5%	0	0.2951	0.4908	0.6104	0.7906	0.9117	1.2705	1.5843	1.8390	1.9337	2.0518	2.1341	2.8175
	I M15 5%	0	0.3282	0.4544	0.5598	0.7172	0.7989	1.1730	1.2681	1.4433	1.4700	1.5398	1.5844	1.9704
	I M20 5%	0	0.3390	0.4969	0.6021	0.7322	0.7965	1.0844	1.2217	1.3606	1.4410	1.4570	1.5184	1.9627
	I M15/L10 5%	0	0.2035	0.3328	0.4486	0.5853	0.6759	1.0131	1.3310	1.5286	1.5940	1.7306	1.8257	2.4229
	I M20/L10 5%	0	0.2660	0.4163	0.5321	0.6824	0.7876	1.1438	1.3166	1.4624	1.5225	1.6157	1.6969	2.2650
	I Control 7%	0	0.2894	0.4375	0.5787	0.7664	0.8681	1.3503	1.7085	2.0082	2.1908	2.2838	2.3975	3.1329
	I M15 7%	0	0.2663	0.3722	0.4797	0.6401	0.7226	1.0886	1.2303	1.3658	1.4109	1.4359	1.5511	1.8937
	I M20 7%	0	0.3336	0.4789	0.5667	0.7167	0.8141	1.0807	1.1844	1.3329	1.3026	1.3377	1.3760	1.7256
	I M15/L10 7%	0	0.3588	0.4861	0.5996	0.8542	0.9324	1.2207	1.4016	1.6286	1.6577	1.7206	1.7681	2.3554
	I M20/L10 7%	0	0.2988	0.4280	0.5089	0.7034	0.7828	1.0879	1.3431	1.5034	1.5314	1.6170	1.6964	2.2738

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 6 Weeks														
Group	VHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
2	I Control 3%	0	0.2507	0.3151	0.4326	0.5644	0.6589	0.9010	1.3422	1.6416	1.8421	2.0441	2.1400	2.9909
	I M15 3%	0	0.2492	0.4052	0.5243	0.6516	0.7516	1.1253	1.4703	1.7537	1.8522	1.9084	1.9590	2.5778
	I M20 3%	0	0.2970	0.4142	0.5381	0.6553	0.7512	0.9311	1.3693	1.6743	1.7662	1.8288	1.9074	2.4762
	I M15/L10 3%	0	0.4102	0.5384	0.6720	0.8083	0.8978	1.0929	1.6487	1.8024	1.9012	2.0242	2.1043	2.6401
	I M20/L10 3%	0	0.2156	0.3334	0.4593	0.5544	0.6481	0.8664	1.2815	1.5534	1.7716	1.9256	2.0301	2.8201
	I Control 5%	0	0.3060	0.4427	0.6026	0.7300	0.8620	1.1913	1.6138	1.9244	2.1559	2.2630	2.3640	3.2338
	I M15 5%	0	0.3207	0.4529	0.5672	0.7172	0.8360	1.1018	1.5457	1.7328	1.9244	1.9957	2.0254	2.6045
	I M20 5%	0	0.3303	0.4983	0.5992	0.6956	0.8082	1.0040	1.3781	1.5739	1.6631	1.7566	1.8472	2.2886
	I M15/L10 5%	0	0.2555	0.4130	0.5199	0.6774	0.7933	1.0473	1.4647	1.7202	1.8658	1.8985	1.9564	2.5075
	I M20/L10 5%	0	0.2886	0.4434	0.6854	0.7921	0.9334	1.1558	1.5571	1.6788	1.8126	1.8893	1.9449	2.5190
	I Control 7%	0	0.3255	0.5356	0.6579	0.8267	0.9731	1.2556	1.7998	1.9652	2.0875	2.1391	2.1822	2.7884
	I M15 7%	0	0.2601	0.4516	0.5684	0.7148	0.8332	1.0512	1.3159	1.6041	1.6663	1.7115	1.7769	2.1522
	I M20 7%	0	0.3240	0.4805	0.5890	0.7534	0.8907	1.1605	1.6043	1.8485	2.0273	2.0608	2.1406	2.6993
	I M15/L10 7%	0	0.3481	0.4340	0.5367	0.6579	0.7944	1.0964	1.5289	1.7789	1.9184	1.9981	2.0672	2.7097
	I M20/L10 7%	0	0.2428	0.4949	0.5727	0.7159	0.8388	1.0723	1.4038	1.5890	1.7477	1.7975	1.8816	2.3936

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 8 Weeks														
Group	VHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
1	I Control 3%	0	0.2493	0.4208	0.5375	0.7695	0.9784	1.2551	1.5534	1.7854	1.9367	2.0923	2.1802	2.9309
	I M15 3%	0	0.2651	0.4355	0.5372	0.7515	0.9163	1.1540	1.3024	1.4329	1.5318	1.5936	1.6678	2.1308
	I M20 3%	0	0.2640	0.3954	0.4807	0.6418	0.8463	1.0467	1.0954	1.2200	1.2958	1.3635	1.4177	1.9390
	I M15/L10 3%	0	0.3695	0.5120	0.5845	0.8170	1.0092	1.0737	1.2403	1.3236	1.4352	1.5333	1.5776	2.2562
	I M20/L10 3%	0	0.2262	0.3256	0.4033	0.5777	0.7221	0.8829	1.0518	1.1499	1.2385	1.3161	1.3679	1.7889
	I Control 5%	0	0.3629	0.5284	0.6369	0.8806	1.0798	1.4072	1.7558	2.0156	2.1792	2.3269	2.4657	3.4121
	I M15 5%	0	0.3297	0.4512	0.5474	0.7367	0.8897	1.0932	1.3125	1.4466	1.5097	1.5964	1.6658	2.3836
	I M20 5%	0	0.3605	0.4998	0.6236	0.8557	1.0213	1.1404	1.2333	1.3075	1.3818	1.4484	1.4839	2.1045
	I M15/L10 5%	0	0.2710	0.4018	0.4874	0.6821	0.8332	1.0076	1.2085	1.3237	1.4094	1.5122	1.5558	2.2535
	I M20/L10 5%	0	0.3031	0.4347	0.5281	0.6919	0.8220	0.9966	1.1680	1.2813	1.3854	1.4573	1.5094	1.9824
	I Control 7%	0	0.4900	0.7383	0.9246	1.2971	1.5166	1.8979	2.1884	2.4189	2.6517	2.8291	2.9045	3.8734
	I M15 7%	0	0.4738	0.6457	0.7573	0.9878	1.1195	1.2750	1.3847	1.5329	1.6280	1.7634	1.7890	2.4127
	I M20 7%	0	0.3523	0.4823	0.5935	0.7885	0.9339	1.1579	1.3786	1.4760	1.5735	1.6402	1.7052	1.9840
	I M15/L10 7%	0	0.2819	0.4132	0.5095	0.6915	0.8228	1.0837	1.3235	1.4443	1.5704	1.6492	1.7157	2.4072
	I M20/L10 7%	0	0.3139	0.4374	0.5523	0.7581	0.8867	1.0891	1.2503	1.3738	1.5025	1.5762	1.6259	2.0770

Sorptivity of Specimens Subjected to Sulfuric Acid Attack with Different Concentrations for 8 Weeks														
Group	VHour	0	0.1291	0.2887	0.4082	0.5774	0.7071	1	1.4142	1.7321	2	2.2361	2.4495	4.8990
2	I Control 3%	0	0.2349	0.3905	0.4928	0.6888	0.8329	1.1268	1.5231	1.7652	1.9136	2.0375	2.1456	2.9036
	I M15 3%	0	0.2308	0.3792	0.4877	0.6828	0.8147	1.0207	1.3353	1.5387	1.6939	1.8354	1.9165	2.5416
	I M20 3%	0	0.3331	0.4942	0.6147	0.8449	0.9871	1.1943	1.5572	1.7725	1.9634	2.1150	2.1800	2.7717
	I M15/L10 3%	0	0.2499	0.4058	0.4932	0.6719	0.8170	1.0280	1.3518	1.6085	1.7899	1.9216	2.0210	2.6378
	I M20/L10 3%	0	0.2207	0.3420	0.4319	0.5859	0.7085	0.9456	1.2739	1.4974	1.6881	1.8366	1.9688	2.7808
	I Control 5%	0	0.3771	0.5639	0.7205	0.9802	1.1208	1.4125	1.7843	2.1099	2.3927	2.6009	2.7788	3.6505
	I M15 5%	0	0.2745	0.4117	0.5237	0.7272	0.8850	1.1216	1.4623	1.7132	1.8772	1.9671	2.0681	2.5745
	I M20 5%	0	0.3033	0.4193	0.5014	0.6685	0.8387	1.0770	1.4406	1.6990	1.8832	1.9745	2.0689	2.6538
	I M15/L10 5%	0	0.3146	0.4641	0.5918	0.7662	0.8830	1.1431	1.5324	1.8127	2.0152	2.1912	2.2971	3.0493
	I M20/L10 5%	0	0.3184	0.4455	0.5649	0.7654	0.9215	1.2047	1.5920	1.8967	2.1523	2.2962	2.4355	3.2009
	I Control 7%	0	0.3814	0.5831	0.7583	1.0022	1.2505	1.5964	2.1307	2.4478	2.7648	3.0287	3.2171	3.9665
	I M15 7%	0	0.4335	0.6073	0.7390	1.0042	1.1853	1.4890	1.9371	2.1731	2.3871	2.5115	2.6249	3.2963
	I M20 7%	0	0.3352	0.4721	0.5747	0.7628	0.8962	1.1545	1.4436	1.6266	1.6471	1.7429	1.8198	2.2474
	I M15/L10 7%	0	0.3852	0.6005	0.7108	0.9611	1.1555	1.3988	1.7472	2.0221	2.1166	2.2199	2.3232	3.0165
	I M20/L10 7%	0	0.3756	0.4957	0.5814	0.7444	0.8884	1.1148	1.4750	1.7323	1.9295	2.0719	2.1628	2.8111

Initial Absorption Rate of Degraded Specimens (mm/vhour)					Initial Absorption Rate of Degraded Specimens (mm/vhour)				
Mix	Exposure Period	SA Concentration	Coefficients	R ²	Mix	Exposure Period	SA Concentration	Coefficients	R ²
Control	2 Weeks	3%	0.8743	0.9883	Control	4 Weeks	3%	0.8126	0.987
M15	2 Weeks	3%	0.6204	0.9898	M15	4 Weeks	3%	0.6548	0.9717
M20	2 Weeks	3%	0.4617	0.958	M20	4 Weeks	3%	0.6237	0.9652
M15/L10	2 Weeks	3%	0.576	0.9714	M15/L10	4 Weeks	3%	0.6632	0.9729
M20/L10	2 Weeks	3%	0.5387	0.9947	M20/L10	4 Weeks	3%	0.7383	0.9851
Control	2 Weeks	5%	0.9245	0.9923	Control	4 Weeks	5%	1.0089	0.9929
M15	2 Weeks	5%	0.7327	0.9828	M15	4 Weeks	5%	0.6876	0.9532
M20	2 Weeks	5%	0.5996	0.9575	M20	4 Weeks	5%	0.6996	0.955
M15/L10	2 Weeks	5%	0.7384	0.9891	M15/L10	4 Weeks	5%	0.7814	0.9777
M20/L10	2 Weeks	5%	0.6106	0.9711	M20/L10	4 Weeks	5%	0.7313	0.9726
Control	2 Weeks	7%	0.9315	0.9899	Control	4 Weeks	7%	1.0351	0.9903
M15	2 Weeks	7%	0.6833	0.9759	M15	4 Weeks	7%	0.853	0.9708
M20	2 Weeks	7%	0.5695	0.9737	M20	4 Weeks	7%	0.701	0.9702
M15/L10	2 Weeks	7%	0.6508	0.9819	M15/L10	4 Weeks	7%	0.7725	0.9798
M20/L10	2 Weeks	7%	0.6091	0.9776	M20/L10	4 Weeks	7%	0.7408	0.9738

Initial Absorption Rate of Degraded Specimens (mm/vhour)					Initial Absorption Rate of Degraded Specimens (mm/vhour)				
Mix	Exposure Period	SA Concentration	Coefficient	R ²	Mix	Exposure Period	SA Concentration	Coefficient	R ²
Control	6 Weeks	3%	0.8524	0.9879	Control	8 Weeks	3%	0.8739	0.9811
M15	6 Weeks	3%	0.7036	0.9634	M15	8 Weeks	3%	0.697	0.9631
M20	6 Weeks	3%	0.6704	0.9677	M20	8 Weeks	3%	0.688	0.9537
M15/L10	6 Weeks	3%	0.7026	0.9592	M15/L10	8 Weeks	3%	0.6796	0.963
M20/L10	6 Weeks	3%	0.6752	0.9871	M20/L10	8 Weeks	3%	0.6548	0.9817
Control	6 Weeks	5%	0.9045	0.9821	Control	8 Weeks	5%	1.0161	0.9841
M15	6 Weeks	5%	0.7122	0.959	M15	8 Weeks	5%	0.726	0.9656
M20	6 Weeks	5%	0.6315	0.9516	M20	8 Weeks	5%	0.6734	0.952
M15/L10	6 Weeks	5%	0.7751	0.9787	M15/L10	8 Weeks	5%	0.7492	0.9772
M20/L10	6 Weeks	5%	0.7101	0.9531	M20/L10	8 Weeks	5%	0.7645	0.9785
Control	6 Weeks	7%	0.9364	0.9725	Control	8 Weeks	7%	1.1878	0.9758
M15	6 Weeks	7%	0.6485	0.9517	M15	8 Weeks	7%	0.8175	0.9488
M20	6 Weeks	7%	0.6839	0.9489	M20	8 Weeks	7%	0.6672	0.9394
M15/L10	6 Weeks	7%	0.7571	0.963	M15/L10	8 Weeks	7%	0.7799	0.9579
M20/L10	6 Weeks	7%	0.6983	0.9618	M20/L10	8 Weeks	7%	0.7239	0.9703

2. Water Porosity

Weights after 2 weeks immersion in 3% sulfuric acid solution						Weights after 2 weeks immersion in 5% sulfuric acid solution					
Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)	Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	260.24	446.62	420.7	13.91	13.59	Control 1	248.49	424.82	402.23	12.81	12.63
Control 2	265.34	453.45	428.47	13.28		Control 2	259.69	444.08	421.12	12.45	
M15 1	278.07	478.54	450.18	14.15	13.89	M15 1	224.65	386.92	364.03	14.11	14.11
M15 2	262.06	448.41	423	13.64		M15 2	233.35	403.27	379.28	14.12	
M20 1	285.41	491.07	462.22	14.03	14.09	M20 1	286.74	496	467.72	13.51	13.65
M20 2	257.25	442.43	416.21	14.16		M20 2	208.09	359.81	338.89	13.79	
M15/L10 1	248.22	430.39	405.28	13.78	13.74	M15/L10 1	262.24	453.71	427.24	13.82	13.86
M15/L10 2	265.09	461.44	434.56	13.69		M15/L10 2	240.17	414.73	390.46	13.90	
M20/L10 1	248.84	433.14	405.58	14.95	14.46	M20/L10 1	271.35	464.62	438.77	13.38	13.55
M20/L10 2	235.34	408.88	384.65	13.96		M20/L10 2	262.33	450.94	425.07	13.72	

Weights after 2 weeks immersion in 7% sulfuric acid solution						Weights after 4 weeks immersion in 3% sulfuric acid solution					
Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)	Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	233.91	400.08	378.29	13.11	13.53	Control 1	258.77	444.50	419.63	13.39	13.25
Control 2	224.32	387.1	364.41	13.94		Control 2	246.52	422.44	399.37	13.11	
M15 1	237.56	406.18	383.4	13.51	13.54	M15 1	255.69	440.45	415.40	13.56	13.56
M15 2	247.45	423.9	399.97	13.56		M15 2	259.96	447.80	422.31	13.57	
M20 1	233.6	404.03	380.85	13.60	13.54	M20 1	263.38	453.31	426.44	14.15	14.22
M20 2	223.42	384.8	363.05	13.48		M20 2	244.42	422.57	397.11	14.29	
M15/L10 1	236.36	408.19	383.76	14.22	14.10	M15/L10 1	238.20	412.61	388.45	13.85	14.25
M15/L10 2	240.89	415.05	390.71	13.98		M15/L10 2	255.27	443.95	416.31	14.65	
M20/L10 1	270.07	463.33	437.13	13.56	14.07	M20/L10 1	265.46	459.96	431.90	14.43	14.49
M20/L10 2	210.79	365.5	342.93	14.59		M20/L10 2	233.77	406.42	381.28	14.56	

Weights after 4 weeks immersion in 5% sulfuric acid solution						Weights after 4 weeks immersion in 7% sulfuric acid solution					
Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)	Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	225.41	386.85	365.99	12.92	12.99	Control 1	170.79	294.91	277.85	13.74	13.61
Control 2	228.89	393.33	371.84	13.07		Control 2	215.51	372.73	351.53	13.48	
M15 1	236.67	406.1	383.46	13.36	13.76	M15 1	236.32	405.41	382.66	13.45	13.83
M15 2	242.48	419.27	394.25	14.15		M15 2	205.74	351.36	330.68	14.20	
M20 1	207.72	359.16	338.56	13.60	13.64	M20 1	214.64	368.3	348.4	12.95	13.83
M20 2	239.56	413.24	389.47	13.69		M20 2	191.84	333.2	312.42	14.70	
M15/L10 1	256.84	441.78	416.42	13.71	13.86	M15/L10 1	191.85	328.15	310.03	13.29	13.94
M15/L10 2	224.71	384.34	361.99	14.00		M15/L10 2	221.81	385.29	361.44	14.59	
M20/L10 1	216.06	376.45	354.72	13.55	13.81	M20/L10 1	225.45	390.55	366.18	14.76	14.32
M20/L10 2	257.07	446.68	420.01	14.07		M20/L10 2	239	414.47	390.12	13.88	

Weights after 6 weeks immersion in 3% sulfuric acid solution						Weights after 6 weeks immersion in 5% sulfuric acid solution					
Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)	Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	233.88	402.39	379.47	13.60	13.40	Control 1	186.76	321.05	303.09	13.37	13.65
Control 2	238.72	409.89	387.30	13.20		Control 2	202.41	350.35	329.74	13.93	
M15 1	238.47	413.87	388.2	14.64	14.29	M15 1	217.66	369.95	349.1	13.69	14.10
M15 2	245.71	424.8	399.82	13.95		M15 2	227.08	388.82	365.36	14.50	
M20 1	258.17	441.79	416.31	13.88	14.12	M20 1	240.6	413.76	389.31	14.12	13.95
M20 2	232.78	402.25	377.9	14.37		M20 2	212.19	366	344.81	13.78	
M15/L10 1	242.37	422.02	396.83	14.02	13.97	M15/L10 1	220.27	378.95	356.47	14.17	14.38
M15/L10 2	244.93	426.36	401.12	13.91		M15/L10 2	241.6	416.57	391.04	14.59	
M20/L10 1	237.73	414.76	388.24	14.98	14.73	M20/L10 1	219.01	379.96	355.71	15.07	14.87
M20/L10 2	240.59	416.2	390.78	14.48		M20/L10 2	223.54	386.08	362.23	14.67	

Weights after 6 weeks immersion in 7% sulfuric acid solution						Weights after 8 weeks immersion in 3% sulfuric acid solution					
Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)	Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	193.02	329.18	310.03	14.06	13.96	Control 1	231.07	396.59	375.84	12.54	13.31
Control 2	169.25	286.88	270.58	13.86		Control 2	215.20	368.03	346.52	14.07	
M15 1	191.68	331.76	310.78	14.98	14.82	M15 1	232.32	398.10	376.22	13.20	14.42
M15 2	199.66	346.25	324.76	14.66		M15 2	251.76	432.98	404.62	15.65	
M20 1	181.34	314.62	294.73	14.92	14.77	M20 1	225.98	389.27	365.57	14.51	13.96
M20 2	202.79	351.53	329.79	14.62		M20 2	247.39	424.99	401.17	13.41	
M15/L10 1	199.1	345.55	323.3	15.19	15.01	M15/L10 1	227.43	394.22	370.50	14.22	14.18
M15/L10 2	199.13	343.5	322.08	14.84		M15/L10 2	240.44	415.47	390.73	14.13	
M20/L10 1	232.71	399.59	375.49	14.44	14.93	M20/L10 1	226.82	395.68	370.04	15.18	14.62
M20/L10 2	207.22	357.68	334.48	15.42		M20/L10 2	220.47	381.79	359.11	14.06	

Weights after 8 weeks in immersion in 5% sulfuric acid solution						Weights after 8 weeks in immersion in 7% sulfuric acid solution					
Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)	Mixes	W Mass	SSD Mass	Dry Mass	Porosity (%)	Average (%)
Control 1	198.04	339.50	318.06	15.16	14.26	Control 1	131.44	224.81	210.76	15.05	15.29
Control 2	159.01	271.56	256.51	13.37		Control 2	117.23	201.03	188.01	15.54	
M15 1	190.46	328.02	309.05	13.79	13.60	M15 1	169.68	289.94	272.87	14.19	14.19
M15 2	185.19	319.70	301.66	13.41		M15 2	179.43	304.84	287.06	14.18	
M20 1	196.98	340.45	320.78	13.71	13.40	M20 1	177.11	306.29	286.88	15.03	15.14
M20 2	212.86	366.95	346.78	13.09		M20 2	155.93	267.55	250.52	15.26	
M15/L10 1	201.73	346.58	326.72	13.71	13.72	M15/L10 1	159.68	278.92	261.13	14.92	14.58
M15/L10 2	213.47	367.94	346.73	13.73		M15/L10 2	194.17	337.40	316.99	14.25	
M20/L10 1	200.33	346.04	325.36	14.19	14.46	M20/L10 1	220.25	378.58	355.65	14.48	14.02
M20/L10 2	199.33	346.72	325.01	14.73		M20/L10 2	183.85	313.74	296.14	13.55	