GAZİANTEP UNIVERSITY GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES

EFFECTIVENESS OF METAKAOLIN ON THE STRENGTH AND DURABILITY PROPERTIES OF AIR-CURED AND WATER-CURED CONCRETES

**M. Sc. THESIS
IN
CIVIL ENGINEERING**

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**KASIM MERMERDAŞ
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Effectiveness of Metakaolin on the Strength and Durability Properties of Air-Cured and Water-Cured Concretes

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Supervisor
Assist. Prof. Dr. Erhan GÜNEYİSİ

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To my father
Hacı Yunus Mermerdaş

ABSTRACT

EFFECTIVENESS OF METAKAOLIN ON THE STRENGTH AND DURABILITY PROPERTIES OF AIR-CURED AND WATER-CURED CONCRETES

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This study investigates experimentally the effectiveness of metakaolin (MK) in improving the strength and particularly durability properties of the air-cured and water-cured concretes. Three MK replacement levels were considered in the study: 0%, 10%, and 20% by weight of cement. The other experimental parameters investigated in the study were: water-to-cementitious material ratio (w/cm), age, curing procedures, and chloride and sulfate exposure periods. The performance characteristics of the plain and MK modified concretes were evaluated by measuring the compressive strength, water sorptivity, water absorption, resistance to chloride ion penetration, drying shrinkage, weight loss due to the corresponding drying, and sulfate resistance. The porosity and pore size distribution of the mortar phase of the concrete were also examined by using mercury intrusion porosimetry. The measurements were conducted at different ages up to 180 days according to the specified test methods. Test results revealed that replacement level of MK and curing procedure adopted had significant effects on the durability characteristics; in particular the most prominent effects were observed on the water-cured MK blended cement concrete, which performed well when the amount of MK used in the mixture increased up to 20%.

Keywords: Metakaolin, Chloride penetration, Curing condition, Drying shrinkage, Durability, Sorptivity, Pore structure, Sulfate attack

ÖZET

METAKAOLİNİN HAVADA VE SUDA KÜR EDİLMİŞ BETONLARIN DAYANIM VE DURABİLİTE ÖZELLİKLERİ ÜZERİNE ETKİSİ

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Bu çalışmada, havada ve suda kür edilmiş betonların dayanım ve özellikle durabilite özellikleri üzerinde metakaolinin (MK) etkisi deneysel olarak incelenmiştir. MK çimentoyla ağırlıkça üç farklı düzeyde (%0, %10 ve %20) yer değiştirilmiştir. Su-bağlayıcı oranı (w/cm), beton yaşı, kür koşulları ile klorür ve sülfata maruz kalma süreleri bu çalışma kapsamında irdelenen diğer deneysel parametrelerdir. Yalın ve MK modifiye betonların performans özelliklerini değerlendirmek maksadıyla; basınç dayanımı, kılcal su geçirimliliği, su emme, klorür iyon geçirimliliği, kuruma rötresi, kurumadan dolayı ağırlık kaybı ve sülfat dayanımı deneyleri gerçekleştirilmiştir. Ayrıca civalı porozimetre deneyi ile betonların harç fazında porozite ve boşluk dağılımları incelenmiştir. Deneyler, 180 günlük süre zarfında, belirtilen test yöntemlerine uygun olarak değişik zamanlarda yapılmıştır. Deneylerden elde edilen sonuçlara göre, MK değişim düzeyinin ve uygulanan kür koşullarının durabilite özelliklerini önemli ölçüde etkilemiştir. Özellikle suda kür edilmiş MK katkılı betonlarda MK katkı oranının %20'ye ulaştığı betonların performanslarında iyileşme tespit edilmiştir.

Anahtar Kelimeler: Metakaolin, Durabilite, Kür koşulları, Kılcal su geçirimliliği, Basınç dayanımı, Su emme, Klorür geçirimliliği, Boşluk yapısı, Sülfat etkisi

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LIST OF SYMBOLS/ABBREVATIONS

AC   Air curing

ASR   Alkali-silica reaction

CH   Calcium hydroxide

CR   Cement replacement

CSL   Compressive strength loss

E_d Dynamic modulus of elasticity

FA   Fly ash

HPC   High performance concrete

HR   High resolution

HRM   High reactivity metakaolin

MIP   Mercury intrusion porosimeter

MK   Metakaolin

MKC   Commercial metakaolin

OPC   Ordinary Portland cement

SEM   Scanning electron microscope

SF   Silica fume

SR   Sand replacement

WA   Water absorption

WC   Water curing

σ Compressive strength

1. INTRODUCTION

1.1 General

Concrete is the most important element of the infrastructure and well-designed concrete can be a durable construction material. However, the environmental aspects of Portland cement are a growing concern, as cement manufacturing is responsible for about 2.5% of total worldwide emissions from industrial sources. One effective way to diminish the environmental impact is to use natural pozzolans and/or supplementary cementing materials, as a partial cement replacement. This strategy will have the potential to reduce costs, conserve energy, and reduced waste volumes [1]. The cementing materials that are widely used, concrete constituents, are fly ash, granulated blast furnace slag, and silica fume, etc. [2]. Recently, there has been a growing interest in the utilization of high-reactivity metakaolin (MK) as a supplementary cementitious material in concrete construction industry. MK is an ultrafine pozzolana, produced by calcining purified kaolinite clay at temperature ranging from 700 to 900 ^{o}C to drive off the chemically bound water and destroy the crystalline structure [3-5]. Unlike industrial by-products, such as fly ash, silica fume, blast-furnace slag, MK is refined carefully to lighten its color, remove inert impurity, and control particle size. The particle size of MK is generally less than 2 µm, which is significantly smaller than that of cement particles, though not as fine as silica fume [4,6]. Moreover, the use of MK in concrete in its present form is relatively a new concept (commercially available since the mid 1990s) [7]. The interest in the use of MK has been focused on the consumption of calcium hydroxide (CH) produced by cement hydration which is associated with poor durability. Thus, the use of metakaolin improves long-term strength and durability. In addition, it is also possible to obtain early strength enhancement through the filling effect [8].

According to the literature, it has been claimed that concrete incorporated with metakaolin exhibits premium-level engineering properties comparable to silica fume concrete [9,10]. This results from the characteristics of its chemical composition, fineness, and poorly crystalline nature [11]. The research work about the use of

metakaolin deals with two main areas. In the first one, the heat treatment parameters, the dehaydroxylation/amorphization process of the kaolinite, and the formation of the metakaolinite have been studied [11-14]. The second one concerns the filling and pozzolanic behavior of metakaolin and its influence on cement and concrete properties [9, 15-23]. Research related to the effect of metakaolin on the performance of concrete is in progress due to the fact that metakaolin is a relatively new mineral admixture for concrete industry, especially its present form. Metakaolin is also considered as an alternative supplementary cementing material. It is comparable to silica fume in pozzolanic reactivity, but is lower in price [22].

It is generally agreed that ingress of aggressive species into concrete leads, in many structures, to long-term deterioration. The concrete performance depends mainly on the environmental conditions, the microstructures, and the chemistry of the concrete. Here, the continuation of hydration reactions in portland cement is essential to improve the potential strength and durability of concrete. This continuation depends on the type (chemical and mineralogical composition) and fineness of cement, the type and the amount of supplementary material present, the w/cm ratio and the curing condition, especially at early ages [24]. It is obvious that those factors are essential to obtain the durable concrete structures. Curing is necessary for concrete to fully realize its potential properties [25,26]. The curing becomes more important for concrete incorporating pozzolans, especially in hot and dry environments [27].

In this thesis, MK was used as a replacement for Portland cement (PC), ranging from 0% to 20% by weight, to evaluate its efficiency upon the concrete properties. For this purpose, six different concrete mixtures with two w/cm ratios of 0.35 and 0.55 were designed. The main focus of the study is to evaluate the effectiveness of MK on strength and durability properties of the concretes, which are subjected to different curing regimes. Permeability related durability properties were examined through long term chloride penetration test as well as water sorptivity and water absorption tests. Resistance of the concretes with and without MK to sulfate attack is also studied under different circumstances (continuous and drying-immersion cyclic exposures). Drying shrinkage and weight loss due to the corresponding drying was also monitored. Furthermore, in order to examine the main effect of MK on the performance properties of the concretes, the porosity and pore size distribution of the

concrete were also examined by using mercury intrusion porosimetry. The influence of the proper and inadequate curing (air-curing) conditions on the plain and MK modified concretes was evaluated and compared to the findings of previous researchers. Based on the test results, the effects of replacement level of MK, w/cm ratio, age, and curing procedure upon strength and particularly durability properties of the concrete were discussed.

1.2 Outline of the Thesis

Chapter 1-Introduction: Aim and objectives of the thesis are introduced.

Chapter 2-Literature review and background: A literature survey was conducted on kaolin and metakaolin. The previous studies on the use of MK as a mineral admixture are investigated.

Chapter 3-Experimental study: Materials, mixtures, casting, curing conditions, and test methods are described.

Chapter4-Test results and discussions: Indication, evaluation, and discussion of test results are presented.

Chapter5-Conclusion: Conclusion of the thesis and recommendation for future studies are given.

2. LITERATURE REVIEW AND BACKGROUND

2.1 Mineral Admixtures

Mineral admixtures are finely divided siliceous materials which are added to concrete in relatively large amounts, generally in the range of 5 to 80 percent by weight of portland cement [28]. Although pozzolans in the raw state or after thermal treatment are being used in some parts of the world, for economic reasons many industrial by-products are fast becoming the primary source of mineral admixtures in concrete.

Power generation units using coal as fuel, metallurgical furnaces producing cast iron, silicon metal, and ferrosilicon alloys are the major source of by-products which are being produced at the rate of millions of tons every year in many industrial countries. Dumping away these by-products reperesents a waste of the material and causes a serious environmental pollution problems. Disposal as aggregates for concrete and roadbase construction is a low-value use which does not utilize the potential of these pozzolanic and cementitious materials. With proper quality control, large amounts of many industrial by-products can be incorporated into concrete, either in the form of blended portland cement or as mineral admixtures. When the pozzolanic or/and cementitious properties of a material are such that it can be used as a partial replacement for portland cement in concrete, this results in significant energy and cost savings [28]. Types of mineral admixtures according to their origin and type of production are shown in Table 2.1.

Table 2.1 Classification of mineral admixtures [28]

Mineral Admixtures	
Natural Materials	**By-Product Materials**
Volcanic Glasses	Fly Ash
Volcanic Tuffs	Blast Furnace slag
Calcined Clays or Shales	Condensed Silica Fume
Diatomaceous Earth	Rice Husk Ash

In the literature there are so many studies covering the investigation on the effects of mineral admixtures on the properties of concretes produced or cured under various conditions [29-42]. Generally the effects of mineral admixtures may be assesed under the following titles;

- Improvement in mechanical properties

- Improvement in workability

- Durability to thermal cracking

- Durability to chemical attacks

- Production of high performance concrete

2.2 Production and Characteristics of Calcined Kaolin (CK)

2.2.1 Chemical Composition and Origin

Kaolin is named after the Chinese locality "Kauling" or "Kao-ling" meaning high ridge. It is the name of a hill near Yaochao Fu, mainland China, where clay was mined centuries ago. Kaolin is a soft, white plastic clay consisting of a loose aggregation of randomly oriented stacks of kaolinite flakes.

The most common mineral by far in the kaolin group of minerals is kaolinite. The physical and chemical properties together with its applications are discussed in this section. The physical and chemical properties of kaolin determine its use as an

industrial mineral. These uses are governed by several factors including the geological conditions under which the kaolin formed, the total mineralogical composition of the kaolin deposit, and the physical and chemical properties. Kaolin deposits can be sedimentary, residual, or hydrothermal and in almost every instance the kaolin has different properties and thus must be fully tested and evaluated to determine its utilization. The occurrences of kaolin are common, but commercially useable deposits are relatively few in number. Kaolin is usually white or near white in color.

Particle size and particle size distribution are also very important in determining the industrial uses of the kaolin. A coarse particle kaolin has very different physical and optical properties relative to a fine particle size kaolin. Other properties that are important are the relatively low surface area in comparison to smectite and palygorskite–sepiolite, and the low absorption capacity, which relates to the minimal layer charge and the low surface area. A relatively low viscosity at high solid concentrations is an important characteristic of some kaolins. This is particularly important in paper coating and paint applications. Viscosity of kaolin products is dependent on several factors including mineral content; particle size, shape and distribution; presence of soluble salts; and dispersability. The presence of a small amount of smectite, illite or halloysite adversely affects viscosity [43].

Ideal Kaolin Composition: $Al_2O_3.2SiO_2.2H_2O$; [44]

In kaolinite

SiO_2 46.54%

Al_2O_3 39.50%

H_2O 13.96%
_____

100%

2.2.2 Microstructure of Kaolin

Kaolinite is a dioctahedral 1:1 layer silicate mineral with well-formed six-sided flakes, frequently with a prominent elongation in one direction [45-47]. Typical microstructure of the standard kaolin is illustrated in Figure 2.1 by Shvarzman et al.

[13]. The High Resolution Scanning Electron Microscopy (HR SEM) was performed using a digital scanning electron microscope, in order to observe the effect of amorphization degree on pozzolanic activity of kaolinite. They investigated the influence of the amorphous phase content on chemical activity in the pastes containing portlandite and both untreated and heat-treated kaolinite based materials (local kaolin clay, standard kaolin, metamax). This effect was shown by data for compressive strength as a function of the amorphous phase content in kaolin admixtures.
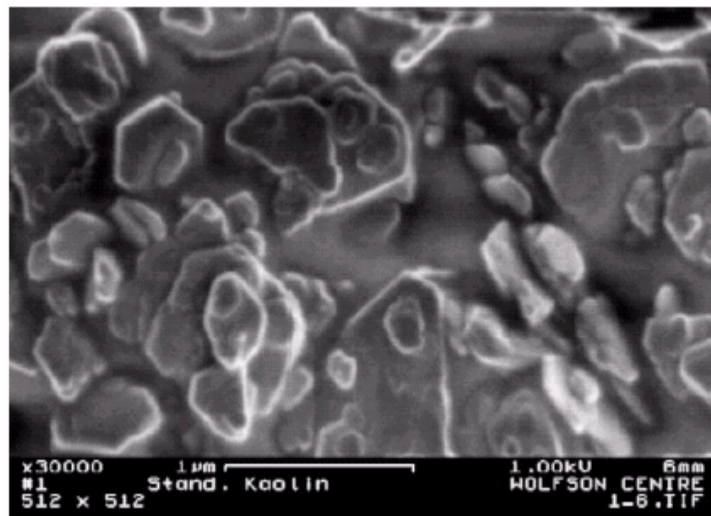
Figure 2.1 HR-SEM micrograph of the pure standard kaolin [13]

Murray [47] studied traditional and new applications of some clay minerals and he showed SEM micrograph of the kaolin plates and stacks (Figure 2.2). There is very little substitution in the structural lattice and thus it has a minimal layer charge and a low base exchange capacity. The kaolinite crystals, which make up most of the kaolin deposits, are pseudo-hexagonal along with plates, some larger books, and vermicular stacks.
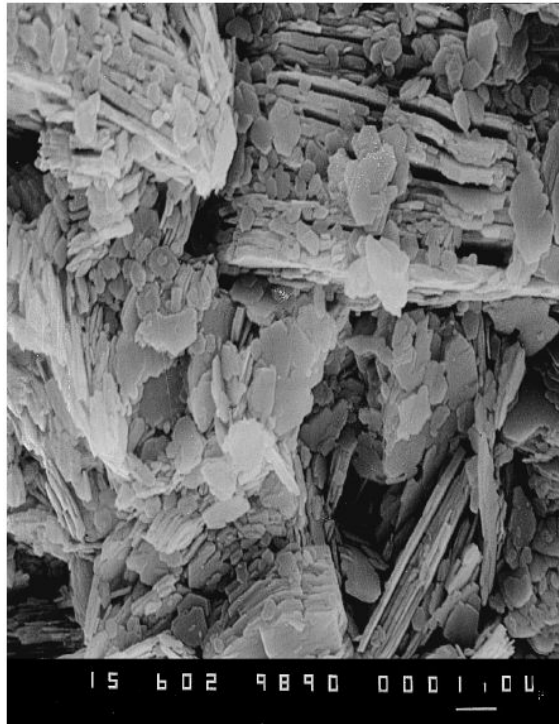
Figure 2.2 SEM showing kaolin plates and stacks [47]

2.2.3 Kaolin as a Trade Asset

Kaolin deposits can be sedimentary, residual, or hydrothermal and in almost every instance the kaolin has different properties and thus must be fully tested and evaluated to determine its utilization.

The USA, UK, Brazil, and China are the largest kaolin producers in the world and together, account for about 58% of world production. In 2002, the major kaolin exporters, in descending order, were the USA, UK, Brazil and China. The major world and US kaolin producer is Imerys, which has a controlled production capacity of nearly 5 Mt per year. Other major kaolin producers include Huber Engineering materials and Engelhard (both in the USA) and CADAM and Para Pigmentos (PPSA) in Brazil.

End-user applications, world kaolin production and world kaolin exports are given in Table 2.2 and Figures 2.3 and 2.4, respectively [43].

Table 2.2 Application of kaolin to the industry [43]

Application/Use	Description
Fertiliser	Used as coating agent to inhibit moisture adsorption and is an anti-caking agent in fertilizers
Insectcide	Kaolin acts as a dilutant and dispersing agent for active components in insecticides
Animal Feed	As a binder and anti-caking agent, kaolin ensures free-flowing properties.
Ceramics	Used in earthenware, chinaware, electrical porcelains, stoneware, sanitaryware and floor tiles. It is used in either the body and/or glaze
Structural Ceramics	Bricks, roof tiles and vitrified pipes.
Civil Engineering	Clay liners and barriers, sealants, liquid retention ponds and cement additives.
Paper	Used in the paper coating, as filler, opacifiers, whitening agents. Kaolin adds brightness, improves ink dispersion, and increases opacity
Pharmaceuticals	Used as a carrier of active agents and as anti-caking agent.
Refractories	Main component in certain acid refractory bricks and monolithic products.
Paint	Used as a filler and extender and can replace TiO_2 pigments in paint recipe.
Plastics	As a filler and extender, kaolin enhances electrical insulation, durability and infrafed adsorption properties.
Rubber	Kaolin fillers improve tensile strength and modulus of rupture.
Other	Detergents, adhesive components, cosmetics, soaps, bathing minerals, crop protection, dust control, printed inks, polymers.
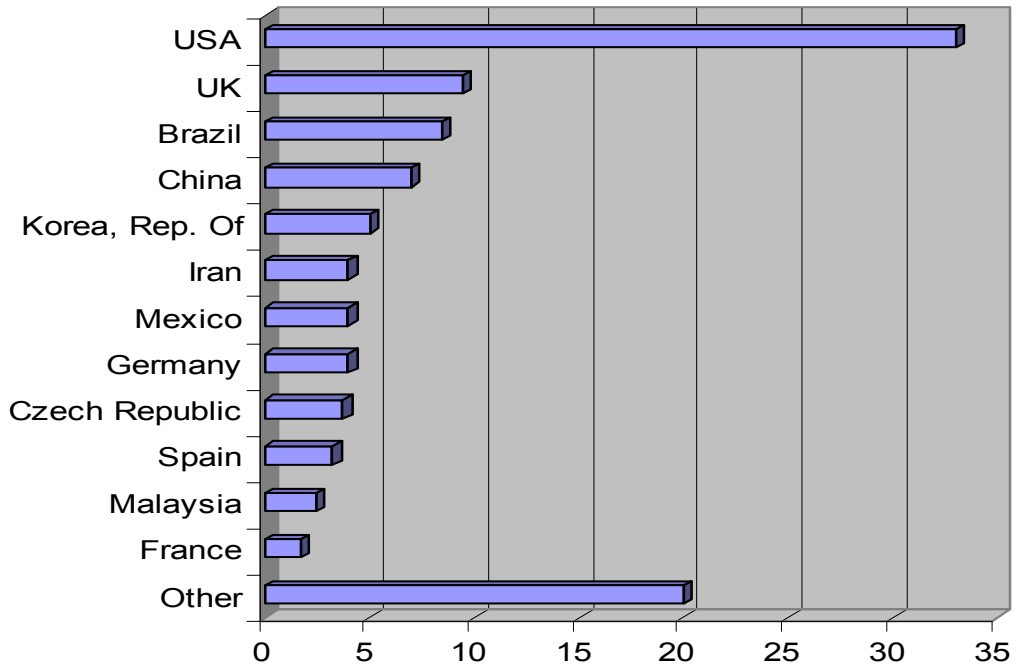
Figure 2.3 Percentage of world kaolin production total 22.5 Mt (2002) [43]
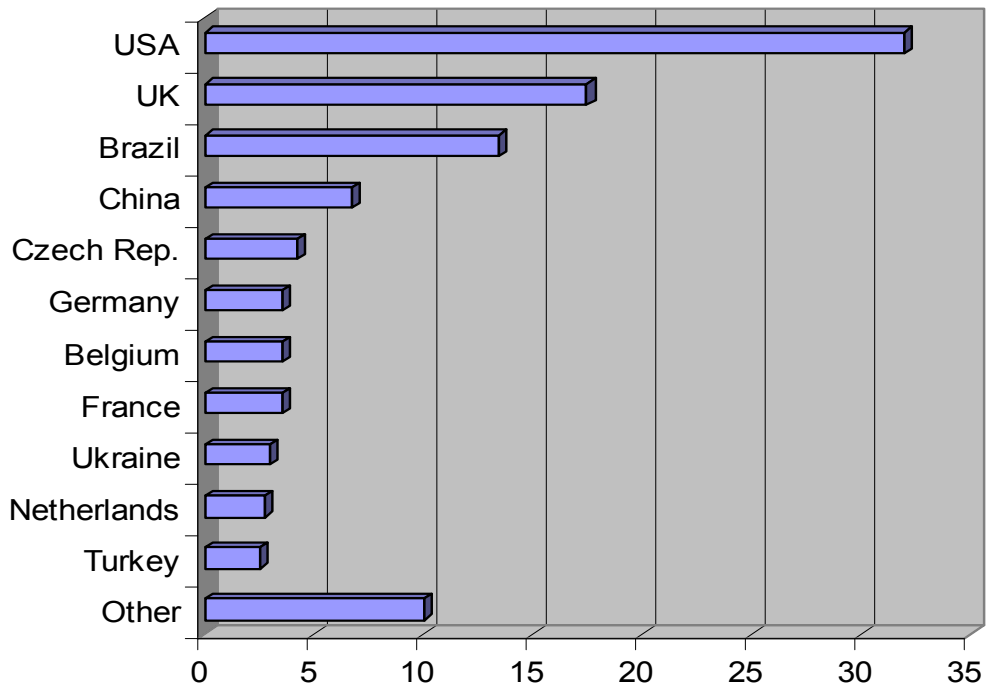
Figure 2.4 World kaolin export total 10.8 Mt (2002) [43]

2.2.4 Kaolin Deposits

Kaolin deposits are classified as either primary or secondary. Primary kaolins result from residual weathering or hydrothermal alteration (or kaolinisation) of alkali feldspar rich rocks such as granite or gneiss, whilst secondary kaolins are of sedimentary origin. The mineralogical and chemical composition of kaolin depends on the nature of the parent rock and the type and degree of alteration [43].

Kaolin deposits in Turkey are reported by Seyhan [48] in terms of their geomorphological formation and location (Figure 2.5).
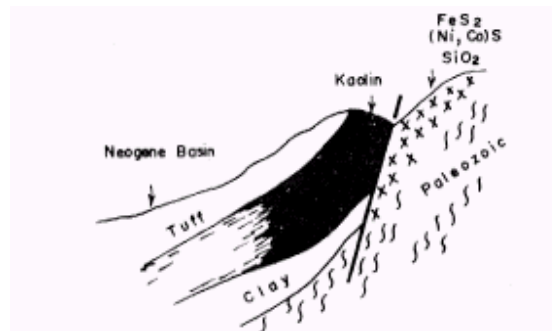
(a) Uşak-Karaçayır

(b) Giresun-Osmaniye

(c) Bingöl-Kurudere
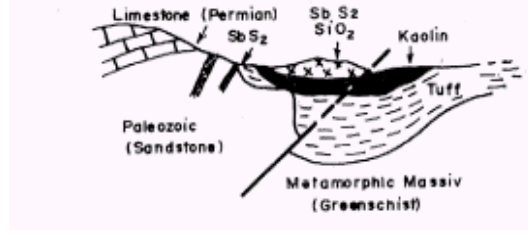
(d) İvrindi
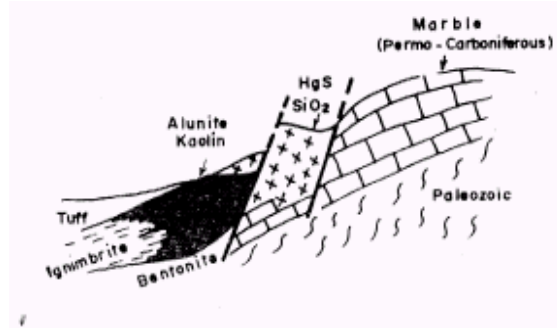
(e) Aksaray-Gelveri
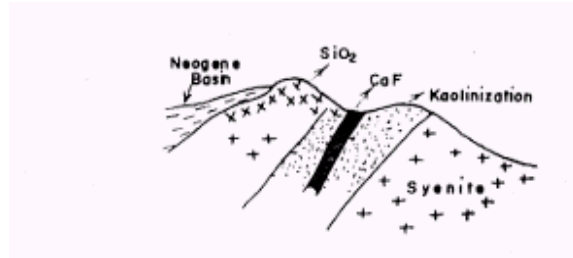
(f) Çiçekdağ
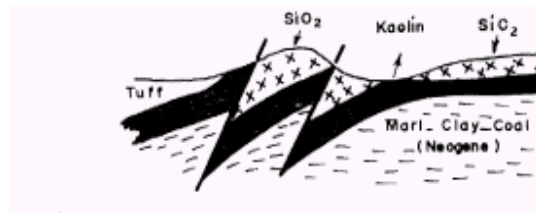
(g) Gevrekseydi Village
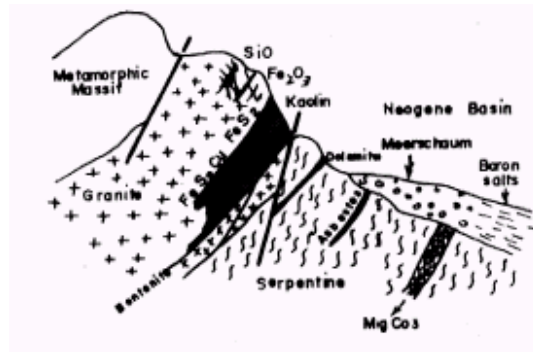
(h) Mıllalıcık

Figure 2.5 Turkey kaolin deposits [48]

2.2.5 The Calcination Process on Kaolin

Calcined kaolin is an anhydrous, thermally structured alumino-silicate product produced by heating ultra-fine natural kaolin to high temperature. Metakaolin, in the form of calcined kaolin (commercially available since the mid 1990s), is produced by calcining purified kaolinite clay at temperature ranging from 600 to 800 °C to drive off the chemically bound water and destroy the crystalline structure [49].

The calcination process alters the particle shape of kaolin and increases its hardness - a meta-kaolin is formed which is highly reactive. Fully calcined kaolin properties include: high colour retention, excellent thermal stability and the absorption of UV light by dissipating the energy as heat. Calcined kaolin contributes to opacity by replacing up to 15-25% of TiO_2 pigments in most applications. The low surface hydroxyl content of calcined kaolin leads to low moisture pick up which gives excellent performance in moisture sensitive applications [43].

Heat treatment in calcination process may vary. There are several studies in the literature revealing the effect of the heat treatment on the chemical and physical properties of calcined kaolin [3,13,50-53]. For example, Shvarzman et al. [13] studied dehydraxilation process occuring during calcination of different kaolin clays at different temperatures. They found that;

- At calcination temperatures below 450 °C, kaolin clays show relatively low level of dehydroxilation degree,

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- In the range from 450 to 570 ^{o}C, the degree of dehydroxylation sharply increased,

- Finally, at the temperatures between 570 and 700 C the kaolinite was fully dehydroxylated.

2.3 Effects of Metakaolin (MK) on Properties of Concrete

Metakaolin is a mineral admixture, which is relatively new to the concrete industry that has the potential for improving the durability of concrete. MK differs from the more commonly used mineral admixtures, such as fly ash and silica fume, in that it is not a by-product; it is manufactured under a carefully controlled process by thermally activating purified kaolinite within a specific temperature range (600-800 ^{o}C). The resulting anhydrous alumino-silicate ($Al_2Si_2O_7$) is mainly amorphous material, which behaves as a highly reactive artificial pozzolan.

Recently, there has been a considerable interest in the use of high reactivity metakaolin (MK) as a supplementary cementitious material in concrete industry. Metakaolin is increasingly being used to produce high-strength, high-performance concrete with improved durability. Metakaolin can also be used in lightweight concrete, marine concrete, precast concrete for architectural, civil, industrial and structural applications. Shotcreting, fibro-cement, ferro-cement products, glass fibre reinforced concrete, mortars, stuccos and pool plasters are some examples to further applications of MK in construction industry [43].

Metakaolin chemically combines with calcium hydroxide to form calcium silicate and calcium alumina hydrates. It can be used as a replacement or additional material for the production of the concrete.

2.3.1 Pozzolanic Property of MK

The reaction between a pozzolan and calcium hydroxide is called the pozzolanic reaction [28]. The chemical mechanism by which pozzolana improves the properties of concrete is explained by the fact that when cement hydrates, calcium hydroxide is liberated. This calcium hydroxide can react with amorphous aluminium silicates to form stable cementing material [54].

The utilisation of calcined kaolin, in the form of metakaolin (MK), as a pozzolanic material for mortar and concrete has received considerable attention in recent years. This interest is part of widely spread attention directed towards the utilisation of wastes and industrial by-products in order to minimise Portland cement (PC) consumption, the manufacture of which being environmentally damaging. Another reason is that mortar and concrete, which contain pozzolanic materials, exhibit considerable enhancement in durability properties [3]. Unlike other mineral admixtures that are mostly by-product pozzolans, which can have variable composition, purity and rectivity, the production of MK can be closely contolled and thus, higher degree of purity and pozzolanic rectivity can be obtained [4].

Originally the term pozzolana was associated with naturally formed volcanic ashes and calcined earths, which react with lime at ambient temperatures in the presence of water. In recent times the term has been extended to cover all siliceous/aluminous materials which, in finely divided form and in the presence of water, will react chemically with calcium hydroxide (CH) to form compounds that posses cementitious properties [3].

The principal reaction is that between the metakaolinite, $(Al_2O_3 \cdot 2SO_2)$ or AS_2, and the CH derived from cement hydration, in the presence of water. This reaction forms additional, cementitious aluminum containing CSH gel, together with crystalline products, which include calcium aluminate hydrates and alumino-silicate hydrates (i.e., C_2ASH_8, C_4AH_{13} and C_3AH_6). The optimum replacement levels of PC by MK are associated with changes in the nature and proportion of the different reaction products (depending on composition) temperature and reaction time, which are formed in the PC-MK system [3].

There are several studies in literature on pozzolanic effect of metakaolin [4,13,49,56-66]. For instance;

In the study of Remlocan et al. [55] when metakaolin is used as a partial replacement for OPC, it is observed that metakaolin is capable of reacting with portlandite to form calcium-silicate-hydrate similar in composition and structure to those obtained from Portland cement. Research has also shown that for metakaolin produced from china clay, the calcium-silicate-hydrate that are formed have a low Ca:Si ratio (in the range

of 0.8 to 1.5), which allows them to entrap alkali ions from the pore solution. Reduction in alkalinity (and associated pH) in the pore solution and depletion of portlandite are considered as the most beneficial effects of pozzolans in reducing expansion due to alkali-silica reaction (ASR). In light of this, the potential for using metakaolin to control alkali-silica expansion in concrete has been reported.

Poon et al. [63] studied the rate of pozzolanic reaction in high performance cement pastes. They assessed the progress of the pozzolanic reaction of MK-blended cement pastes with a water-binder ratio (w/b) of 0.30. A series of tests on the compressive strength, porosity and pore size distribution, degree of pozzolanic reaction, and $Ca(OH)_2$ content of MK-blended cement pastes has been carried out. Comparisons have been made with the results obtained from SF- and FA-blended cement pastes, and with those obtained by other researchers for MK pastes with higher w/b ratios and obtained the following results;

- At early ages, the rates of pozzolanic reaction and CH consumption in MK-blended cement pastes were higher than in SF- or FA-blended cement pastes. This indicates that the MK used in this study had a higher initial reactivity than the SF and the FA when used in cement pastes with a w/b ratio of 0.30.

- Due to its high initial reactivity, MK resulted in a higher rate of compressive strength development and pore structure refinement for the high-performance cement pastes when compared with SF. It also resulted in lower mercury-intruded porosity than the control.

- The rate of pozzolanic reaction in MK pastes became slower after 28 days of curing. After that, the pore size distribution of MK pastes was slightly coarsened. This coarsening happened at a later age in a cement paste with a lower w/b ratio than in a paste with a higher w/b ratio. However, the pozzolanic reaction of MK was still not completed at the age of 90 days with about half of the MK unreacted. The degree of pozzolanic reaction and CH consumption level of the SF pastes reached or exceeded those of MK pastes at the ages of 28–90 days.

2.3.2 Effect of MK on Pore Structure of Concrete

One of the most important effect of the pozzolans is pore size refinement. Filling up large capillary spaces is important in terms of improving the strength and impermeability of the concrete [28]. Thus, modifiers should be used in order to provide pore size refinement in concrete.

Bredy et al. [66] conducted a study on porosity and pore size distribution of pastes containing MK. Pastes were prepared with MK content of 0–50% at different water to binder (w/b) ratios to maintain the same consistency. They concluded that the total porosity of paste decreased if the MK content was below 20%. Beyond 30%, an increase in porosity was found. Larbi and Bijen [67] reported that at 100 days of curing the pore volume of mortar and the threshold diameter decreased in the presence of MK. Khatib et al. [57] found a slight increase in pore volume for pastes containing up to 15% MK as partial replacement of cement and at a constant water/(cement +MK), and this increase is dependent upon the MK content. The presence of MK, however, causes refinement in pore structure, in that pastes containing MK decrease the threshold diameter and increase the percentage of small pores.

Poon et al. [58] conducted a study on pore structure of high performance MK and SF concrete. They used mercury intrusion porosimeter (MIP) to measure pore size distribution of the concrete. Their finding about pore structure of concretes incorporated with MK and SF was the incorporation of MK in the cement pastes resulted in a very dense microstructure of the paste, with a lower total porosity and finer pore size distribution compared with the plain Portland cement pastes and SF blended cement pastes.

In the study of Singh and Garg [65], the microstructure of the metakaolin modified mortar has been reported. The effect of addition of metakaolin up to 25% in the Portland cement mortars was investigated. An increase in compressive strength and decrease of porosity and pore diameter of cement mortars containing metakaolin (10%) was reported over the cement mortars without metakaolin. The hydration of metakaolin blended cement mortars was investigated by differential thermal analysis (DTA) and scanning electron microscopy (SEM). DTA of hydrated cement showed

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(Fig. 2.6) formation of endotherms of major hydraulic products such as C-S-H (130–135 ^{o}C), hexagonal calcium aluminate hydrate (C$_4$AH$_{13}$) (180–200 ^{o}C), and Ca(OH)$_2$ (480–500 ^{o}C) due to their decomposition reactions. The endotherms at 750–770 ^{o}C is due to decomposition of calcium carbonate (CaCO$_3$). An increase in peak areas of C-S-H and C$_4$AH$_{13}$ was observed with increase in metakaolin up to 10%. SEM (Fig. 2.7) showed formation of dense subhedral to euhedral crystals of C-S-H and C$_4$AH$_{13}$ interspersed with short length ettringite at 3 days (a) of curing. Appearance of partially hydrated amorphous SiO$_2$ and Al$_2$O$_3$ can also be seen. At 7 and 28 days of hydration (b and c), well-crystallized CSH formed. With the increase in curing period (d), well-developed euhedral CSH crystals with little unhydrated metakaolin are formed. The formation of these crystals is responsible for increase in strength of OPC–metakaolin mortar than the plain OPC mortar. Replacement of metakaolin with silica fume (up to 5%) did not show appreciable improvement in compressive strength of the cement.
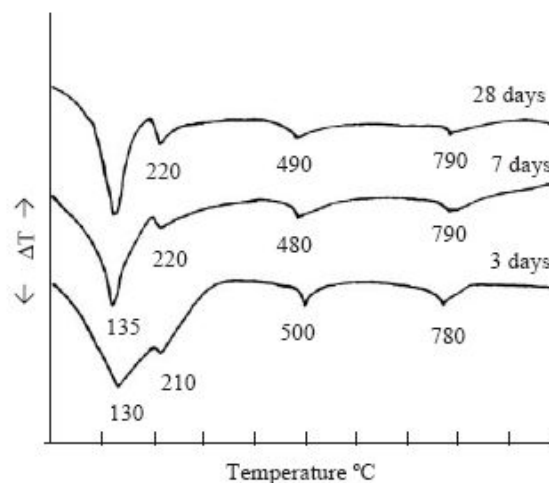
Figure 2.6 Differential thermograms of OPC-metakaolin mix hydrated for different periods [65]

They also used mercury intrusion porosimeter in order to observe the average pore diameter and porosity of mortars with and without MK. The mortar samples were moulded into 2.5x2.5x2.5 cm cubes at normal consistency and hydrated for different periods, crushed and soaked in acetone and then placed in a vacuum oven at 60 ^{o}C to remove acetone and dried for 48 h. The cement mortars were reduced to 3 mm in size

for pore-size distribution and porosity using a "Pore sizer 9320" mercury intrusion porosimeter (Micromeritics) with a maximum mercury intrusion pressure of 210 MPa.They summarized the results of mercury intrusion porosimetre in Table 2.3.
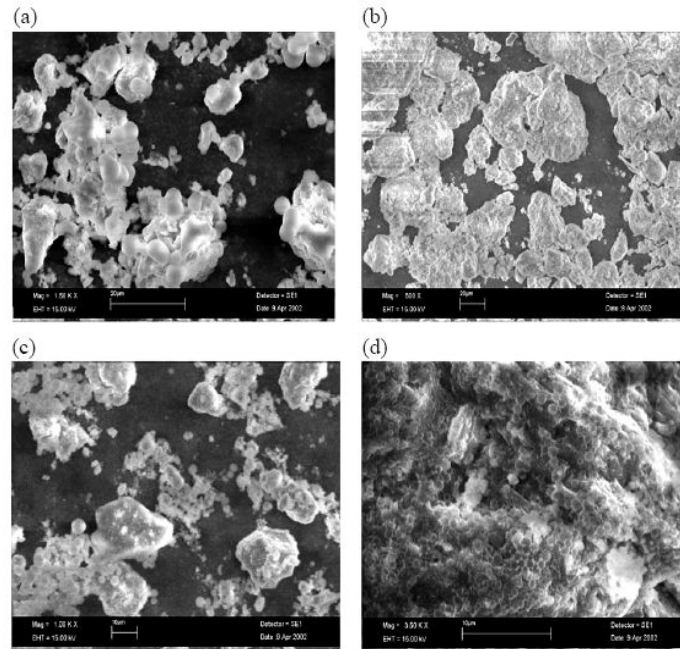
Figure 2.7 SEM of OPC-metakaolin mixture hydrated for different periods (a) 3 days, (b) 7 days, (c) 28 days, and (d) 90 days [65]

Table 2.3 Average pore diameter and porosity of cement mortars with and without MK

Curing Period	Average pore diameter (μm)		Total porosity (%v/v)	
	OPC-10% MK	OPC mortar	OPC-10% MK	OPC mortar
3 days	0.0266	0.0371	15.22	21.11
7 days	0.0252	0.0362	15.10	18.10
28 days	0.0187	0.0342	13.38	16.58
90 days	0.0176	0.0336	11.20	13.40

2.3.3 Fresh Concrete Properties

Wong and Razak [60] studied efficiency of calcined kaolin and silica fume as cement replacement material on the fresh properties of concrete. They noted the following results about workability properties of concretes produced by different water-cementitious ratio (w/cm) at different replacement levels of SF and MK.

The workability characteristics of fresh concrete were assessed with respect to slump and Vebe[1] time. Results are summarized in Table 2.4. The mixtures had slump values ranging from 30 to 260 mm while Vebe time was in the range of 1 to 15 s. The large variation of workability across mixtures was due to the constant superplasticizer dosage used for mixtures with the same w/cm ratio. The superplasticizer content was fixed with the intention of maintaining a standard material proportion and avoiding any effects of variation in superplasticizer content on fresh properties. Consequently, the slump reduced systematically as the amount of mineral admixture used in the mixture increased. It was observed that SF caused a more severe loss of workability compared with MK. This is attributed to its extremely high surface area of 21.3 m^2/g, measured via nitrogen adsorption, which is double that of MK (9.5 m^2/g) [60].

Table 2.4 Workability characteristics with some MK and SF replacement levels for different w/cm ratios [60]

w/cm	Mixture	Slump (mm)	Vebe* (s)
0.27	C	165	8
	MK5	155	8
	MK10	150	10
	MK15	115	10
	SF5	100	8
	SF10	50	12
	SF15	35	15
0.30	C	225	3
	MK5	220	3
	MK10	210	3
	MK15	205	4
	SF5	215	3
	SF10	117	5
	SF15	30	16

* indicates the consistency of the fresh concrete.

Badogiannis et al. [62] studied metakaolin as a main cement constituent. The metakaolin used in their study was either commercial (MKC) or that produced from poor Greek kaolin (MK). In the study, they replaced MK by cement (CR) and sand (SR). Fresh concrete properties are shown in the Table 2.5.

Table 2.5 Properties of fresh concrete [62]

Sample	Slump (mm)	Unit weight (kg/m^3)	Air content (%)
OPC	70	2.453	1.4
MKC-CR10	90	2.434	1.5
MKC-CR20	60	2.440	1.0
MK-CR10	50	2.433	1.5
MK-CR20	70	2.427	1.0
MKC-SR20	60	2.443	1.0
MKC-SR10	100	2.449	1.1
MK-SR20	40	2.439	1.0
MK-SR10	70	2.452	1.1

In the study of Qian and Li [68], the obtained results on workability of MK concrete are shown in the Figure 2.8, which explains the relationship between the metakaolin content and the slump value in fresh concrete. For concrete with a 1% superplasticizer addition, the slump progressively decreases with increasing metakaolin content. However, by increasing the superplasticizer dosage to 1.2%, the slump showed only minor variation with increasing metakaolin content.
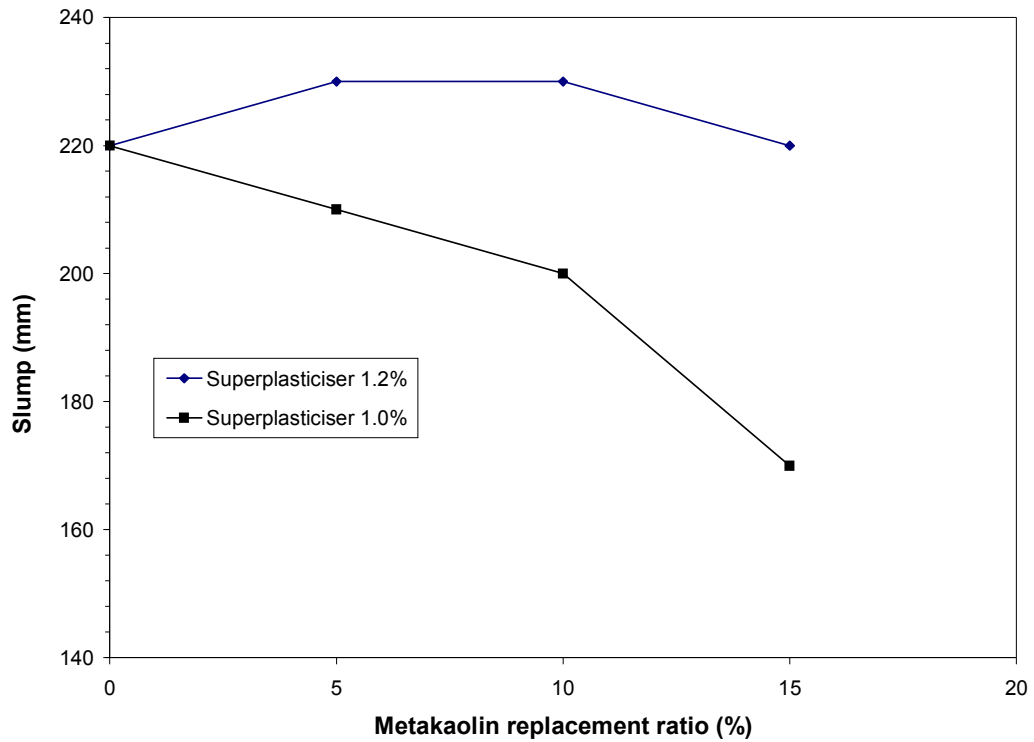
Figure 2.8 Effect of MK replacement levels on slump [68]

Effects of MK on setting time and cosistency of mortars were determined by Batis et al. [21]. The MK blended cements demand significantly more water than the relatively pure cement and this phenomenon is attributed to the high fineness of metakaolin. The increase of the metakaolin content causes a significant increase of the water demand. PC with 10% MK (MK-10) showed the lowest water demand, compared with the other blended cements. The initial and final setting time of metakaolin cements is higher than the setting time of pure cement. Table 2.6 shows the results of their study on the physical properties of the blended cements with metakaolin.

Table 2.6 Physical properties of blended cements with metakaolin [21]

Sample	Water Demand (%)	Setting time (min)	
		Initial	Final
PC	27.5	105	140
MK-10	32.5	155	180
MK-20	41.0	205	230
MKC-20	37.5	140	170

2.3.4 Hardened Concrete Properties

2.3.4.1 Strength and Elastic Properties

In metakaolin blended cements concretes, metakaolin contributes to the strength of concrete not only at early ages mainly by the filling effect, but also at later ages due to the fast pozzolanic reaction [58]. Khatib and Clay [57] showed the relationship between compressive strength and dynamic modulus of elasticity of concretes containing different MK replacement levels. Cement was partially replaced with up to 20% MK. The values of dynamic modulus of elasticity (E_d) for all mixes at all curing times are presented in Table 2.7. The E_d increases rapidly with curing time up to 7 days. However, there is a little increase in E_d after 7 days of curing. This applies to mixes with and without MK. At 1 and 7 days curing, the values of E_d for the control mix are higher than the E_d values for the MK mixes. Beyond 14 days of curing, there is a slight increase in E_d for mixes with and without MK.

Table 2.7 Dynamic modulus of elasticity (E_d, in kN/mm^2) for concrete mixes [57]

Mix no.	Mix code	Curing time (days)				
		1	7	14	28	90
1	0% MK	33.8	47.1	48.3	49.8	51.5
2	5% MK	28.5	46.6	48.6	50.1	51.5
3	10% MK	31.7	46.1	48.7	50.3	51.7
4	15% MK	27.2	46.9	49.3	51.0	52.2
5	20% MK	31.6	46.1	49.3	50.9	52.3

In Fig. 2.9, the strength versus E_d is plotted. When fitting the best exponential curve to the results, the following equation is obtained:

$$\text{Strength} = me^{bE_d} \qquad \text{(Eqn. 2.1)}$$

where m = 3.15 and b = 0.062 for the results of the current investigation with a coefficient of correlation $R^2 = 0.94$, indicating that exponential relationship between strength and E_d is appropriate.
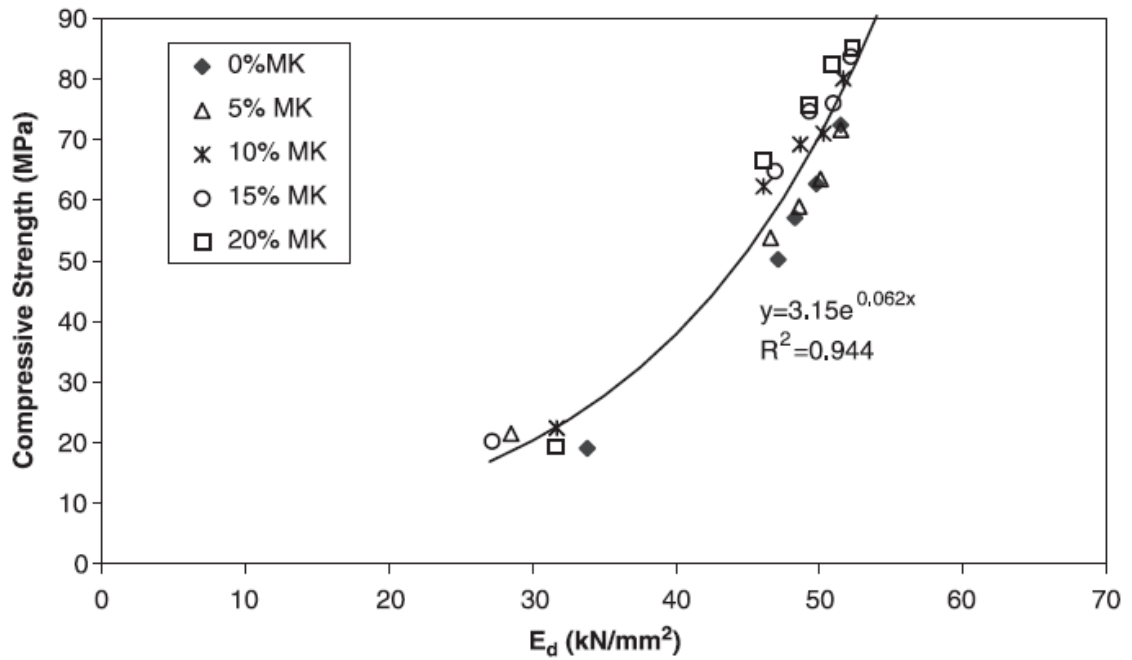
Figure 2.9 Compressive strength vs. dynamic modulus of elasticity (E_d) [57]

Qian and Li studied [68] the relationships between stress and strain for high-performance concrete incorporating 0%, 5%, 10%, and 15% with metakaolin. Table 2.8 shows the results of the experimental study.

Table 2.8 Compressive strength vs. modulus of elasticity of concretes with or without MK [68]

Mixtures	Compressive Strength (MPa)			Modulus of Elasticity (GPa)		
	3 days	28 days	60 days	3 days	28 days	60 days
MK0	27.9	37.8	58.0	24.1	30.0	30.4
MK5	36.3	45.7	62.4	25.6	31.5	33.1
MK10	39.1	63.8	66.5	26.0	33.2	34.4
MK15	42.2	69.7	77.8	26.2	33.2	34.7

According to the results shown in Table 2.8, the elasticity modulus of the concretes exhibited only small increases with increase in metakaolin content. They also noted that the brittleness of the concrete increases with increasing metakaolin content.

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Poon et al. [58] used two different water to binder ratio and different replacement levels of SF and MK. The results of the compressive strength test are shown in Table 2.9, where each value is averaged from the results of three cubes.

Table 2.9 Compressive strength of control and blended concretes [58]

Series	w/cm	Mix	Compressive strength (MPa)			
			3 days	7 days	28 days	90 days
1	0.30	Control	68.5	81.1	96.5	102.5
		5% MK	73.0	88.2	103.6	112.9
		10% MK	85.9	99.8	116.8	120.3
		20% MK	70.8	87.6	99.6	113.8
		5% SF	67.0	79.3	106.5	110.2
		10% SF	63.2	76.9	107.9	115.6
2	0.50	Control	28.6	41.2	52.1	60.4
		5% MK	32.6	45.9	57.1	66.5
		10% MK	40.4	55.2	66.2	71.6
		20% MK	30.0	43.2	58.4	69.1
		5% SF	27.4	47.0	54.3	67.5
		10% SF	25.8	47.4	58.4	69.1

The results showed that the metakaolin used in this study is superior to silica fume in terms of the strength enhancement of concrete. Among different replacement levels, the use of metakaolin at the replacement level of 10% performed the best, which resulted in the highest strength increase over the control concretes at all the test ages, particularly at the age of 3 days. However, the incorporation of silica fume did not result in any strength increase for the concrete at 3 days, although it increased the strength at the ages of or after 7 days.

Batis et al. [21] investigated the influence of metakaolin on the compressive strength of the cement mortars. In this study they used two types of metakaolin. A poor Greek kaolin with a low kaolinite content was thermally treated and the produced metakaolin (MK) was ground to the appropriate fineness. In addition, a commercial metakaolin (MKC) of high purity was used. They produced mortars with 0%, 10%, 20% MK and 20% MKC replacement. Compressive strength values at 1, 2, 7, 28, 180 days are shown in Figure 2.10.
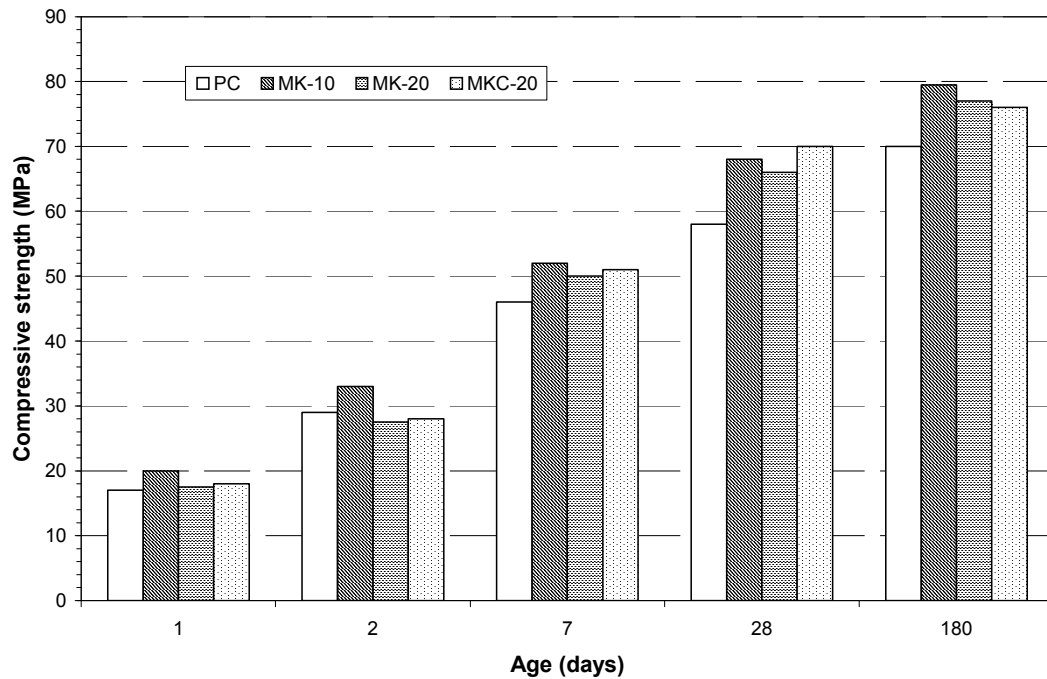
Figure 2.10 Compressive strength of blended cements with metakaolin [21]

2.3.4.2 Time Dependent Behavior

One of the most important characteristics of the concrete is time dependent behavior, which are known as shrinkage and creep.

Brooks and Johari [4] studied the effect of MK on the creep and shrinkage of properties of concrete mixtures. The replacement level of MK was considered as 0%, 5%, 10% and 15% by weight of cement. According to their results, the early age autogenous shrinkage measured from the time of initial set of the concrete was reduced with the inclusion of MK, but long-term autogenous shrinkage measured from the age of 24 h was increased. At 5% replacement level, the effect of MK was

to increase the total autogenous shrinkage considered from the time of initial set. While at replacement levels of 10% and 15%, it reduced the total autogenous shrinkage. The total shrinkage (autogenous plus drying shrinkage) measured from 24 h was reduced by the use of MK, while the drying shrinkage was significantly less for the MK concretes than for the control concrete. The total creep, basic creep as well as drying creep were significantly reduced particularly at higher MK replacement levels. Compared with estimated values, total creep of all concretes was overestimated, especially in the mixes containing the higher values of MK. For basic creep, estimates for low levels of MK were acceptable but, for the higher levels, creep was overestimated. Figure 2.11 shows the effect of MK replacement levels on total shrinkage of concrete specimens. In Figure 2.12, the effect of metakaolin on total creep of concrete loaded to an initial stress/strength ratio of 0.20 at the age of 28 days was presented.
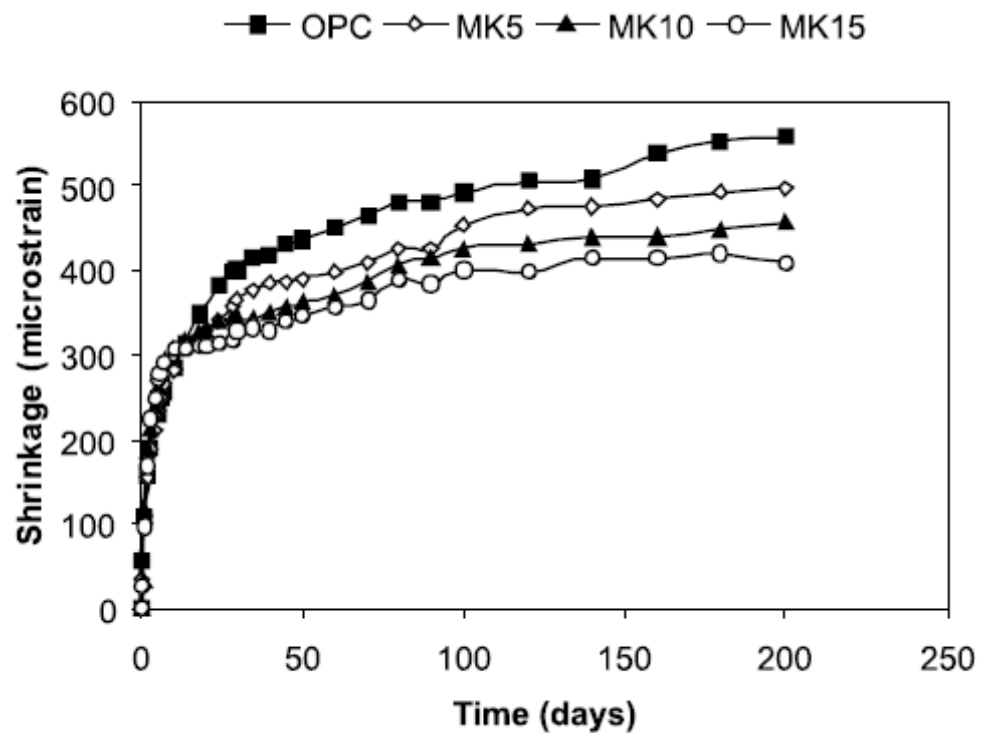
Figure 2.11 Total shrinkage of drying concrete specimens from 24 h [4]
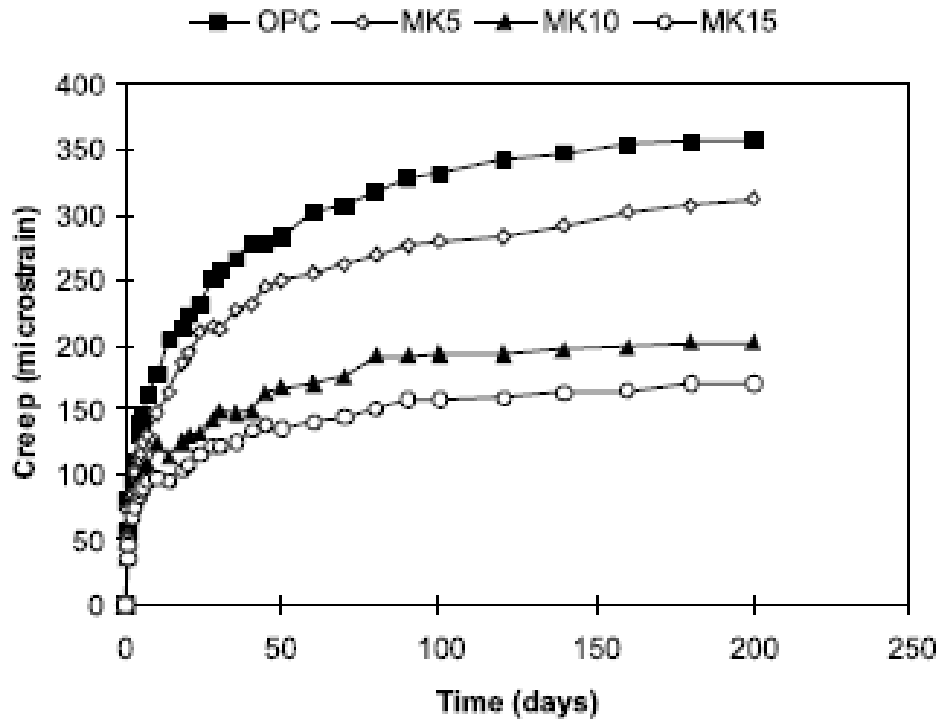
Figure 2.12 Influence of metakaolin on total creep of concrete [4]

2.3.4.3 Resistance to Permeability

Permeability of concrete is the property that measures the flow of fluid through concrete under a pressure gradient. Permeability is of importance in water-retaining structure, whereas in structures situated above ground such as buildings, tests on water penetration by capillary action is more appropriate to define the quality of concrete [57]. Moisture transport in porous media plays an important role in a wide variety of processes of environmental and technological concern, such as the degradation of mortar and concrete.

Mineral admixtures lead to pore refinement and reduce the permeability of the binder matrix [69]. The use of MK in concrete in its present form is relatively a new concept. Little information is available in the literature on the absorption characteristics of concrete containing MK, especially at dry and hot environments. Absorption by capillary action is a key durability parameter [57].

An important term relating to the permeability of concrete is sorptivity. Sorptivity is defined as the slope of plots between the volume of water absorbed per unit wetted

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surface area and the square root of time. In most cases, the plots are linear up to 49 h of absorption, but in some cases where the sorption is very quick (e.g., for air-cured specimens), the linearity is confined to a shorter duration, reflecting the much higher sorptivity [70]. Minimising sorptivity is important in order to reduce the ingress of chloride-containing or sulphate-containing water into concrete, which can cause serious damage [71]. Bai et al. used pulverised fuel ash (PFA) and MK blended portland cement (PC) for air cured and water cured concretes. According to their findings: Increasing the MK content of water-cured PC–PFA–MK concrete reduces the sorptivity to values below that of the control, whereas the sorptivities of PC–PFA concrete exceed that of the control [71].

2.3.4.4 Water Absorption

Water absorption (WA) by total (shallow) immersion is generally measured by drying a specimen to constant mass, immersing it in water for a specific time and measuring its increase in mass as a percentage of the dry mass. Capillary water absorption of concrete, however, is the phenomenon by which water is absorbed into the concrete by capillary action. It involves placing a sample with one surface just in contact with water and the mass or height of water absorbed by capillary action is measured at different time intervals. The fineness of the capillary pores in concrete causes absorption of water by capillary action, hence a measure of the rate of absorption provides a useful indication of the pore structure of concrete.

Khatib and Clay [57] studied the water absorption by total immersion and by capillary rise of concrete containing MK. MK was used up to 20% replacement levels and the following result was obtained; the partial replacement of cement with MK reduces the water penetration into concrete by capillary action. The WA of concrete by total immersion, is slightly increased in concrete containing MK as seen in Figure 2.13. However, it was noted that the range of WA values was very narrow.
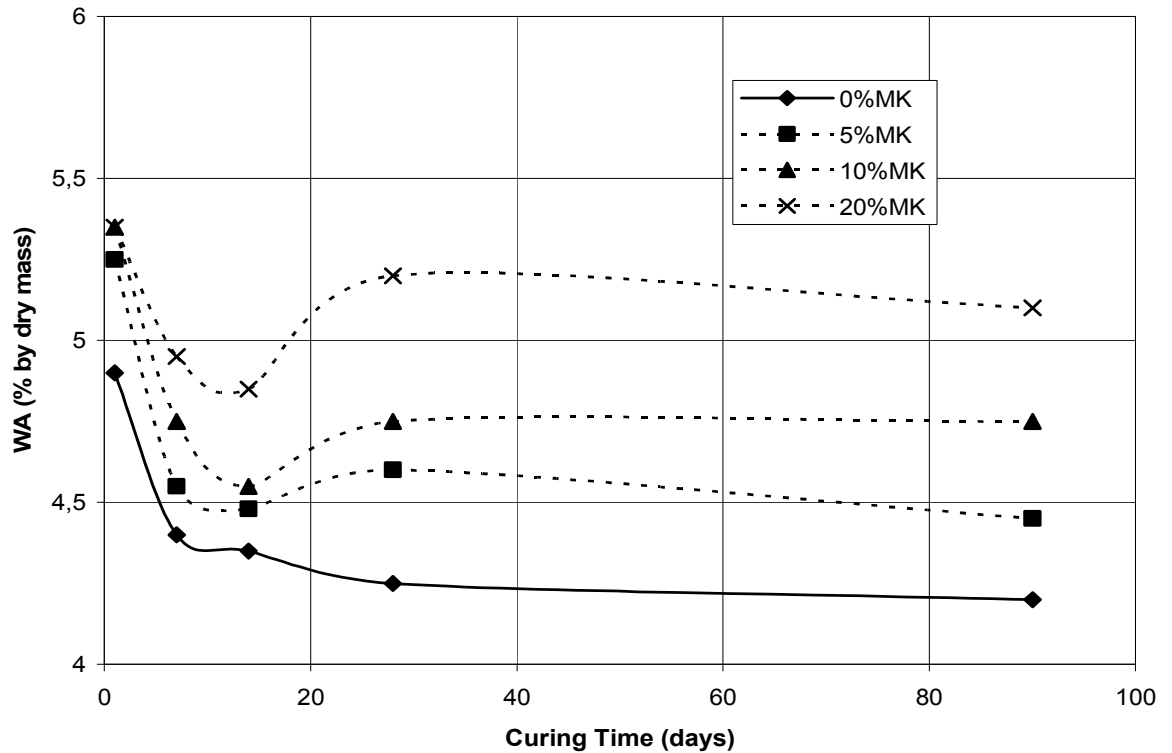
Figure 2.13 Variation of WA with curing time for concrete containing different MK replacement levels [57]

2.3.4.5 Chloride Ion Ingress

Corrosion of reinforced steel resulting from the ingress of chloride ion is one of the most important issues concerning the durability of concrete structures. When the chloride concentration of the concrete exceeds a certain threshold value, steel reinforcement embedded in concrete would start to corrode [72]. To reduce chloride ion ingress, some researchers have used mineral admixtures. Recent works have shown that MK is effective as a supplementary cementitious material on improving the durability of concrete, such as resistance to chloride ingress [73].

Poon et al. [58] studied the properties of high performance metakaolin (MK) and silica fume concretes. In the study, the compressive strength and chloride penetrability of MK blended concretes are determined and compared with those of SF concretes. The results of the rapid chloride penetration test are shown in Table

2.10. Both the MK and SF concretes showed lower total charges passed than the control.

Table 2.10 Chloride penetrability of control and blended concretes [58]

Series	w/cm	Mix	Total Charge passed (C)			
			3 days	7 days	28 days	90 days
1	0.30	Control	2461	2151	1035	931
		5% MK	1327	1244	862	646
		10% MK	417	347	199	135
		20% MK	406	395	240	124
		5% SF	1060	945	665	426
		10% SF	567	445	360	336
2	0.50	Control	5312	4054	2971	2789
		5% MK	4215	3765	2079	1065
		10% MK	1580	1247	918	752
		20% MK	751	740	640	580
		5% SF	3156	2047	1641	1235
		10% SF	3140	1877	1523	1053

According to their results given in the Table 2.10, it can be seen that a 5% SF replacement in concrete resulted in a lower total charge passed than a 5% MK replacement, but a 10% MK replacement resulted in a lower total charge passed than a 10% SF replacement, at both w/b ratios of 0.30 and 0.50. The difference in the total charge passed between the MK concrete and the SF concrete with a 10% replacement level is particularly significant when they were prepared at the w/b ratio of 0.50. This indicates that the use of MK is more effective than SF in improving the resistance of concretes against chloride penetration according to the results of the rapid chloride permeability test. However, it was noted that the results of the rapid test should be proved by long term tests.

2.3.4.6 Sulfate Resistance

Sulfate attack is one of the most aggressive environmental deteriorations that affect the long-term durability of the concrete structures. The sulfate attack of the concrete leads to expansion, cracking, and deterioration of many civil engineering structures exposed to sulfate environment such as piers, bridges, foundations, concrete pipes, etc.

The sulfate attack is generally attributed to the reaction of sulfate ions with calcium hydroxide and calcium aluminate hydrate to form gypsum and ettringite. The gypsum and ettringite formed as a result of sulfate attack is significantly more voluminous (1.2 to 2.2 times) than the initial reactants [74]. The formation of gypsum and ettringite leads to expansion, cracking, deterioration, and disruption of the concrete structures. In addition to the formation of ettringate and gypsum and its subsequent expansion, the deterioration due to sulfate attack is partially caused by the degradation of calcium silicate hydrate (C–S–H) gel through leaching of the calcium compounds. This process leads to loss of C–S–H gel stiffness and overall deterioration of the cement paste matrix [75].

Al-Akhras [49] investigated the effect of metakaolin (MK) replacement of cement on the durability of concrete to sulfate attack. They used three MK replacement levels in the study: 5%, 10%, and 15% by weight of cement. The other experimental parameters investigated in the study were: water to binder ratio (0.50 and 0.60), initial moist curing period (3, 7, and 28 days), curing type (moist and autoclaving), and air content (1.5% and 5%). After the specified initial moist curing period, the concrete specimens were immersed in 5% sodium sulfate solution (Na_2SO_4) for a total period of 18 month (Figure 2.14). The degree of sulfate attack was evaluated by measuring expansion of concrete prisms, compressive strength reduction of concrete cubes, and visual inspection of concrete specimens to cracks.
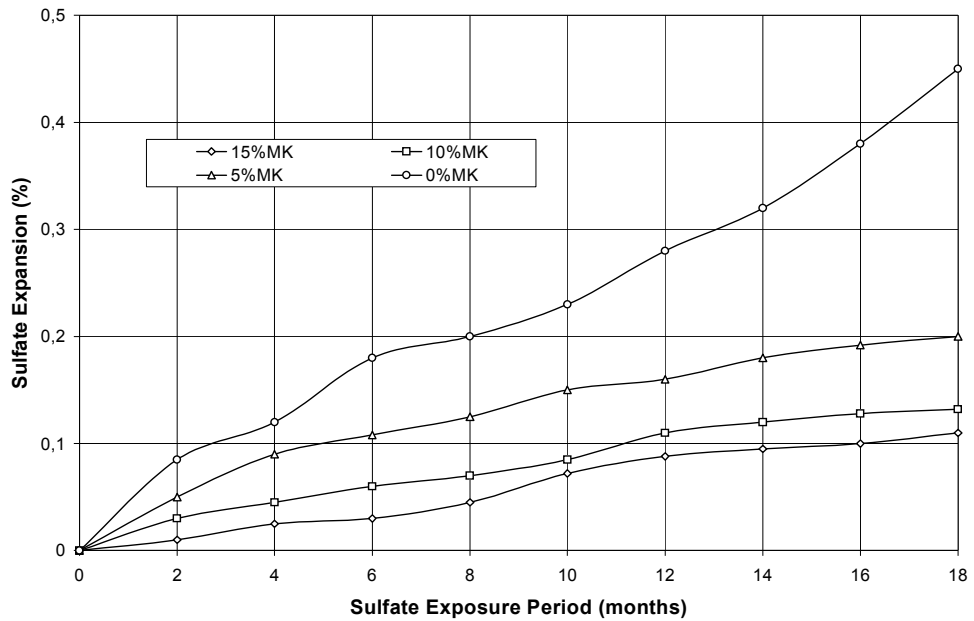
Figure 2.14 Effect of MK replacement level on the variation of sulfate

expansion with sulfate exposure period at w/b ratio of 0.60 [49]

The study showed that MK replacement of cement increased the sulfate resistance of concrete. The sulfate resistance of MK concrete increased with increasing the MK replacement level. As it seen from Figures 2.15 and 2.16, the sulfate resistance of MK concrete at w/b ratio of 0.50 was found higher than that at w/b ratio of 0.60. Autoclaved MK concrete specimens showed superior sulfate resistance compared to the moist cured ones. The pore volume of the autoclaved MK concrete was found less than that of the moist cured MK concrete. The air entrained MK concrete showed higher improvement in the sulfate resistance than the non-air entrained MK concrete. However, the air entrained plain concrete showed lower improvement in the sulfate resistance than the non-air entrained concrete.
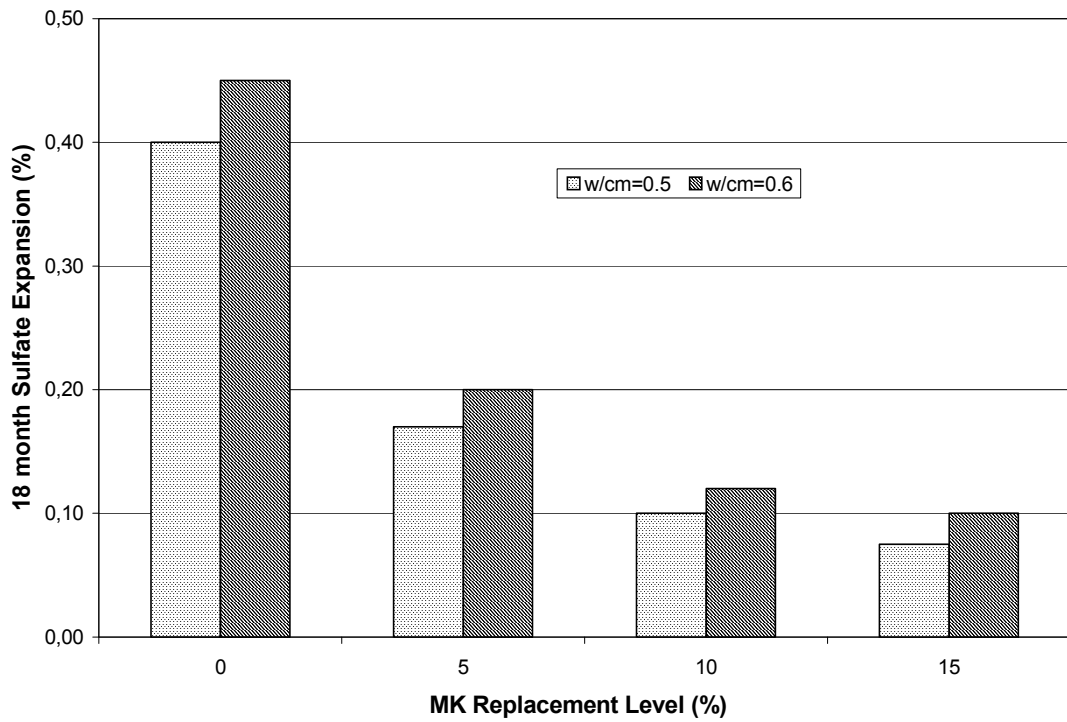
Figure 2.15 Effect of w/cm ratio on the 18 month sulfate expansion of MK concrete [49]
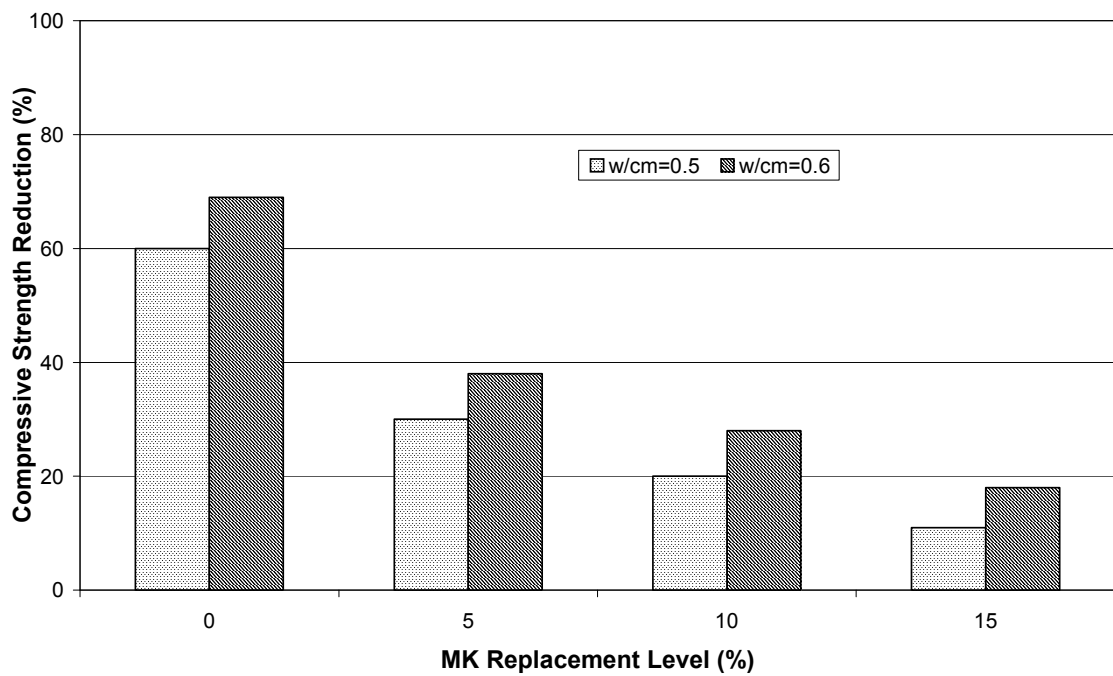
Figure 2.16 Effect of w/cm ratio on the compressive strength reduction of MK concrete [49]

Lee et al. [73] studied the effect of solution concentrations and replacement levels of metakaolin on the resistance of mortars exposed to magnesium sulfate solutions. In the study, the mortar and the paste specimens incorporating 0%, 5%, 10% and 15% metakaolin (MK) were prepared. The resistance of the mortar specimens was evaluated using visual examination, reduction in compressive strength and expansion measurements.

Results confirmed that the mortar specimens with a high replacement level of metakaolin showed lower resistance to a higher sulfate concentration of magnesium solution. However, in a lower concentration, there were no visibly remarkable differences in the deterioration of mortar specimens, even up to 360 days of exposure, regardless of replacement levels of metakaolin. It is concluded that it is necessary to pay special attention when using metakaolin in concrete exposed to highly concentrated magnesium sulfate solution.

Effect of solution concentrations and MK replacement levels on the reduction in the compressive strength of mortar specimens exposed to magnesium sulfate solutions is shown in the Figure 2.17 below.

Some works have reported that MK improves the sulfate resistance of concrete. However, there are also different conclusions in literature. Information about the behaviour of metakaolin-modified concrete under the effect of sulfate ions is still limited and somewhat contradictory, which retards its application in the construction practice.
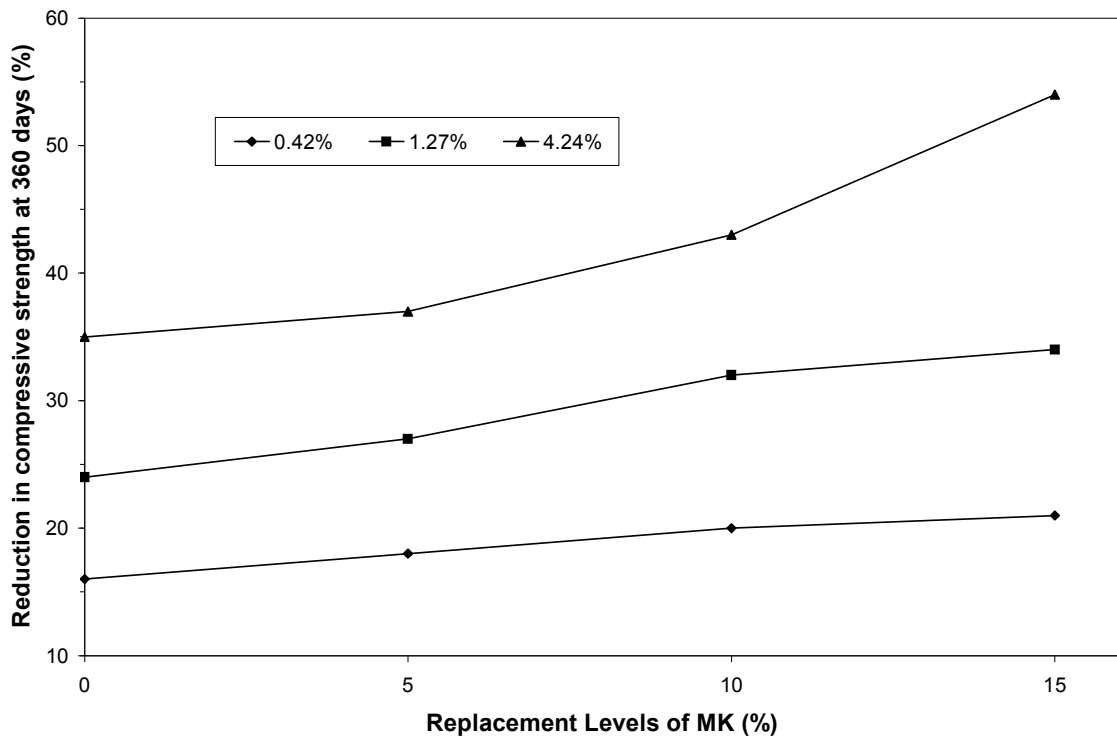
Figure 2.17 Effect of solution concentrations and MK replacement levels on the reduction in the compressive strength of mortar specimens exposed to magnesium sulfate solutions [73]

2.3.4.7 Alkali-Silica Reaction

Alkali silica reaction is a heterogeneous chemical reaction which takes place in aggregate particles between the alkaline pore solution of the cement paste and silica in the aggregate particles. Hydroxyl ions penetrate the surface regions of the aggregate and break the silicon-oxygen bonds. Positive sodium, potassium, and calcium ions in the pore liquid follow the hydroxyl ions so that electro neutrality is maintained. Water is imbibed into the reaction sites and eventually alkali-calcium silica gel is formed.

The reaction products occupy more space than the original silica so the surface reaction sites are put under pressure. The surface pressure is balanced by tensile stresses in the center of the aggregate particle and in the ambient cement paste. At a certain point in time, the tensile stresses may exceed the tensile strength and

eventually brittle cracks propagate. The cracks radiate from the interior of the aggregate out into the surrounding paste.

The cracks are empty (not gel-filled) when formed. Small or large amounts of gel may subsequently exude into the cracks. Small particles may undergo complete reaction without cracking. Formation of the alkali silica gel does not cause expansion of the aggregate. Observation of gel in concrete is therefore no indication for that the aggregate or concrete would crack [76].

Ramlochan et al. [55] used high reactivity metakaolin (HRM) with 0-20% replacement levels in concrete and mortar prisms to observe the expansion due to alkali-silica reaction (Figure 2.18).
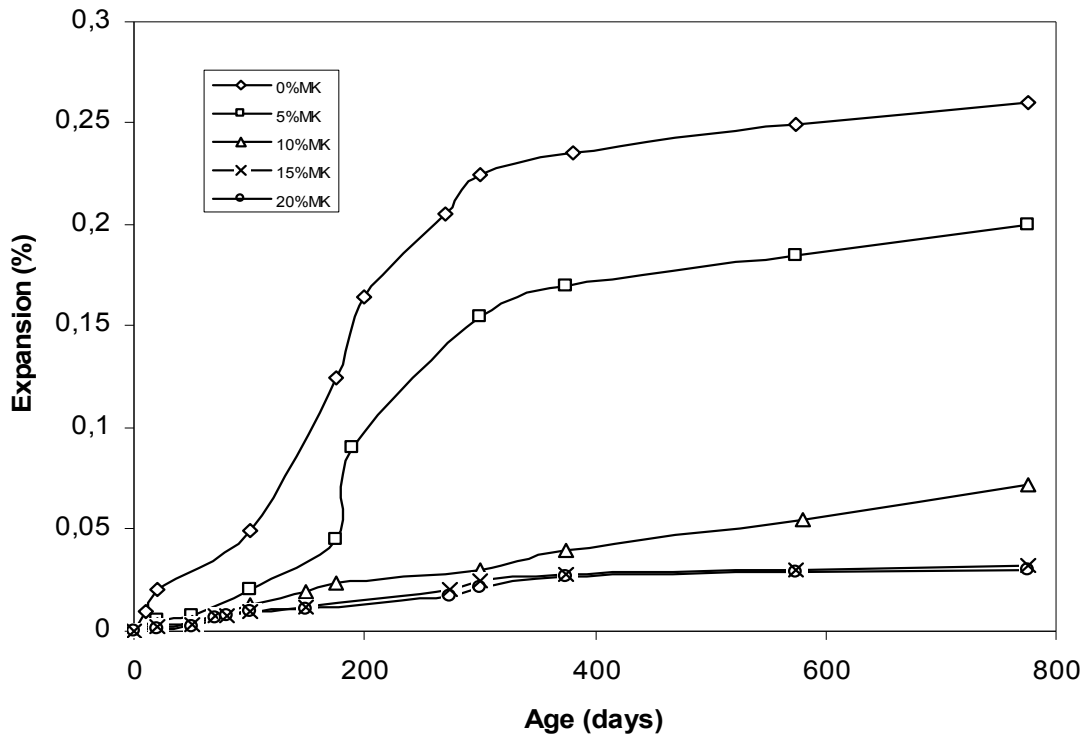
(a
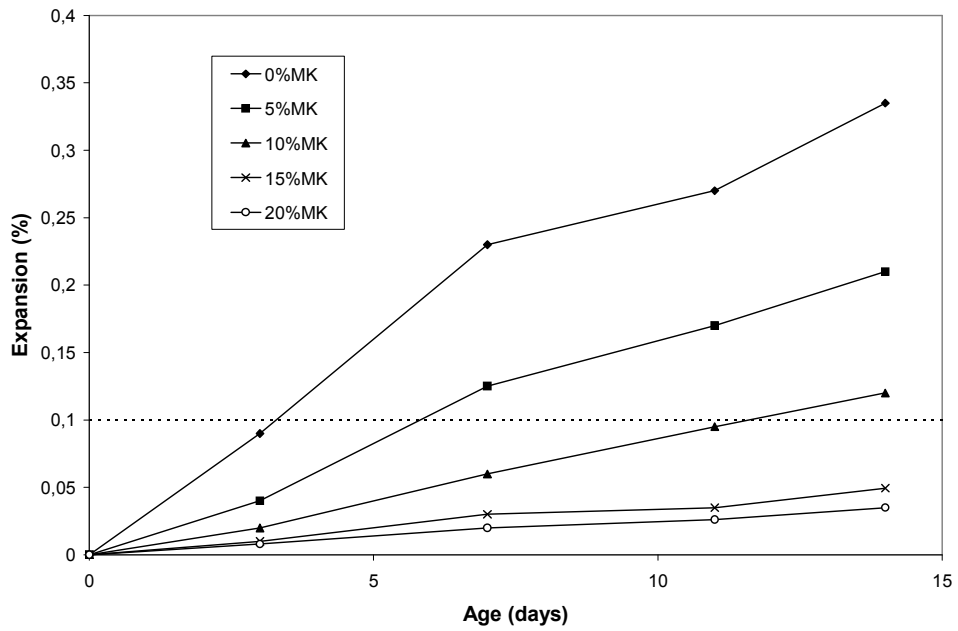
(b

Figure 2.18 Expansion evolution of (a) concrete prisms, (b) mortar bars containing
high-reactivity-metakaolin and cement [55]

The aim of their study is to evaluate the efficacy of a commercial grade of HRM in controlling the expansion due to ASR. Two laboratory test methods were performed to determine the minimum effective level of HRM required as a partial cement replacement to control deleterious expansion in the presence of reactive aggregates. The results of the expansion tests are compared to the chemistry of expressed pore solutions to help elucidate the mechanisms by which HRM may suppress expansion.

At the end of tests, they reported the following conclusions;

- The alkali concentration of the pore solutions expressed from the pastes was significantly reduced when HRM was used to replace up to 20% of the OPC. The long-term hydroxyl ion concentration was reduced to below 0.2 mol/l for both moderate-alkali cement and high-alkali cement.

- Incorporation of HRM as a partial cement replacement between 10% and 15% may be sufficient to control deleterious expansion due to the alkali-silica reaction in concrete, depending on the nature of the aggregate.

- The mechanism by which HRM may suppress expansion due to alkali-silica reaction appears to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions.

3. EXPERIMENTAL STUDY

3.1 Materials

3.1.1 Cement

The cement used in this study is Portland cement (CEM I 42.5R) conforming to the Turkish standard TS EN 197-1 (which mainly based on the European EN 197-1). It has a specific gravity of 3.14 and a surface area (Blaine) of 327 m^2/kg. The physical and chemical properties of the cement used are given in Table 3.1. It was supplied by Adana Cement Factory.

3.1.2 Metakaolin

The metakaolin used in this study is a white powder with a Hunter L whiteness value greater than 90 (on a scale from "0-black" to "100-maximum whiteness"). It has a specific gravity of about 2.60, a specific surface area (Nitrogen BET Surface Area) of 8600 m^2/kg, and an average particle size less than 2 μm. Physical and chemical properties of MK used in this study are given in Table 3.1. The origin of the raw material is from India.

3.1.3 Aggregate

Both fine and coarse aggregates were used to produce the plain and metakaolin modified concrete. The fine aggregate was a mix of river sand and crushed sand whereas the coarse aggregate was a river gravel with a maximum particle size of 16 mm. Both aggregates were obtained from local sources. Properties of the aggregates are presented in Table 3.2. Grading of the aggregates is shown in the Figure 3.1.

Table 3.1 Chemical compositions and physical properties of Portland cement and metakaolin

Item	Portland cement	Metakaolin
SiO_2 (%)	19.73	51.8
Al_2O_3 (%)	5.09	45.8
Fe_2O_3 (%)	3.99	0.35
CaO (%)	62.86	0.01
MgO (%)	1.61	0.03
SO_3 (%)	2.62	-
Na_2O (%)	0.18	0.13
K_2O (%)	0.80	0.06
Cl^- (%)	0.01	-
Insoluble residue (%)	0.24	-
Loss on ignition (%)	1.90	0.91
Free lime (%)	0.57	-
Specific gravity (g/cm^3)	3.14	2.60
Setting time, Vicat needle Initial/Final (h-min)	2-46/3-44	-
Le chatelier (mm)	1	-
Specific surface area (m^2/kg)	327 (Blaine)	8600 (BET)
Color	Gray	White

Table 3.2 Sieve analysis and physical properties of aggregates

Sieve size (mm)	Fine aggregate		Coarse aggregate	
	River sand	Crushed sand	No I	No II
16.0	100	100	100	100
8.0	100	100	31.5	1.9
4.0	86.6	95.4	1.0	1.1
2.0	56.7	63.3	0.5	1.0
1.0	37.7	39.1	0.5	0.9
0.50	25.7	28.4	0.5	0.9
0.25	6.7	16.4	0.4	0.8
Fineness modulus	2.87	2.57	5.66	5.93
Specific gravity	2.66	2.45	2.72	2.73
Absorption, %	0.55	0.92	0.45	0.42
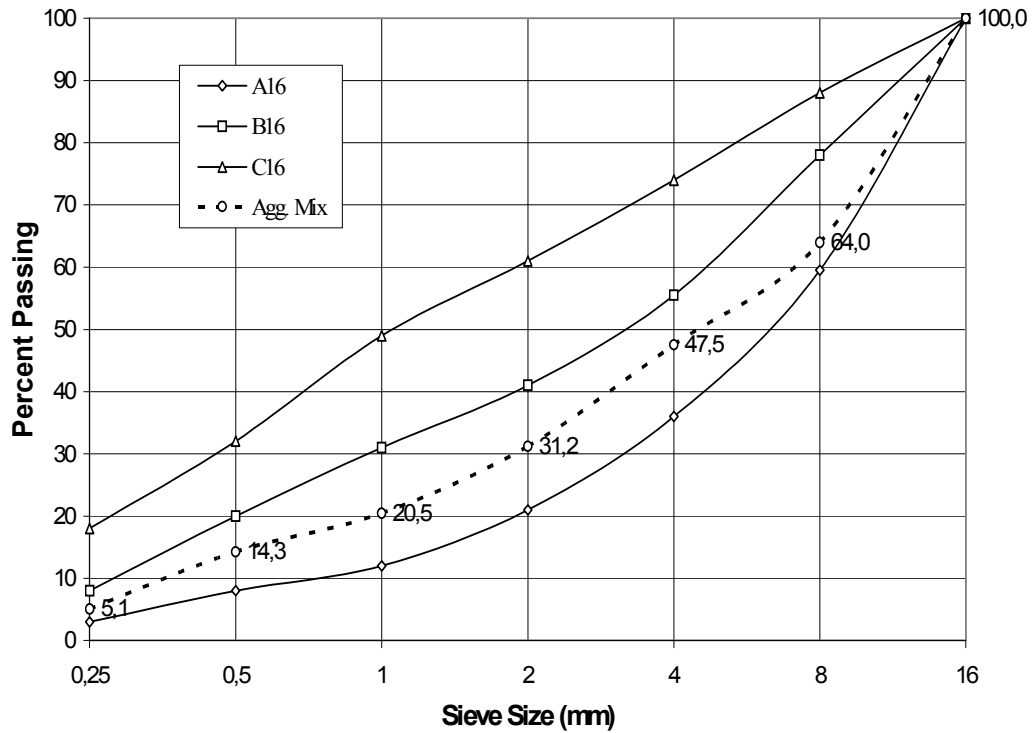
Figure 3.1 Aggregate grading curve and zones

3.1.4 Superplasticizer

A commercially available sulphonated naphthalene formaldehyde-based superplasticizer was used to give a consistent workability. The properties of the superplasticizer are given in Table 3.3. It was supplied by Grace Chemical Corp.

Table 3.3 Properties of the superplasticizer

Color	Dark brown
State	Liquid
Specific gravity (g/cm^3)	1.22
Freezing point	-4 ^{o}C
Chloride content	None
Nitrate content	None

3.1.5 Industry Salt and Sulfate

Industry type sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) were utilized in the preparation of 4% NaCl and 10% Na_2SO_4 solutions for the exposure conditions, respectively.

3.2 Details of Concrete Mixtures

Two series of control mixtures with w/cm ratios of 0.35 (Series 1) and 0.55 (Series 2) were designed. To develop the metakaolin-modified concrete mixtures, the Portland cement was partially replaced with 10% and 20% metakaolin (by weight) for both series. Thus, totally six different mixtures were prepared in this study. Details of the mixtures are given in Table 3.4. Grading of the aggregate mixture was kept constant for all concretes. The mixtures given in Table 3.4 were designed to have slump values of 140 ± 20 mm and 180 ± 20 mm for w/cm ratios of 0.35 and 0.55, respectively for the ease of handling, placing, and consolidation. The superplasticizer was added at the time of mixing to achieve the specified slump at each w/cm ratio.

3.3 Casting and Curing Conditions of Test Specimens

All concretes were mixed in accordance with ASTM C192 standard in a power-driven revolving pan mixer. Specimens cast from each mixture consisted of eighteen 100x100x100 mm cubes for compressive strength testing, eighteen 100x100x100 mm cubes for sorptivity and water absorption tests, two 100x100x500 mm prisms for chloride ion permeability test, ninety 100x100x100 mm cubes for sulfate resistance measurements. To monitor the free shrinkage and weight loss, two 70x70x280 mm prisms from each mixture were also cast. All specimens were poured into the steel moulds in two layers, each of which being vibrated for a couple of seconds. After casting, except for the shrinkage specimens, all the other moulded specimens were covered with a plastic sheet and left in the casting room for 24 hr. They were then demoulded and divided into two equal groups. Then, two different curing regimes (water-curing and air-curing) were applied. Thereafter, they were tested in accordance with the specified test methods. Curing regimes for the test specimens are;

a) **Air curing (AC):** specimens were left to cure continuously in the laboratory under ambient condition until the test age. The temperature was moderately controlled at 20 ^{o}C, but humidity was uncontrolled and generally ranged between 50 to 80%. Specimens were designated as AC and are called air-cured at ambient temperature.

b) **Water curing (WC):** specimens were left to cure continuously in water at 20 ± 2 ^{o}C until the test age. Specimens were designated as WC and are called water-cured at controlled temperature.

Moreover, drying shrinkage specimens were cured for 24 h at 20 ^{o}C and 100% relative humidity and were then demoulded. After that, the specimens were exposed to drying in a humidity cabinet at 23 ± 2 ^{o}C and 50 ± 5% relative humidity, as per ASTM C157 for about 60 days.

Table 3.4 Mixture proportions of the concrete in kg/m^3

Materials		Concrete series					
		Series 1 (w/cm=0.35)			Series 2 (w/cm=0.55)		
		MK0	MK10	MK20	MK0	MK10	MK20
Cement		450	405	360	350	315	280
Metakaolin		0	45	90	0	35	70
Water		158	158	158	193	193	193
Fine Aggregate	River sand	724	720	717	726	723	721
	Crushed sand	233	232	231	234	233	232
Coarse Aggregate	No I	611	608	605	612	610	608
	No II	241	240	239	242	241	240
Superplasticizer		7.9	10.1	12.4	3.5	4.4	6.1

3.4 Test Procedures

3.4.1 Compressive Strength

The concrete cubes (100x100x100 mm) were used for the compressive strength test at various ages. The compression test was carried out on the specimens by a 3000 kN capacity testing machine. The test procedure followed during the test was in conformity with ASTM C39. Three specimens from each mixture were tested at each testing age. The test was performed at the ages of 28, 90, and 120 days.

3.4.2 Sorptivity

The sorptivity test measures the rate at which water is drawn into the pores of concrete. For this, three test specimens having a dimension of 100x100x100 mm were employed. The specimens were dried in an oven at about 50 ^{o}C until constant mass and then allowed to cool to the ambient temperature in a sealed container. Afterwards, the sides of the specimens were coated by paraffin and as shown in Figure 3.2, the sorptivity test was carried out by placing the specimens on glass rods in a tray such that their bottom surface up to a height of 5 mm is in contact with water. This procedure was considered to allow free water movement through the bottom surface. The total surface area of water within the tray should not be less than 10 times that of the specimen cross-sectional area. The specimens were removed from the tray and weighed at different time intervals up to 1 hour to evaluate mass gain. The volume of water absorbed was calculated by dividing the mass gained by the nominal surface area of the specimen and by the density of water. These values were plotted against the square root of time. The slope of the line of the best fit was defined as the sorptivity coefficient of concrete. For each test, the measurements were obtained from three specimens and the average values were reported. The test was conducted at the ages of 28, 90, and 120 days.
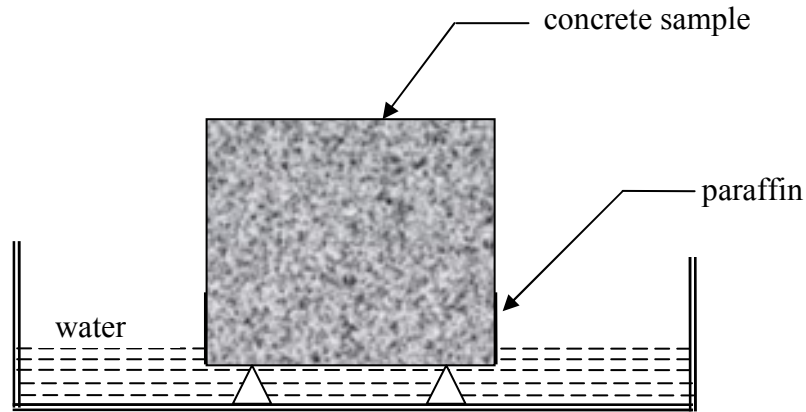
Figure 3.2 Measurement of concrete sorptivity

3.4.3 Water Absorption

Water absorption (WA) by total immersion is generally measured by drying a specimen to constant mass, immersing it in water for a specific time and measuring its increase in mass as a percentage of the dry mass [57]. In this study the specimens, after sorptivity test, were left in water for three days and then removed from water to measure surface dry saturated weight (W_1). Then, they were put in oven and kept under 100 ± 5 °C temperature until they reached a constant mass. Oven dry weights (W_2) of the specimens were recorded and water absorption for each sample is calculated (Eqn 3.1). Water absorption value for each sample group is an average of three specimens. The test was conducted at the ages of 28, 90, and 120 days.

$$WA \ (\%) = \frac{W_1 - W_2}{W_2} \times 100 \qquad \text{(Eqn 3.1)}$$

3.4.4 Chloride Ion Penetration

The prismatic test specimens (100x100x500-mm) after being subjected to 28 days of initial curing procedures were soaked continuously in 4% NaCl solution for 90 days. During the 90-day chloride exposure period, the test specimens were withdrawn from the soaking tank (at 7, 14, 28, 56, and 90) to determine the depth of chloride penetration into the plain and the metakaolin-modified concretes. For this purpose, the prisms were first split at mid point and the freshly split surfaces were soon

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sprayed with 0.1N silver nitrate (AgNO₃) solution. The AgNO₃ solution preferentially reacts with the free chloride present in the harden matrix to form a white precipitate of silver chloride (AgCl); whereas at greater depths, where free chlorides are absent, AgNO₃ reacts with the hydroxides to form a brown precipitate of silver oxide (AgO). Thus, the depth of chloride penetration is clearly indicated as the boundary of color change. View of the boundary of color change after spraying AgNO₃ solution for the plain and the metakaolin-modified concrete specimens is illustrated in Figure 3.3.The white coloring (formation of silver chloride) occurs wherever the concentration of free chloride ion is greater than 0.15% by weight of cement. Measuring the depth of color change was performed from the four sides of the split section at intervals of 20 mm. Measurements made close to the corners of the section and ahead of the coarse aggregates were ignored. The test method followed in the present investigation to determine the depth of chloride penetration is reliable and accurate, and has also been recommended by other researchers [78,79,83,84]

a)   b)
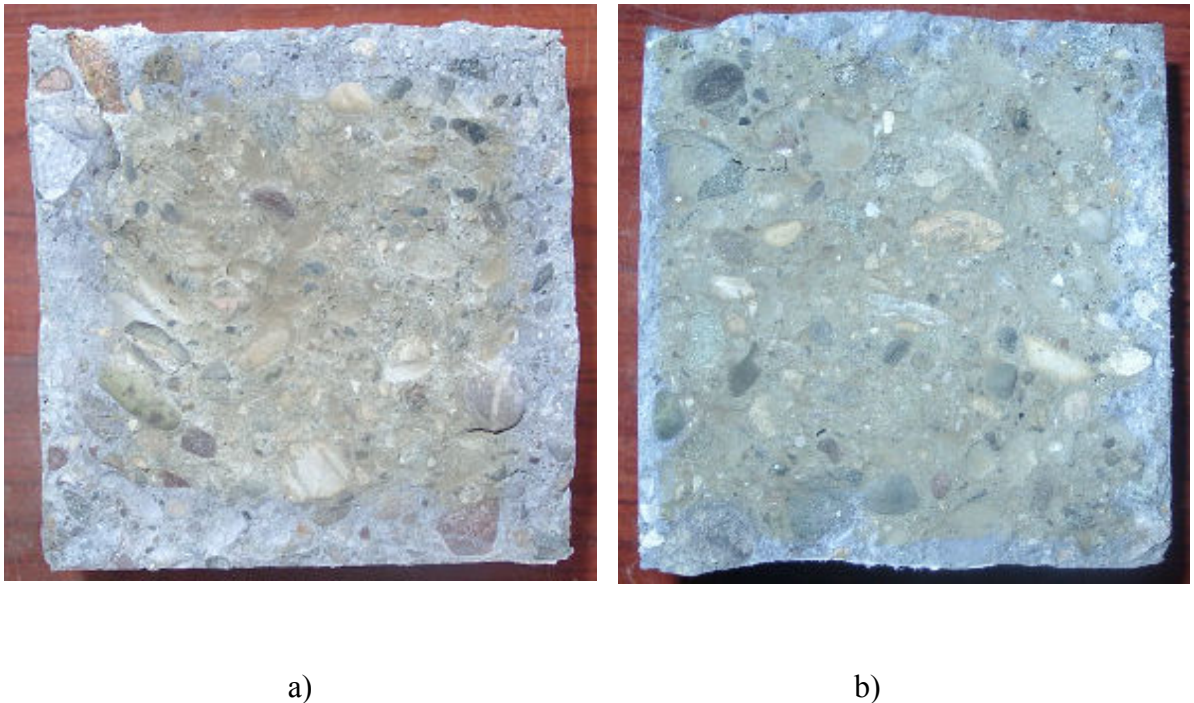
Figure 3.3 Photographs showing the typical boundary of color change on the specimens after the 28 day chloride exposure period a) plain concrete (MK0) and b) metakaolin concrete (MK20)

3.4.5 Drying Shrinkage and Weight Loss

Free shrinkage test specimens having a dimension of 70x70x280 mm for each mixture were cured for 24 h at 20 ^{o}C and 100% relative humidity and then were demoulded. After that, the specimens were exposed to drying in a humidity cabinet at 23 ± 2 ^{o}C and 50 ± 5% relative humidity, as per ASTM C157 for about 60 days. The length change was measured by means of a dial gage extensometer with a 200 mm gage length. The shape of the shrinkage specimens as well as the location of the reference pins are shown in Figure 3.4. Measurements were carried out every 24 h for the first 3 weeks and then 3 times a week. At the same time, weight loss measurements were also performed on the same specimens. Variations in the free shrinkage strain and the weight loss were monitored during the 60-day drying period (at 23 ± 2 ^{o}C and 50 ± 5% relative humidity) and the average of two prism specimens were used for each property.
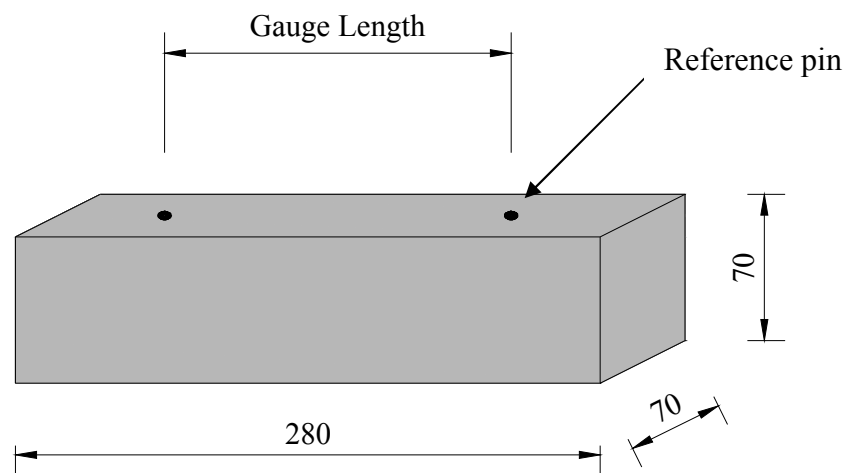
Figure 3.4 Shrinkage sample

3.4.6 Sulfate Resistance

To evaluate the resistance of the proposed mixtures to sulfate attack, 100x100x100 cube specimens were used. After 28-day initial curing conditions of AC and WC, the specimens were transferred into tap water, 10% sodium sulfate solution, and 10% sodium sulfate solution with drying-immersion cycles at laboratory temperature. Drying-immersion cycles were conducted each 10 days. This type of testing

condition is considered as an accelerated testing procedure, which indicates the performance of a particular concrete mixture to sulfate attack under wetting and drying cycles. Compressive strength, weight loss, and UPV tests were used to evaluate the degree of sulfate attack for all samples after 60, 90, 180, 270, 365 days from the beginning of the exposure period. Visual inspection of concrete specimens to cracks was also observed at each testing time. The compressive strength loss may be calculated through the Eqn. 3.2.

$$\text{CSL (\%)} = \frac{\sigma_m - \sigma_s}{\sigma_m} \times 100 \qquad \text{(Eqn. 3.2)}$$

Where σ_m is the average compressive strength (in MPa) of three concrete cubes subjected to initial AC or WC for specified periods and σ_s is the average compressive strength (in MPa) of three concrete cubes exposed to sulfate attack in the form of permenant exposure or drying-immersion cycle.

3.4.7 Mercury Intrusion Porosimetry

The tests of pore structure of the concrete samples were conducted at the age of 120 days using a mercury intrusion porosimetry (MIP). More specifically, the porosity of the specimen, as well as its pore size distribution was measured. For this, the samples without coarse aggregate for microstructure testing were separated from the concrete cube specimens after the compressive strength testing due to the limitation of sample size for the porosimeter. The samples were dried at about 105 $^{\circ}$C before mercury intrusion porosimeter test. The samples were subjected to a maximum pressure of up to 227 MPa. A cylindrical pore geometry, a constant contact angle of 140°, and a constant surface tension of 483 dynes/cm were assumed [77,78]. The mercury intruded pore diameter d at a pressure of P was calculated by using the following equation [78]:

$$d = -(1/P)4\gamma\cos\theta \qquad \text{(Eqn. 3.2)}$$

where d is the pore diameter (μm), P is the applied pressure (MPa), γ is the surface tension of mercury (dynes/cm), and θ is the contact angle (degree).

4. TEST RESULTS AND DISCUSSIONS

4.1 Compressive Strength

The data concerning the variation of compressive strength with w/cm ratio, concrete age, and curing condition for concretes incorporated with 0%, 10%, and 20% MK are given in Table 4.1. The strength values for the plain and metakaolin-modified concretes ranged from 36.1 to 76.8 MPa and from 37.4 to 98.5 MPa, respectively. The effect of MK on compressive strength of concrete is well observed in Figure 4.1. The figure indicated that there was a systematic increase in compressive strength with the increase in MK content. This is more pronounced for concretes subjected to water curing (WC). The degree of strength enhancement (due to MK) is in direct relation to the parameters of age, curing condition, and the amount of MK used. MK not only increases the 28-day strength of concrete but also increases the later strengths (90 and 120 days). For example, the increase in compressive strength with increasing age reached approximately 11% and 20% at 90 days for the plain and metakaolin-modified concretes, respectively, depending mainly on the MK content. In the study of Poon et al. [58], the strength properties of the high performance metakaolin and silica fume was also investigated. Regarding the use of MK, they demonstrated that MK concretes had relatively higher strength development than control concretes. It was reported that the ratio of the 90 day compressive strength to the 28 day compressive strength for the MK concretes was found as up to 1.18, depending mainly on replacement level of MK and w/cm ratio.

It was also noted that for both w/cm ratios, the concretes with MK had remarkably higher compressive strength than the plain concretes. The percent increase in the strength with the use of MK ranged from approximately 10% to 30% for the water-cured concretes but from 2% to 17% for the air-cured concretes, depending mainly on the variation in w/cm ratio, age, and replacement level of MK. The addition of metakaolin into the matrix improves the bond between the cement paste and aggregate particles as well as increasing the density of the cement paste which in turn significantly improves the compressive strength of the concretes. According to the

literature, the main factors that affect the contribution of metakaolin in the strength are a) the filling effect, b) the dilution effect, and c) the pozzolanic reaction of metakaolin with CH [17].

The effect of curing procedures on the 28, 90, and 120-day compressive strength of the plain and the metakaolin-modified concretes is illustrated in Figure 4.2. For both concrete types, air curing (AC) resulted in significantly lower 28, 90 and 120-day strengths as compared to water curing (WC). It was observed that the ratios for the plain and metakaolin-modified concretes subjected to AC did not fall within 10% of equality and deviated up to approximately -28% and -35% from those cured under WC, respectively. This implies that the reduction in strength is particularly large for concretes with MK, especially at later ages (90 and 120 days). For inadequate curing (air curing, AC), the absence of moist curing resulted in lower strengths where the concrete containing MK suffered more at all testing ages. This can be attributed to the lack of development of hydration and pozzolanic reactions to produce a dense microstructure as well as the extensive shrinkage cracking, which may have developed due to continuous air curing which has also been indicated by other researchers [29, 38, 51].

Table 4.1 Compressive strength values of plain MK modified concretes at the ages 28, 90 and 120 days

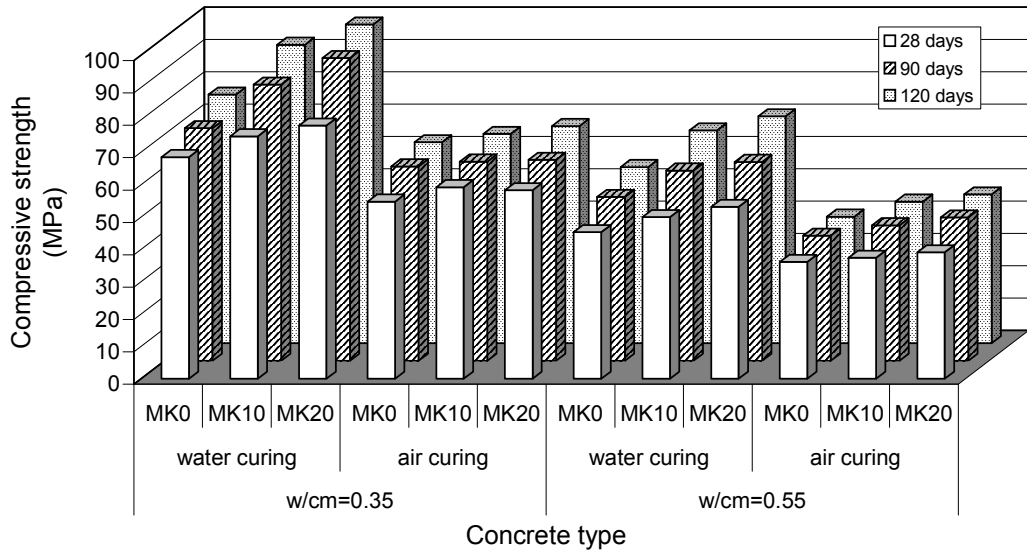| w/cm	Curing regime	Replacement level of MK	Compressive strength (MPa)		
			28 days	90 days	120 days
0.35	WC	0%	68.5	72.0	76.8
		10%	74.9	85.4	92.2
		20%	78.2	93.6	98.5
	AC	0%	54.8	60.1	62.1
		10%	59.3	61.6	64.7
		20%	58.3	62.2	67.1
0.55	WC	0%	45.3	50.7	54.4
		10%	50.0	58.8	65.7
		20%	53.1	61.5	70.1
	AC	0%	36.1	38.7	39.1
		10%	37.4	41.9	43.7
		20%	39.1	44.3	45.9

Figure 4.1 Variation in compressive strength of plain and metakaolin modified
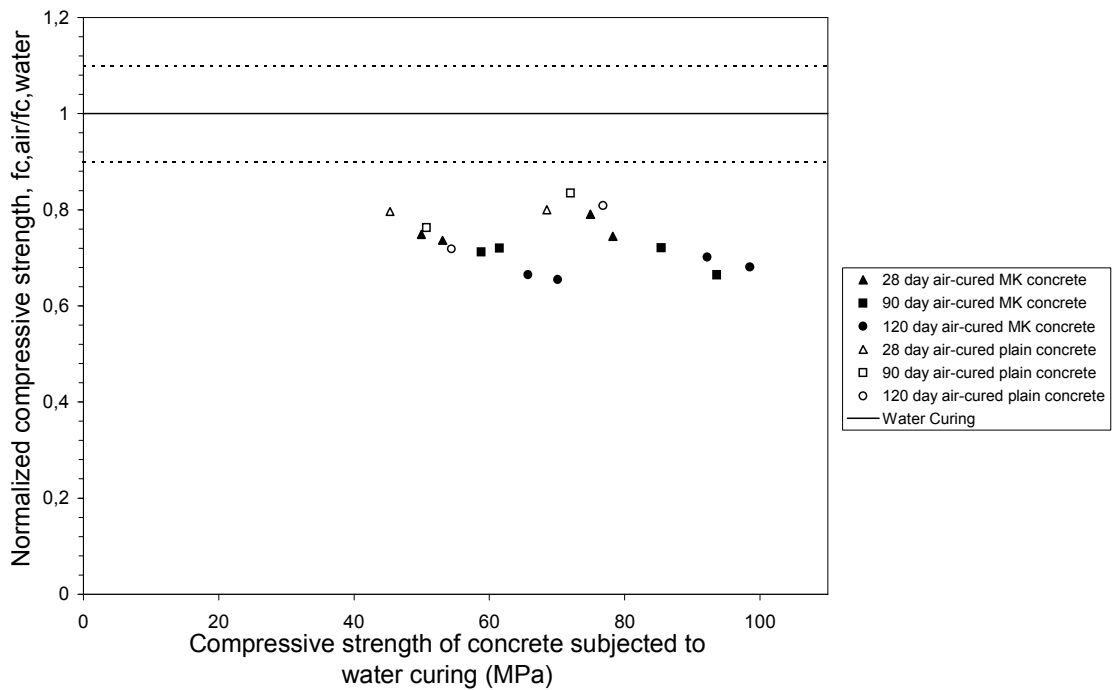concretes subjected to different curing regimes

Figure 4.2 Influence of curing condition on 28, 90 and 120 day compressive
strengths of concretes incorporated with or without metakaolin

4.2 Sorptivity

The change in sorptivity with w/cm ratio, concrete age, and curing condition for the plain and metakaolin-modified concretes are given in Table 4.2 and plotted in Figure 4.3. It is apparent that sorptivity decreases systematically with an increase in curing period (from 28 to 120 days), and the gradients of the sorptivity tends to decrease with increase in the replacement level of MK. At early age (28 days), the sorptivity values are clearly reflected in the strength values. Thus, the concretes with the lowest sorptivities have the highest strengths, especially for those subjected to water curing regime. Increasing the MK content reduced the 28-,90-, and 120-day sorptivities of the concrete. This is particularly for the high w/cm ratio water-cured concretes. The sorptivity values of the concrete containing MK were approximately from 2% to 36% and from 8% to 60% lower than that of the plain concretes at 28 and 90 days, respectively, depending on w/cm ratio, amount of MK used, and curing regime. At later age (120 days), the range determined for 90 days was almost unchanged (7-62%). Generally, metakaolin concrete performed better than the control concrete and marked improvements in terms of lower rate of water penetration through capillary suction were apparent, particularly under water curing condition. This reduced sorptivity reflects a finer pore structure that would, for example, inhibit ingress of aggressive elements into the pore system [72]. Taşdemir [38] have also shown that type and fineness of mineral admixtures (such as fly ash, limestone filler, sandstone filler, and silica fume) together with curing condition affect greatly the pore structure of concrete and it was reported that a significant reduction in sorptivity for the blended mixtures was obtained when the proper curing was applied.

A comparison of air-cured and water-cured concrete sorptivity with age for the plain and metakaolin-modified concretes is given in Figure 4.4. The figure distinguishes the prevailing effect of water curing on the metakaolin specimens, especially tested at later age (120 days). It was noted that air curing caused significant increase in sorptivity of both plain and especially metakaolin concretes as compared to water curing. Results showed that ratios for plain and metakaolin concrete specimens under air curing condition lied within a range of 1.2 to 1.5 and 1.4 to 3.2, respectively. This implies that MK concretes are very sensitive to curing method adopted. Figure 4.4 also revealed that there is a marked difference in sorptivity values for the plain and

metakaolin-modified concretes at 120 days as a result of pozzolanic reaction which effectively reduces the volume of pore space.

Table 4.2 Sorptivities of plain and MK modified concretes

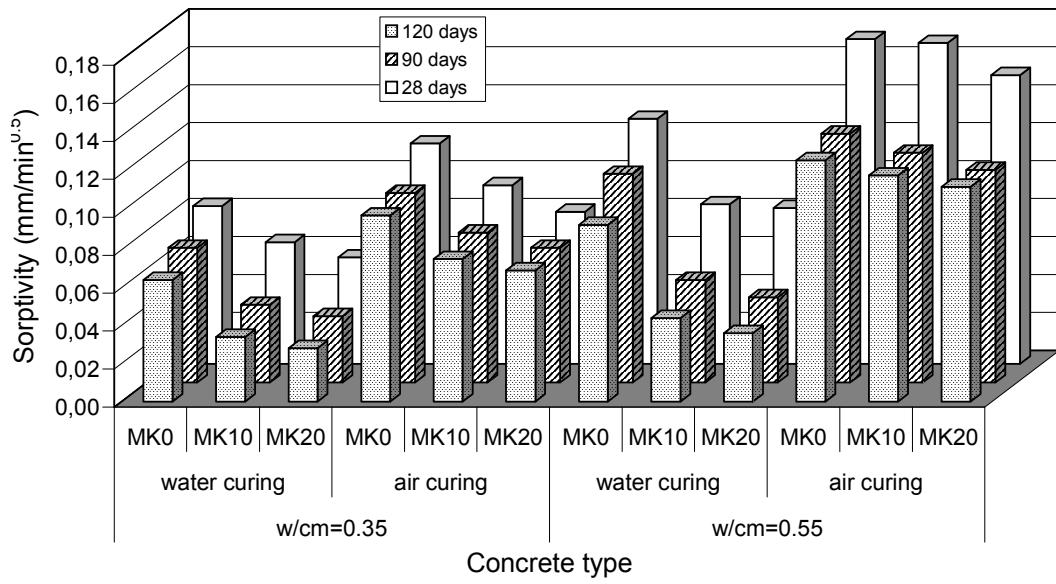| w/cm	Curing regime	Replacement level of MK	Sorptivity (mm/min$^{0.5}$)		
			28 days	90 days	120 days
0.35	WC	0%	0.083	0.071	0.064
		10%	0.064	0.041	0.034
		20%	0.056	0.035	0.028
	AC	0%	0.116	0.100	0.098
		10%	0.094	0.079	0.075
		20%	0.080	0.071	0.069
0.55	WC	0%	0.129	0.110	0.093
		10%	0.084	0.054	0.044
		20%	0.082	0.045	0.036
	AC	0%	0.171	0.131	0.127
		10%	0.169	0.121	0.119
		20%	0.152	0.112	0.113

Figure 4.3 Variation in sorptivity of plain and metakaolin-modified concretes
subjected to different curing regimes
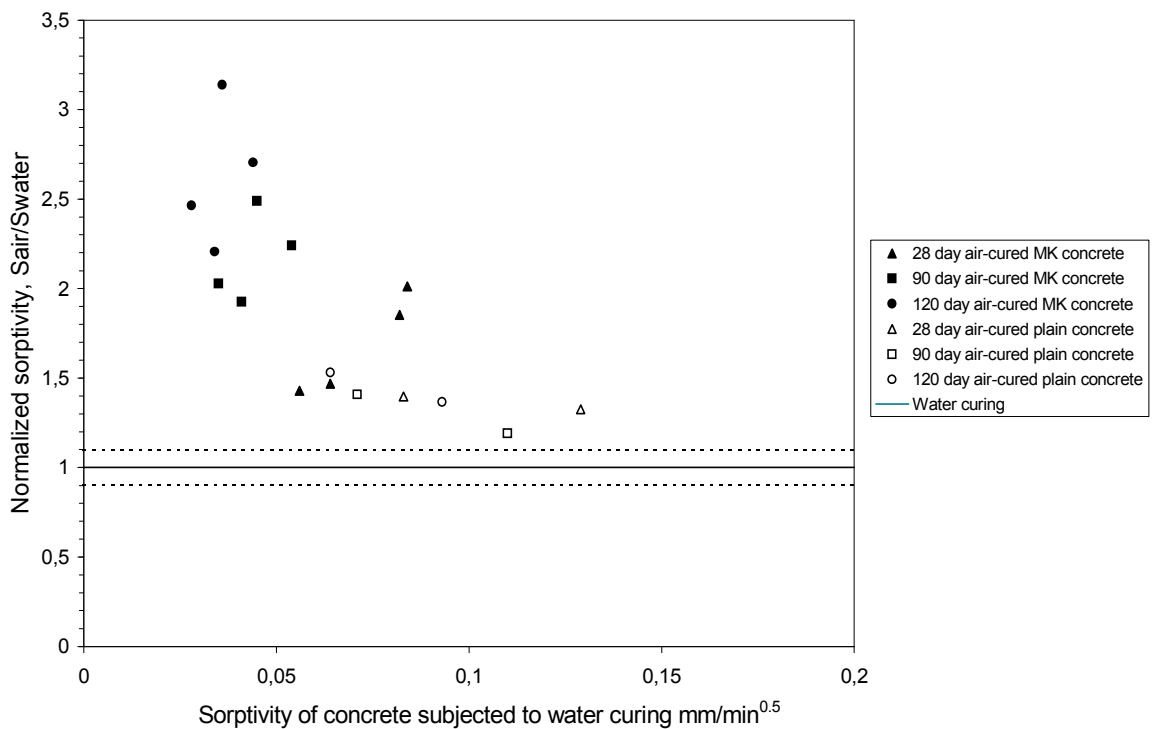
Figure 4.4 Influence of curing condition on 28, 90 and 120 day sorptivity coefficients
of concretes incorporated with or without metakaolin

4.3 Water Absorption

Table 4.3 shows water absorption (WA) values measured at 28, 90, and 120 days. It is clear from the table that water absorption decreases with increasing age and MK content. The tendency of the decrease can also be observed from Figure 4.5 as well. The water absorption of the concretes ranged from 2.0 to 7.3%, depending mainly on w/cm ratio, MK content, curing condition, and testing age. It was evident from Figure 4.5 that there was a systematic decrease in WA values due to the incorporation of MK, irrespective of w/cm ratio. This is more pronounced for the specimens subjected to WC. The percent reduction in WA values due to the inclusion of MK was in the ranges of 3-17% and 15-40% for the concretes subjected to AC and WC, respectively. However,in the study of Khatib and Clay [57] the WA of concrete by total immersion, is slightly increased in concrete containing MK. On the other hand, it was noted that the range of WA values was very narrow (4.2-5.1%).

A comparison of air-cured and water-cured concrete on WA with different test ages for the plain and metakaolin-modified concretes is given in Figure 4.6. The figure made a distinction on the prevailing effect of water curing, particularly on the metakaolin specimens. According to the results shown in the figure, the ratios for the plain and metakaolin concrete specimens under air curing condition lied within a range of 1.5 to 1.8 and 1.5 to 2.6, respectively. Figure 4.6 also indicated that there is a remarkable difference in WA values for the plain and metakaolin-modified concretes, especially at later ages (90 and 120 days).

Table 4.3 Water absorption values of plain and MK modified concretes

w/cm	Curing Regime	MK Replacement Levels	Water Absorption (%)		
			28 days	90 days	120 days
0.35	WC	0%	3.7	3.4	3.2
		10%	3.2	2.8	2.5
		20%	2.8	2.7	2.0
	AC	0%	5.7	5.4	4.9
		10%	5.4	4.9	4.5
		20%	5.3	4.5	4.6
0.55	WC	0%	4.8	4.0	3.8
		10%	4.7	3.0	2.6
		20%	3.9	2.8	2.4
	AC	0%	7.3	6.9	6.8
		10%	7.1	6.6	6.4
		20%	7.0	6.4	6.1
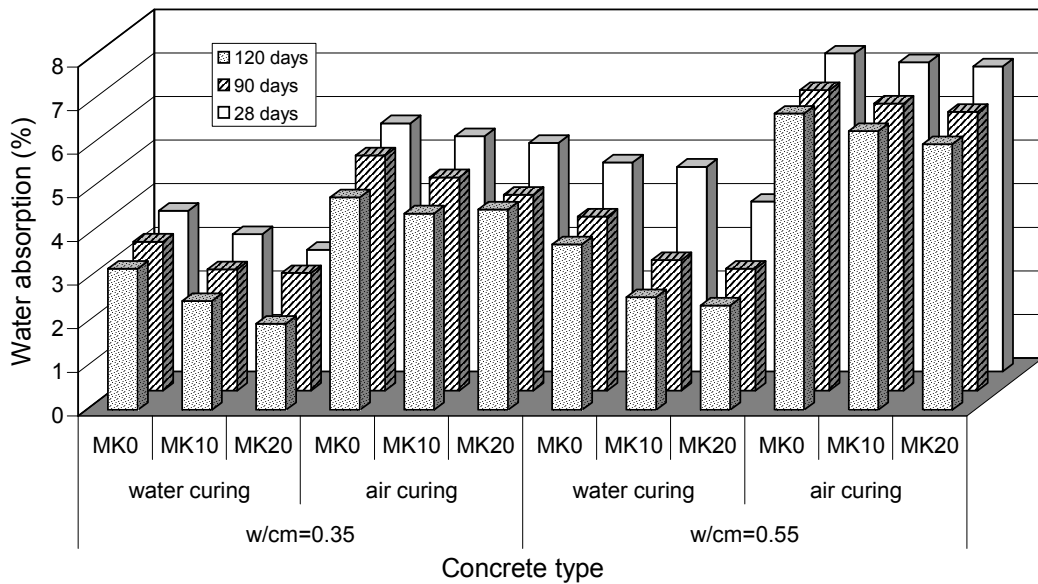
Figure 4.5 Variation in water absorption of plain and metakaolin-modified concretes to different curing regimes

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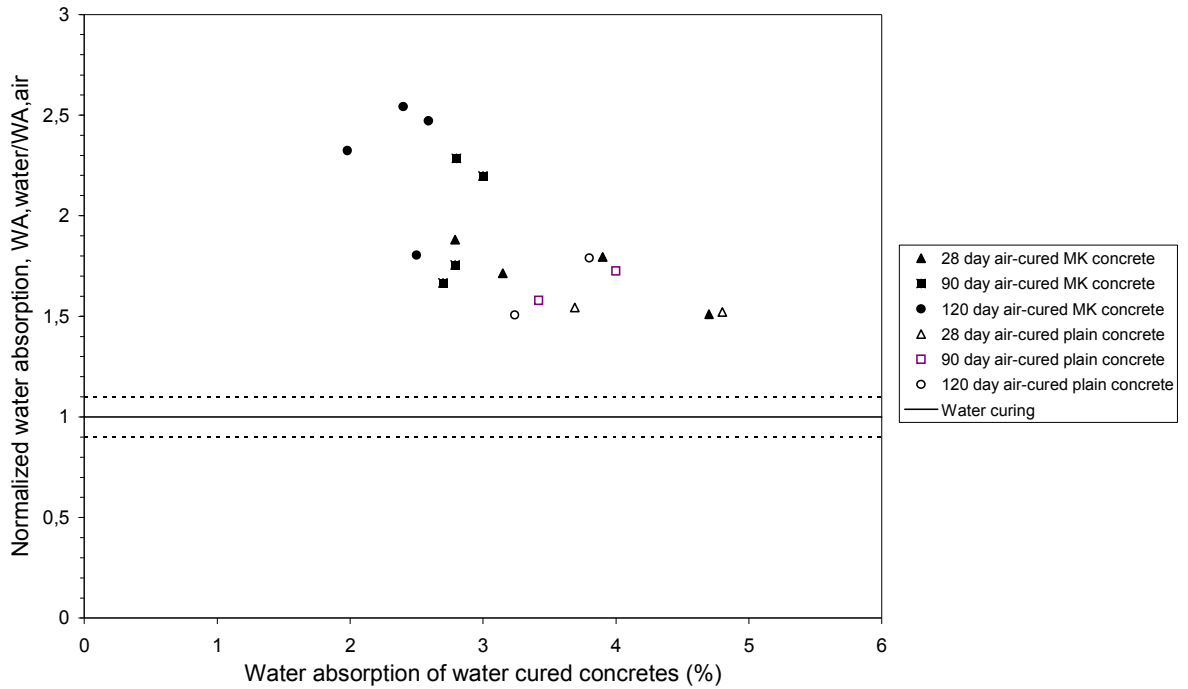
Figure 4.6 Influence of curing condition on water absorption of concretes
incorporated with metakaolin

4.4 Resistance to Chloride Ion Penetration

Figure 4.7 demonstrates the chloride penetration depth measured periodically (at 7, 14, 28, 56, and 90 days) through the plain and metakaolin-modified concretes subjected to two different initial curing followed by immersion in salt solution. Depths of chloride penetration for plain concretes subjected to the initial curing conditions of AC and WC were in the range of about 8 to 23 mm and 6 to 17 mm, respectively, depending mainly upon w/cm ratio and immersion period in salt solution. However, the concretes incorporating metakaolin had comparatively lower chloride penetration depths which ranged from 6 to 20 mm for the initial curing of AC and from 2 to 15 mm for the initial curing of WC. It was also observed that the chloride penetration depths of all concretes decreased with decreasing w/cm ratio from 0.55 to 0.35, irrespective of initial curing conditions. The effect of w/cm ratio was well observed at the end of the 7-day chloride exposure period for all initial curing conditions. The plain concretes with high w/cm ratio gave about 2.0 and 1.8 times greater chloride penetration depths than those with low w/cm ratio for the

initial curing conditions of AC and WC, respectively. However, these values for the metakaolin-modified concretes ranged from 1.7 to 2.3, depending on replacement level of MK and initial curing period. The order of the increase reduced with the increasing chloride immersion period (from 7 to 90 days) for both concretes. In addition, the test results exhibited that metakaolin-modified concretes had noticeably lower chloride penetration depth in comparison to the plain concretes during the 90-day chloride exposure period, particularly under the initial water curing condition. For example, at the end of the 90-day immersion period, the depth of chloride penetration for high and low w/cm ratio water-cured concretes containing 10% MK were approximately 7% and 10% lower than that of the control concrete at similar condition, respectively. However, those for concretes with 20% MK were about 17% and 21%. This result agrees well with the results from a previous study by Ding and Li [19]. They demonstrated that the incorporation of MK in concrete reduced the chloride diffusion rate significantly. It was concluded that 5% MK had some improvement on the chloride diffusivity while 15% MK has a significant improvement.

The chloride penetration depths measured for both plain and metakaolin-modified concrete specimens during the 90-day chloride exposure period were then used to compute the chloride penetration coefficient, K (mm per square root of week). The magnitudes of K were estimated by using the empirical relationship (Eqn. 3.1) between the depth of chloride penetration (X) and duration of immersion in salt solution (t) as proposed by Bakker [79].

$$X = a + K \sqrt{t} \qquad \text{(Eqn. 3.1)}$$

The chloride penetration coefficient, K, is used in the present investigation as an indicator of the resistance of concrete against chloride penetration. Several authors previously used the similar test method to calculate this parameter for comparing the resistance to chloride ion penetration of different mortars and concretes [80,81].

Figure 4.8 shows the chloride penetration coefficients (K) of all concretes. The figure indicated that for the plain and metakaolin-modified concrete specimens pre-cured for a similar condition, an increase in w/cm ratio leads to a larger K or faster rate of chloride penetration. Moreover, as expected, for the concretes of all w/cm ratios, K marginally decreased with improving pre-curing condition. For a given pre-curing condition and w/cm ratio of the mix, the magnitudes of K for the plain concrete specimens were also relatively higher compared to the corresponding K for the metakaolin-modified concrete specimens. It was also noted that increasing the replacement level of MK decreased considerably the chloride diffusivity. Moreover, graphs in Figure 4.8 showed that the concretes made with 20% MK had the lowest chloride penetration coefficient, irrespective of w/cm ratio and pre-curing condition.

The effect of initial curing condition on the chloride penetration coefficient of the plain and metakaolin-modified concretes is illustrated in Figure 4.9. Lack of proper curing produced similar effect on the chloride ingress to that on the sorptivity of concrete. Air curing leads to higher chloride penetration coefficient for both plain and especially MK concretes. It was observed that the ratio of the chloride penetration coefficient of the specimens pre-cured under air curing to those pre-cured under water curing for the plain concrete deviated up to 30%. However, this ratio for concretes containing MK lied within a range of 32 to 52%. This indicates that the chloride penetration of the concretes containing MK is more sensitive to the lack of curing. This is due to the change in hydration kinetics of total cementitious material and the hydration development at the curing cessation time [61].
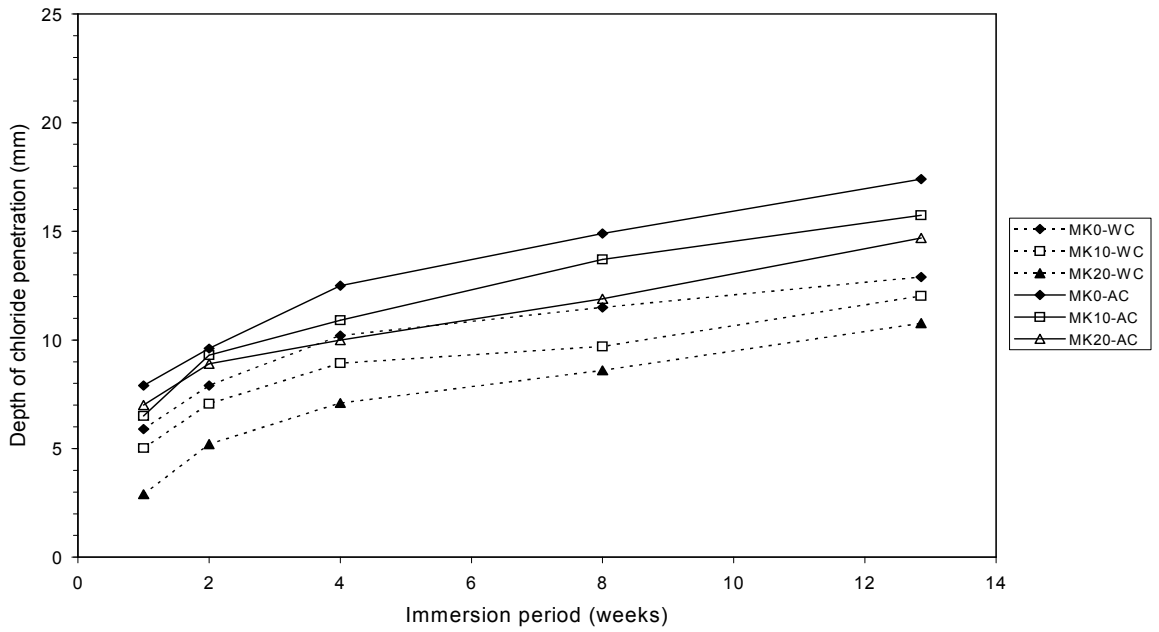
a)
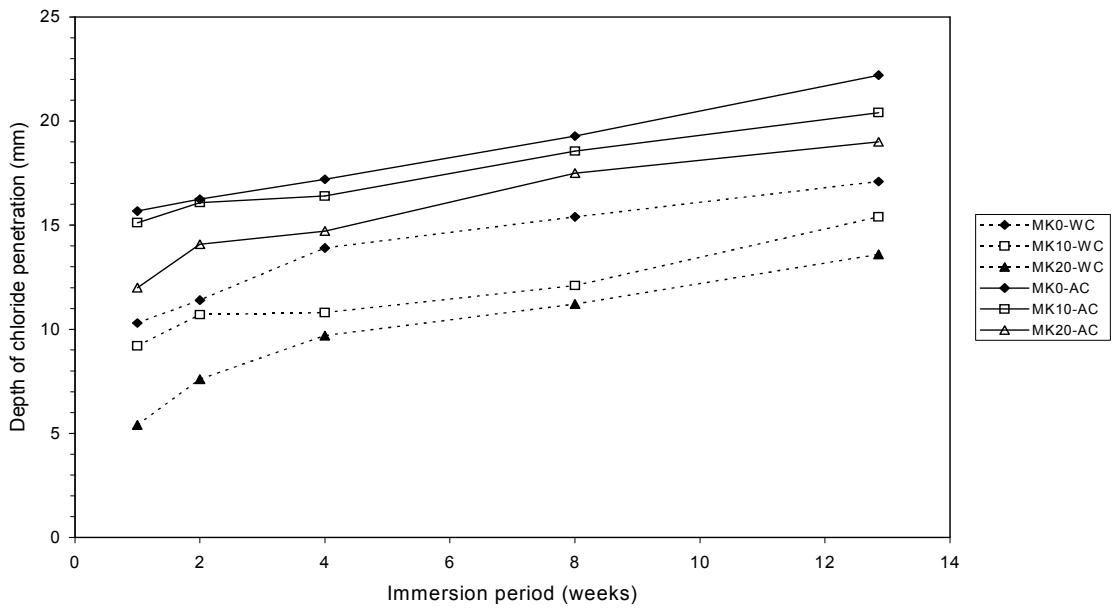
b)

Figure 4.7 Variation in chloride penetration depth with immersion period for plain
and metakaolin-modified concretes subjected to different curing regimes a) w/cm
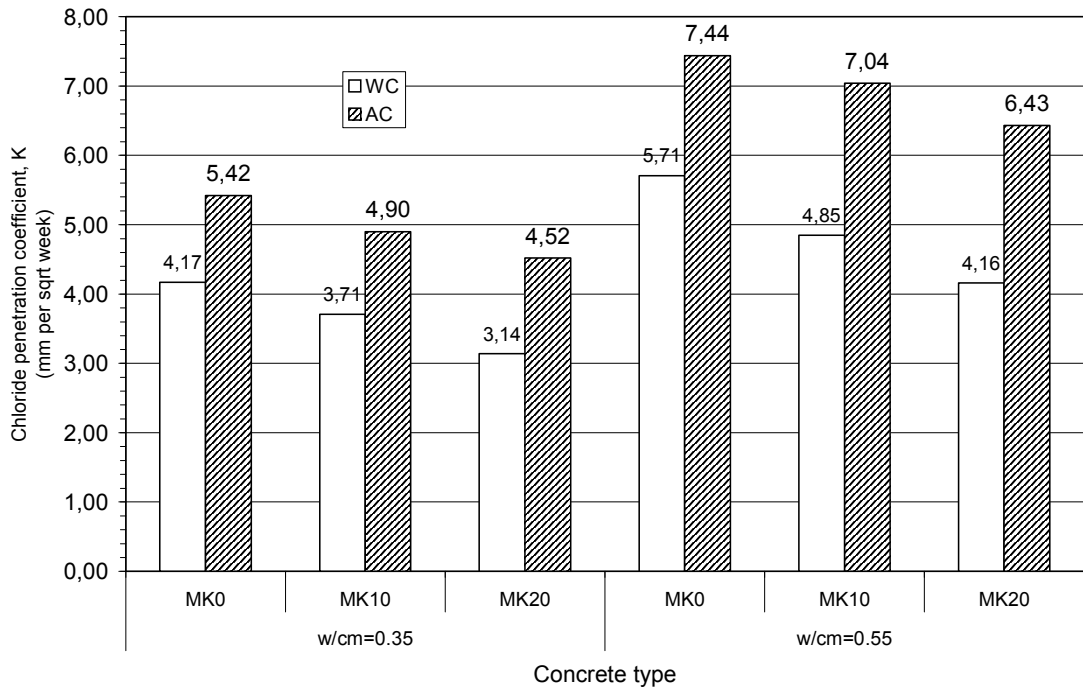ratio: 0.35 and b) w/cm ratio: 0.55

Figure 4.8 Variation in chloride penetration coefficient of plain and metakaolin-
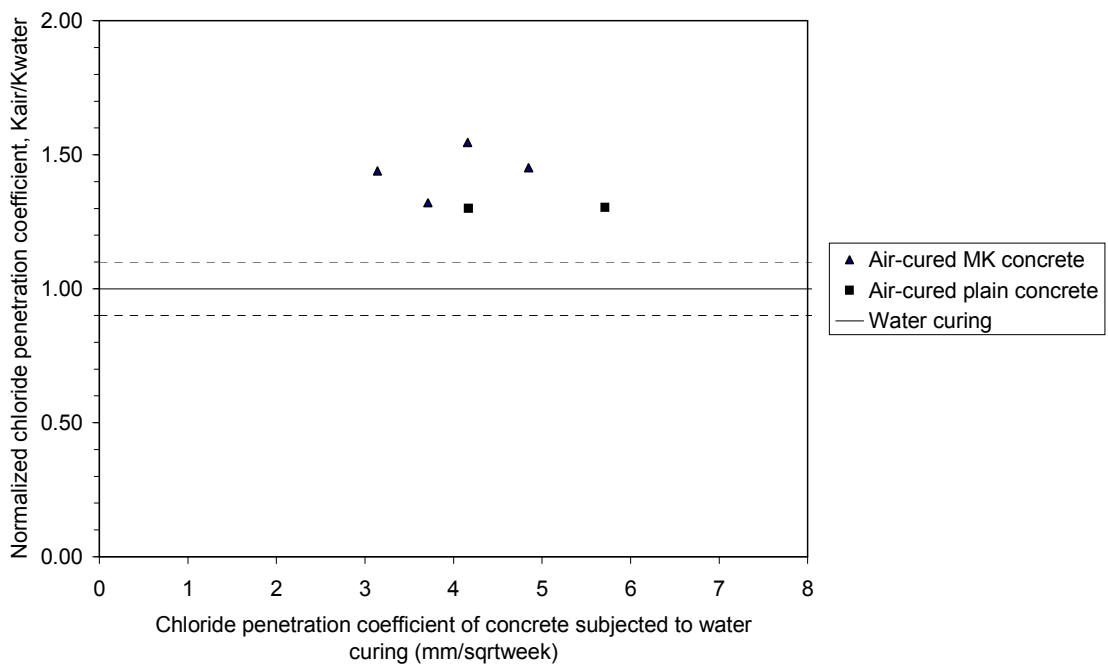modified concretes subjected to different curing regimes

Figure 4.9 Influence of curing condition on chloride penetration coefficient of
concretes incorporated with metakaolin

4.5 Drying Shrinkage and Weight Loss

Drying shrinkage tests alone can not offer sufficient information on the behavior of concrete structures since virtually all concrete structures are restrained in some way, either by reinforcement or by the structure. However, drying shrinkage tests can provide necessary information on how the drying shrinkage stresses develop [82].

The strain developments versus time of the drying shrinkage specimens produced with two w/cm ratios are presented in Figure 4.10. It was observed from the figure that drying shrinkage of the concretes having 0.35 and 0.55 w/cm have decreasing tendency with little fluctuations through the time passed. At early test ages, the shrinkage of all of the specimens developed quickly up to approximately 2 weeks and the difference between amount of drying shrinkage of plain and MK modified concretes was small, especially for low w/cm ratio. But after 2 weeks that difference has become more clear and the shrinkage of concrete with MK decreased with increasing replacement levels. When the shrinkage value at 60 days was considered, the shrinkage of MK concrete specimens exhibited remarkable reduction in comparison to plain concrete shrinkage. It was pointed out that the more the replacement of MK, the more the reduction in shrinkage, irrespective of w/cm ratio. For example, at low w/cm ratio, the drying shrinkage of the concrete mixtures incorporated with 10 and 20% MK were approximately 5 and 15% less than that of the plain concrete, respectively. However, at high w/cm ratio, the effect of MK is more pronounced and concretes with 10 and 20% MK had about 13 and 18% lower shrinkage than plain concrete. This agrees with the observations of Al-Khaja [83] and Jainyong and Yan [84] for the effect of the ultrafine mineral admixtures. In the study of Al-Khaja [83], it was concluded that the shrinkage and creep of plain concrete were considerably or moderately reduced with the incorporation of silica fume, showing a one-month reduction in strain of 34.9 and 18.5% for shrinkage and creep, respectively, which led to a reduction in the total deformation of 20.8%. Jainyong and Yan [84] have also showed that ultrafine ground granulated blast-furnace slag and silica fume can substantially promote hydration of cement and increase in the amount of AFt crystal hydrates and C-S-H gel hydrates in cement paste, which offers hardened concrete a stronger structure and higher resistance to deformation caused by applied forced. As well, these two binders may fill small

pores and voids harmful to the structure of concrete. That might be the mechanism of reducing effect of ultrafine mineral admixtures (i.e. GGBS, SF) on creep and drying shrinkage of concrete.
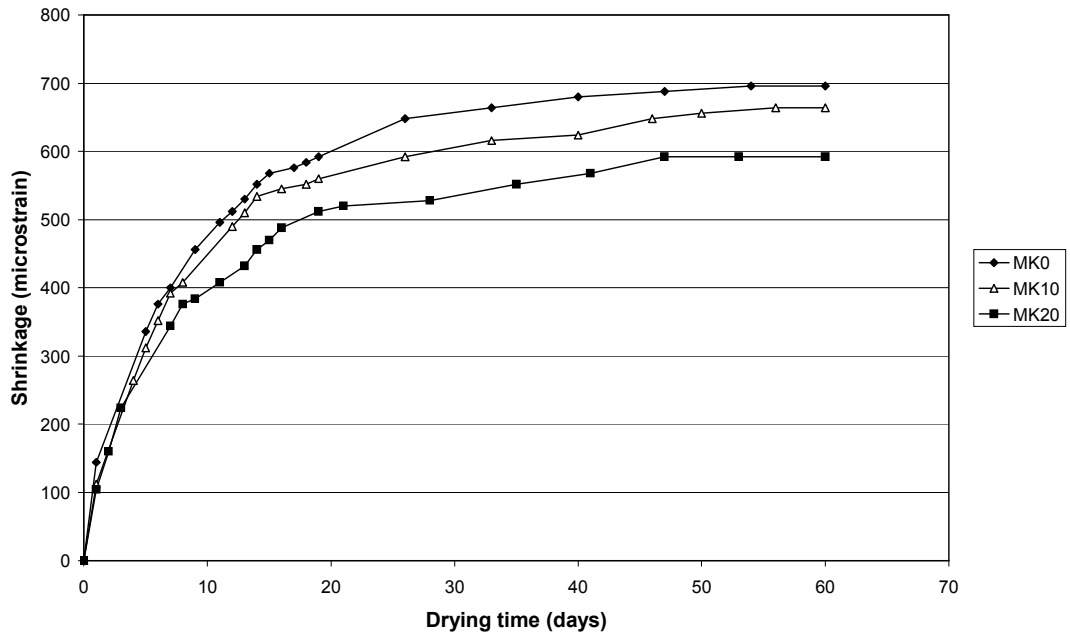
a)
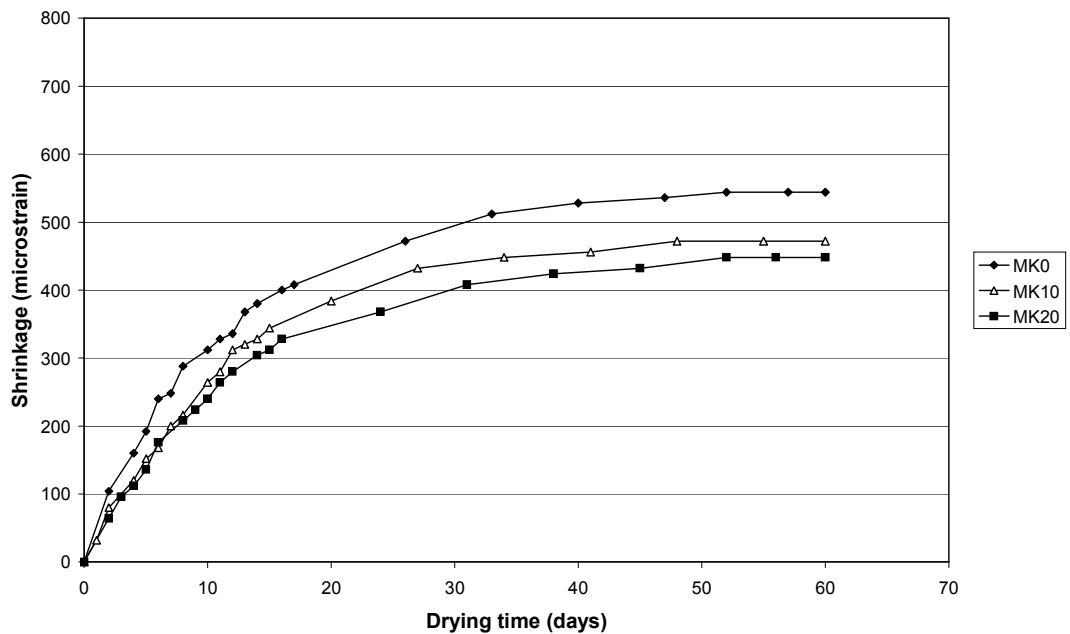
b)

Figure 4.10 Drying shrinkage vs. drying time graph of plain and MK concretes having w/cm ratios of a) 0.35 and b) 0.55

The relationship between shrinkage after 60 days and replacement levels of MK can be seen in Figure 4.11. It was observed that there was an inverse type of relationship between them and the drying shrinkage of the concrete for both w/cm ratios decreased linearly with increasing MK content. This indicates that the two are interdepended. It was also noticed that MK had shrinkage-reducing or compensating properties. It might be used as an additive in concrete application where high shrinkage should be avoided or undesirable.
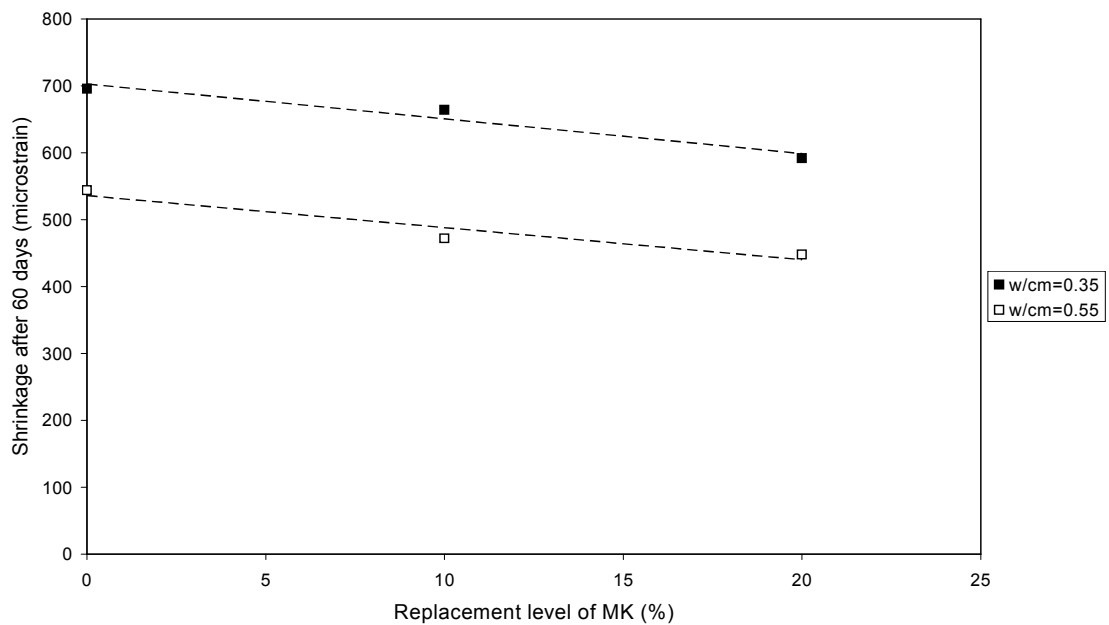
Figure 4.11 Relationship between shrinkage after 60 days and replacement level of MK

Reductions in shrinkage strains due to MK are surely a result of the decrease in the shrinkage rate. The shrinkage rates have been calculated and presented in Figure 4.12. The critical comparison of the curves given in Figure 4.12 for the plain and MK modified concretes indicated that the average shrinkage rates of MK blended cement concretes were lower than the plain concretes during 60 day drying period, irrespective of replacement level and w/cm ratio. It is evident from the figure that the higher MK content, the slower the shrinkage rate of concrete, especially for high w/cm ratio. It was also noted that both plain and MK concretes with low w/cm ratio showed a somewhat faster development of shrinkage than those with high w/cm ratio.
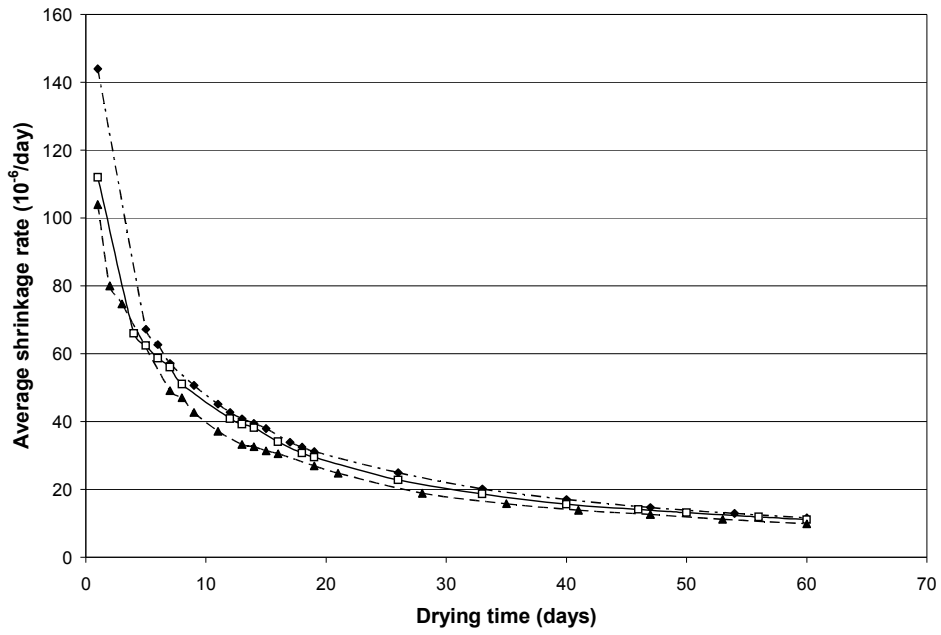
a)
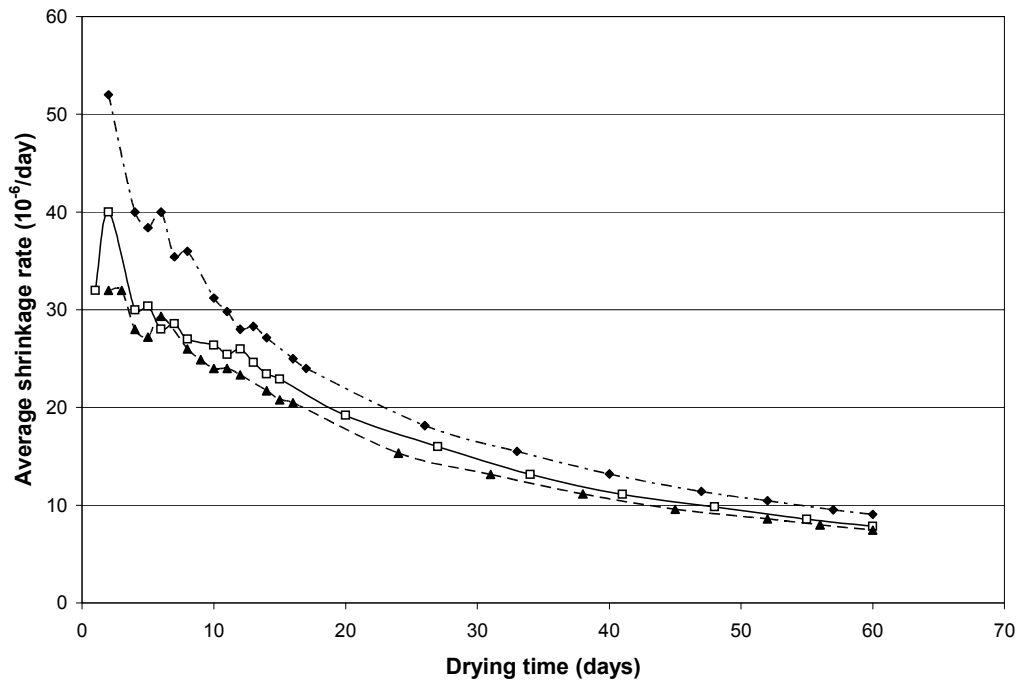
b)

Figure 4.12 Average shrinkage rate vs. drying time graphs of plain and MK concretes
having w/cm ratios of a) 0.35 and b) 0.55

The results of weight loss due to drying for different concrete mixtures are also shown in Figure 4.13. It was clear from the figure that concrete mixes with higher unit water contents showed higher weight loss. Similar to the drying shrinkage test results, inclusion of MK to the concrete mixes decreased considerably the weight loss for both w/cm ratios. During 60 day drying period, the difference of weight loss between plain and MK blended cement concretes were more distinguishable. This is true for all drying time and the difference increases with increasing the drying time. It was observed that after 60 day drying, the MK concretes exhibited up to 48% less weight loss compared to plain concretes, depending mainly on replacement level and w/cm ratio. It seems that the rate of weight loss for MK concretes slows down earlier than that for plain concrete. This may be because there is less water available in the mixes.
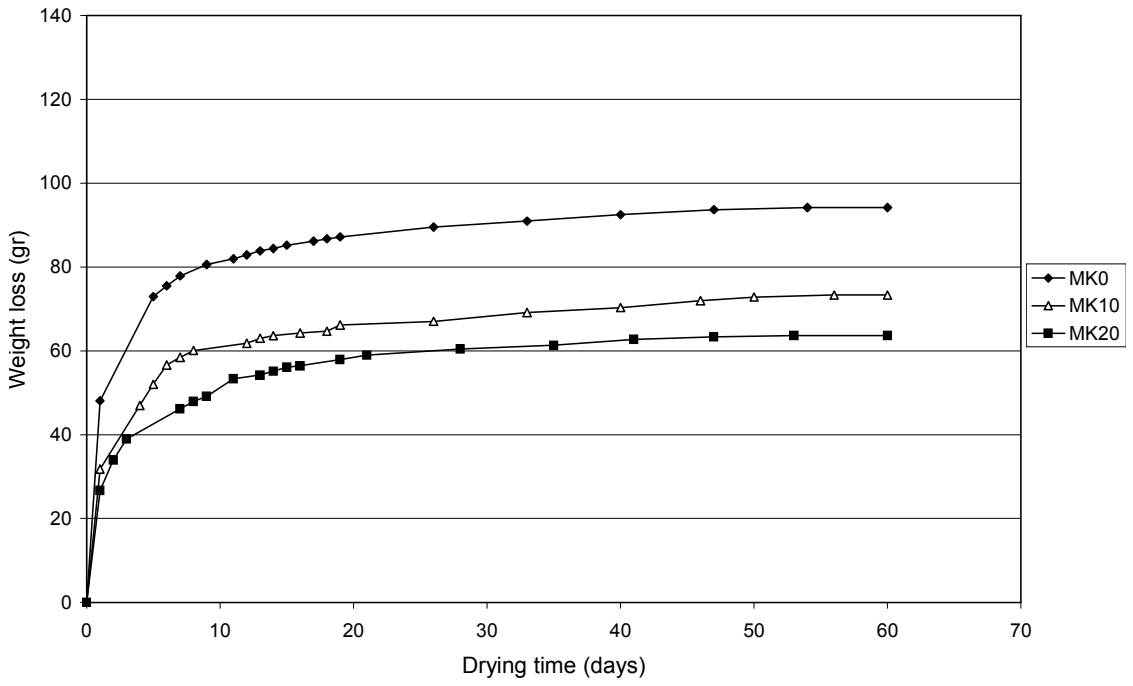
a)
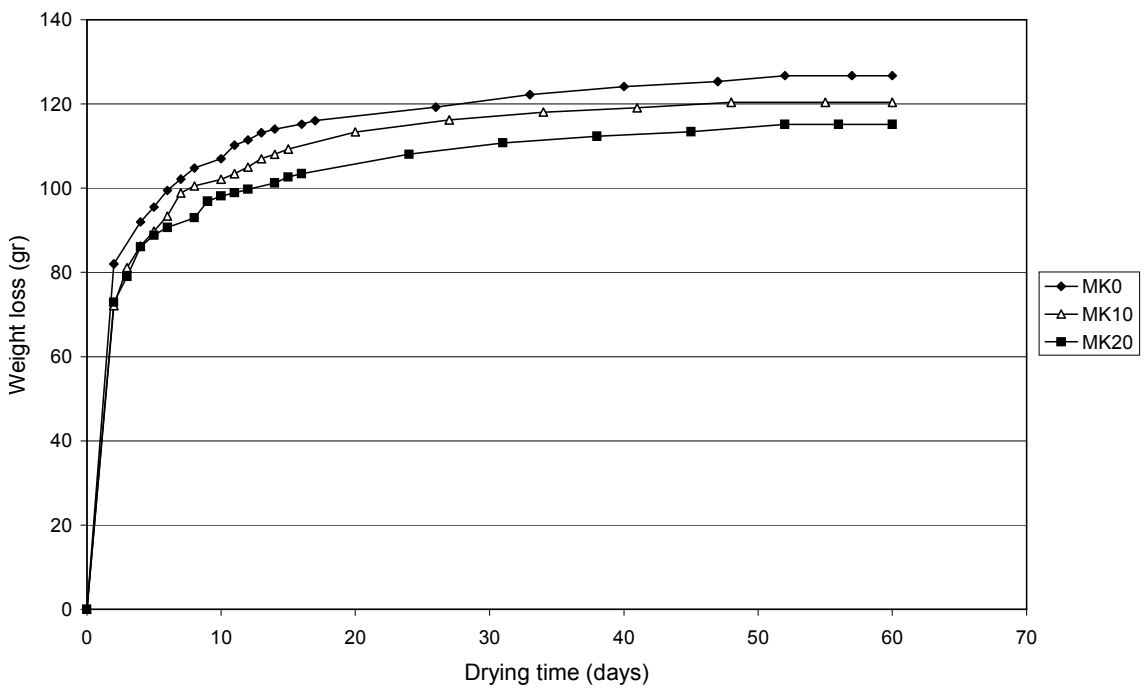
b)

Figure 4.13 Weight loss vs. drying time graphs of plain and MK concretes having

w/cm ratios of a) 0.35 and b) 0.55

4.6 Sulfate Resistance

In this part of the investigation, the resistance of the plain and MK concretes against sulfate attack under different circumstances is examined by monitoring the change in compressive strength as well as the weight loss and UPV during the 1 year exposure period. Herein, the preliminary results obtained at the end of the 180 day sulfate exposure period were given and discussed, especially the results on the variation in the compressive strength. The results are presented in Tables 4.4 and 4.5. Variations in the compressive strength loss (CSL) of concretes with and without MK exposed to the continuous immersion in sulfate solution (SO_4) and drying-immersion cycle (SO_4-cyclic) are shown in Figures 4.14 and 4.15 for the specimens with w/cm ratios of 0.35 and 0.55, respectively. The compressive strength of the specimens immersed in tap water was used as reference in order to evaluate the CSL.

It is clear from the figures that w/cm ratio has a paramount importance on the improvement of the sulfate resistance of the concrete. The lower the w/cm ratio, the lower CSL was observed. For example, the degree of CSL at the end of 180 days of cyclic exposure was observed to be about 13% and 23% for MK10 concretes of 0.35 and 0.55 w/cm ratios, respectively, depending mainly on initial curing condition adopted. According to the test results, the use of MK in concrete was also more effective in decreasing the CSL. For instance, the plain and MK concrete specimens subjected to continuous immersion in sulfate solution, after the 28 day initial water curing had compressive strength reductions of about 16% and 7%, respectively, depending on w/cm ratio. However, in case of cyclic exposure, 21% and 12% of CSL were observed for initially water-cured plain and MK concretes, respectively. It is apparent from the figures that the use of MK is mostly useful in reducing the CSL, irrespective of w/cm ratio and regardless of initial curing condition. Critical comparison of the tables and figures exhibited that MK incorporation provided a better performance to the concrete under sulfate attack, depending on the replacement levels of MK. Although the effect of MK replacement level was not so distinguishable at early exposure period (60 days), it became more apparent at the later exposure periods (90 and 180 days). As a result, the partial replacement of Portland cement by MK was found to be efficient in the improvement of the

resistance of concrete against sulfate attack. The sulfate resistance of concretes increased with increasing MK content.

According to the results of the CSL, for both sulfate exposure conditions (continuous SO_4 and SO_4-cyclic), initially water-cured (WC) concretes had better performance against sulfate attack in comparison to initially air-cured (AC) concretes, irrespective of w/cm ratio and MK content. According to the test results given in Tables 4.4 and 4.5, it was also observed that the drying-immersion cycle (SO_4-cyclic) causes a worse deterioration than the continuous immersion (SO_4). For example, at 60-day exposure, the maximum CSL of 17% was measured in drying-immersion cycle while 8% of CSL in continuous immersion for the concrete specimens.

Table 4.4 Effect of sulfate exposure on initially water-cured plain and MK modified concretes

| Series (w/cm) | Immersion Period | MK content | Sulfate Exposure | | | | |
| | | | Tap Water | SO$_4$ | | SO$_4$ (cyclic) | |
			σ (MPa)	σ (MPa)	CSL (%)	σ (MPa)	CSL (%)
0.35	Prior to immersion	MK0	68.5	68.5	0	68.5	0
		MK10	74.9	74.9	0	74.9	0
		MK20	78.2	78.2	0	78.2	0
	60 days	MK0	72	69.6	3.3	67.4	6.4
		MK10	85.4	84.1	1.5	81.6	4.4
		MK20	93.6	92.9	0.7	91.7	2.0
	90 days	MK0	76.8	70.2	8.6	67.6	12.0
		MK10	92.2	87.3	5.3	82.7	10.3
		MK20	98.5	95.4	3.1	88.2	10.5
	180 days	MK0	83.3	74.6	10.4	70.4	15.5
		MK10	93.9	85.5	8.9	81.4	13.3
		MK20	97	89.7	7.5	85	12.4
0.55	Prior to immersion	MK0	45.3	45.3	0	45.3	0
		MK10	50	50	0	50	0
		MK20	53.1	53.1	0	53.1	0
	60 days	MK0	50.7	48.2	4.9	44.9	11.4
		MK10	58.8	56.9	3.2	53.1	9.7
		MK20	61.5	59.6	3.1	57	7.3
	90 days	MK0	54.4	47.7	12.3	45.3	16.7
		MK10	65.7	60.6	7.8	57.7	12.2
		MK20	70.1	65.6	6.4	61.2	12.7
	180 days	MK0	56.3	47.5	15.6	44.7	20.6
		MK10	69.1	60.6	12.3	57.9	16.2
		MK20	76.2	67.8	11.0	65.7	13.8

Table 4.5 Effect of sulfate exposure on initially air-cured plain and MK modified concretes

Series (w/cm)	Immersion Period	MK content	Sulfate Exposure				
			Tap Water	SO$_4$		SO$_4$ (cyclic)	
			σ (MPa)	σ (MPa)	CSL (%)	σ (MPa)	CSL (%)
0.35	Prior to immersion	MK0	60.3	60.3	0	60.3	0
		MK10	65.2	65.2	0	65.2	0
		MK20	64.1	64.1	0	64.1	0
	60 days	MK0	64.1	59.5	7.2	57.5	10.3
		MK10	68.8	67.4	2.0	62.4	9.3
		MK20	67.4	66.5	1.3	62.8	6.8
	90 days	MK0	69.3	62.3	10.1	58.3	15.9
		MK10	70.2	64.7	7.8	61.5	12.4
		MK20	73.8	69.7	5.6	64.3	12.9
	180 days	MK0	82.1	69.3	15.6	65.9	19.7
		MK10	89.3	79.4	11.1	74.1	17.0
		MK20	88.6	79.6	10.2	74.5	15.9
0.55	Prior to immersion	MK0	38.7	38.7	0	38.7	0
		MK10	40.1	40.1	0	40.1	0
		MK20	42	42	0	42	0
	60 days	MK0	43.6	39.8	8.7	36.4	16.5
		MK10	47.1	43.5	7.6	41	13.0
		MK20	49.7	45.5	8.5	43.9	11.7
	90 days	MK0	42.5	36.2	14.8	33.4	21.4
		MK10	50.1	43.1	14.0	40.4	19.4
		MK20	51.5	45.4	11.8	42.3	17.9
	180 days	MK0	45.5	35.8	21.3	33.6	26.2
		MK10	52.6	42.7	18.8	40.5	23.0
		MK20	54.9	45.3	17.5	42.7	22.2
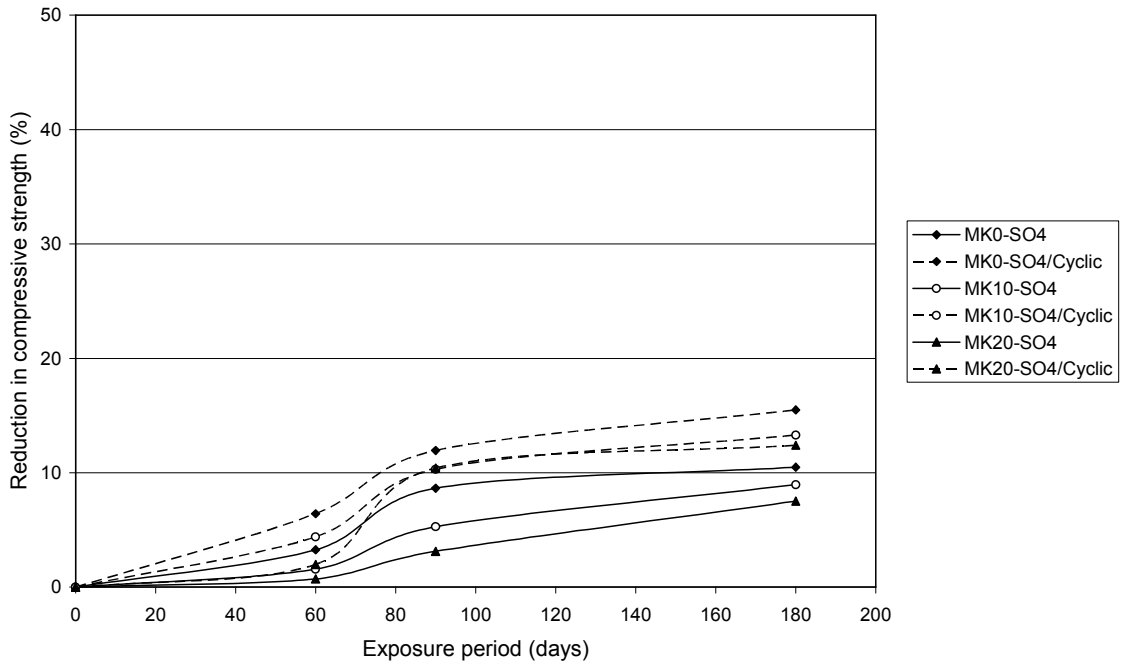
a)
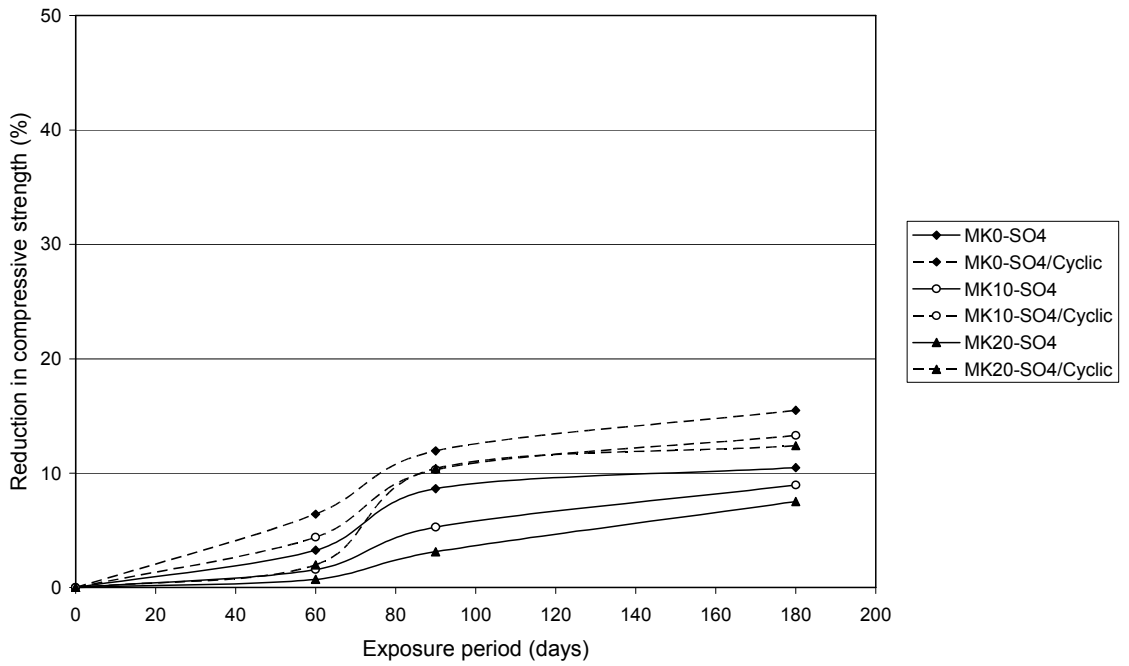
b)

Figure 4.14 CSL for w/cm ratio of 0.35 initially a) WC, b) AC concretes

a)

b)

Figure 4.15 CSL for w/cm ratio of 0.55 initially a) WC, b) AC concretes

4.7 Pore Structure

The results of strength and durability tests indicated that MK had beneficial effect on the properties of concrete. It was observed that partial replacement of Portland cement by MK at levels up to 20% remarkably improved the perf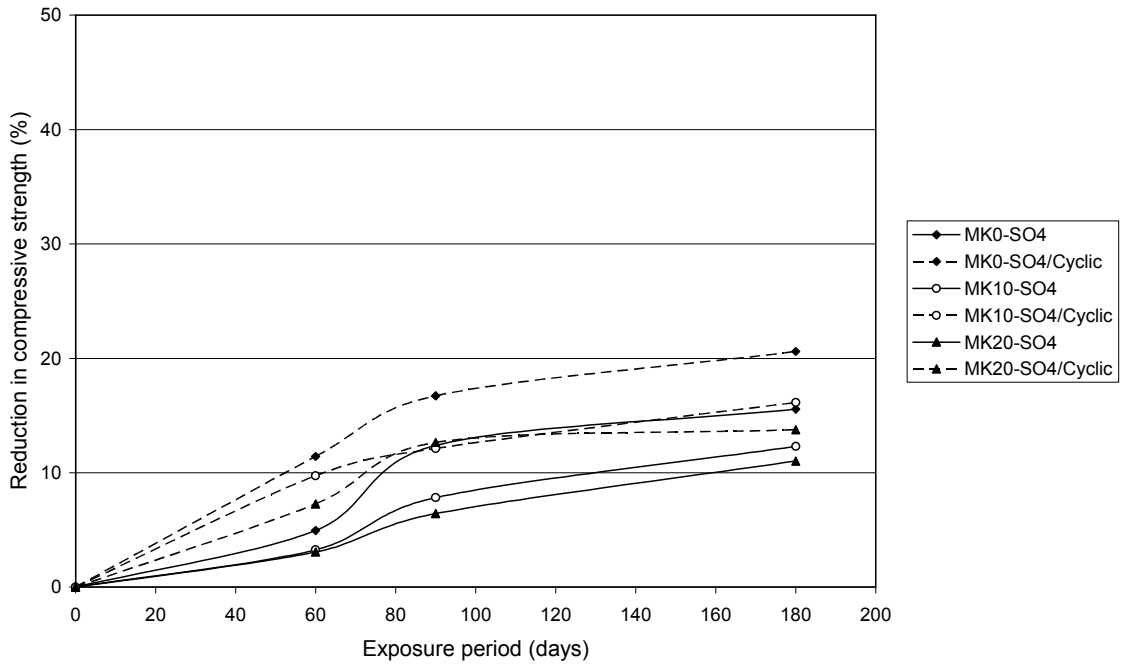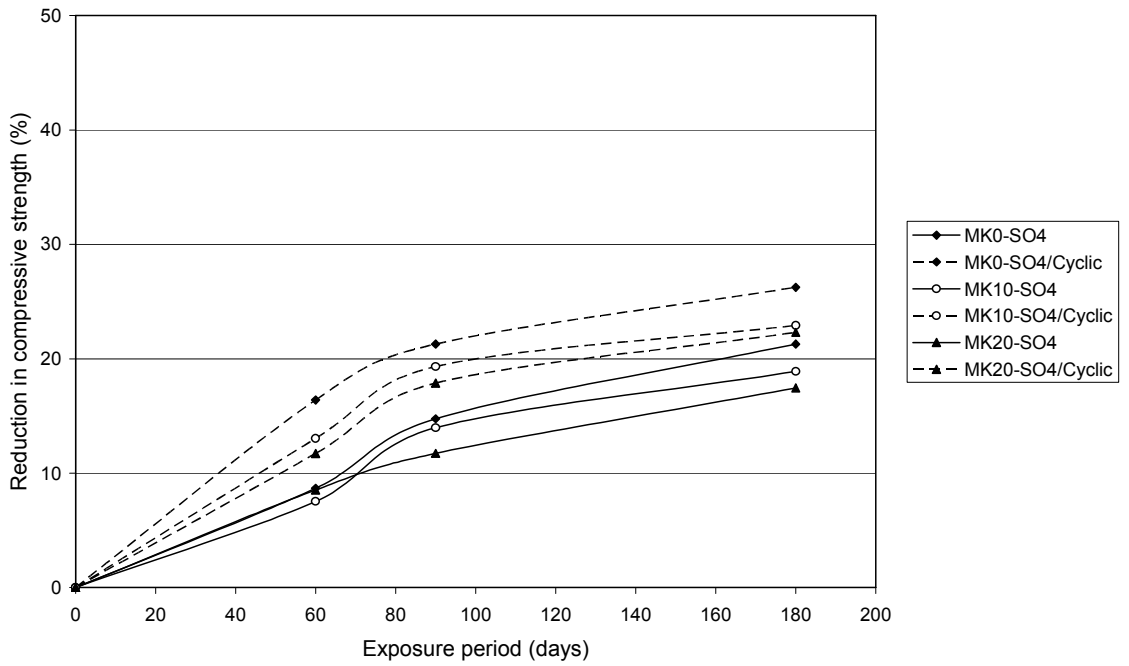ormance characteristics of the air cured and especially water cured concretes, irrespective of w/cm ratios. In order to illustrate the effect of MK inclusion on the pore structure of the concrete subjected to AC and WC conditions, the pore size distribution and porosity of the plain and MK mortar samples having w/cm ratio of 0.35 was determined at the age of 120 days by means of mercury intrusion porosimetry and the results are presented in Table 4.6 and Figure 4.16. It was found that the porosity of the mortars ranged from 5.5 to 13.9%, depending on MK content and curing procedure adopted. It was pointed out that the porosity of the mortar sample decreased remarkably in both initial curing conditions due to incorporation of MK. However, the effectiveness of MK is more evident for the samples subjected to WC. For instance, the decrease in porosity of the mortar sample having 20% MK was observed to be about 7% and 49% for AC and WC conditions, respectively.

It was also noted that there was a considerable reduction in mean (or median) pore diameter of the samples due to the inclusion of MK. The effect is particularly beneficial at 20% MK content, where the lowest porosity and pore diameter are achieved, irrespective of curing method. Poon et al. [58] investigated the effect of MK on pore size distribution of mortars containing MK. The mortars were designed at a water/binder ratio of 0.30 and tested at the end of 28 days curing period. They found that the average pore diameter of control mortar was about 0.0322 μm while that of MK mortars ranged from 0.0186 to 0.0289 μm, depending on MK content. The clear shift towards finer pore structure can be quantified by expressing the pore size distribution in terms of the mean pore diameter. In order to evaluate the central tendency of pore size distribution, the mean and median pore diameters of plain and MK mortar samples are compared as seen in Table 4.6. In water cured MK samples, the deviation from the mean value is smaller than that of plain concrete, but this deviation is not distinguishable in air cured concretes due to uncontrolled, inadequate curing conditions. In addition, As previously mentioned, the data concerning the variations of pore size distribution are plotted in Figure 4.16. The figures show that,

the finer the pore structure the higher the percentage of small pores, irrespective of curing condition and MK content. It is clear from the figure that the incorporation of MK provides a finer pore structure in both AC and particularly WC mortars. In addition to the pozzolanic reaction, the filler action of MK due to the fine particle size of MK (1 μm) compared to the particle size of cement (12 μm) further densifies the pore structure of MK concrete [49]. It was also evident from Figure 4.16, the pore size distributions of mortars exposed to WC are more uniform and finer than those of samples exposed to AC. Thus, it may be concluded that the water curing contributes better to the pore structural refinement of samples than air curing.

The ability of MK replacement to improve durability properties depends on a refinement of pore structure rather than any change in hydration chemistry [52]. Improvements observed in strength, resistance to water and chloride penetration, sulfate attack, shrinkage strain development characteristics of the concretes mentioned in this thesis can be considered as a consequence of refinement in pore structure due to MK inclusion.

Table 4.6 Results of mercury intrusion porosimetry test for the low w/cm ratio samples tested at 120 days and subjected to AC and WC

Curing conditions	MK (%)	Porosity (%)	Mean pore diameter (μm)	Median pore diameter (μm)
AC	0	13.9	0.517	0.305
	10	11.2	0.382	0.222
	20	12.9	0.337	0.143
WC	0	10.7	0.286	0.098
	10	7.3	0.139	0.058
	20	5.5	0.088	0.037
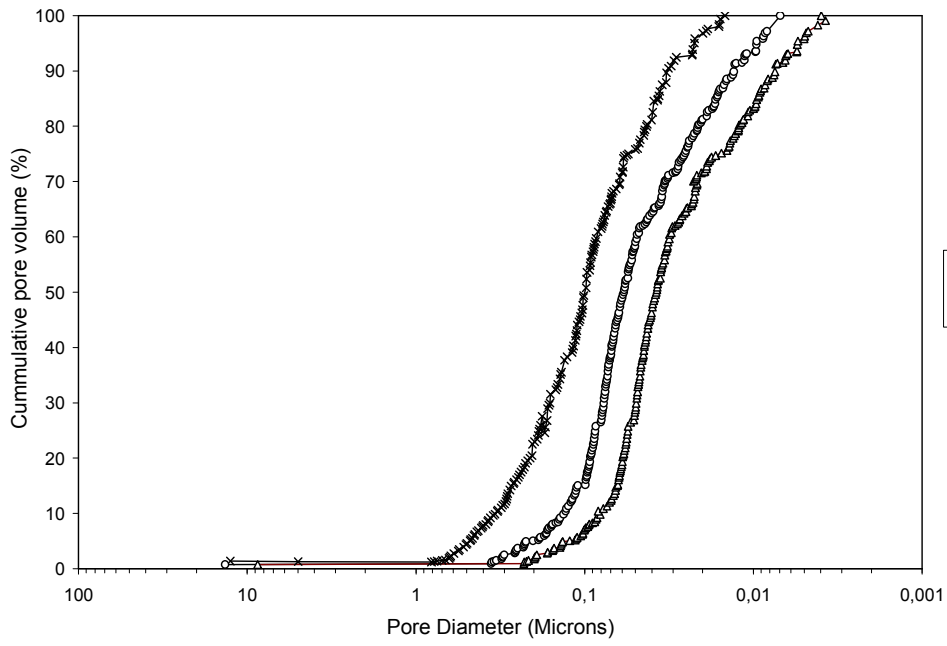
a)
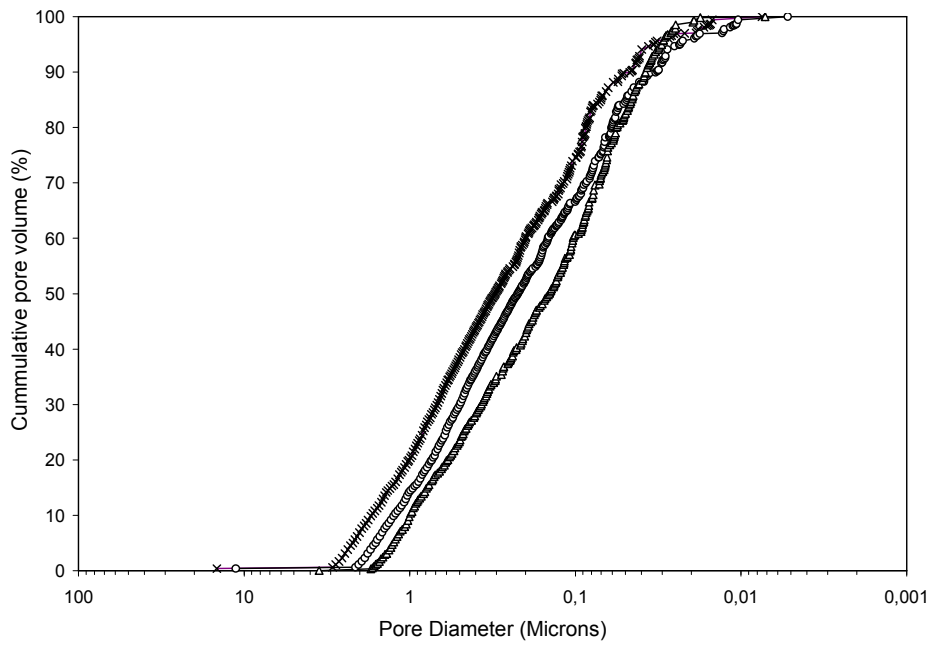
b)

Figure 4.16 Normalized intruded pore volume of concrete with 0.35 w/cm ratio as a function of pore size a) water cured, b) air cured concrete

5. CONCLUSION

In this thesis, the effectiveness of metakaolin on the properties of air-cured and water-cured concretes were investigated. According to the results obtained from the experimental study, the following conclusions can be drawn:

- This study indicated that the inclusion of metakaolin into concrete significantly enhanced the strength and especially permeability-related durability characteristics of the concrete in varying magnitudes. The Concrete containing MK shows higher strength than that of the plain concrete associated with the marginally lower chloride penetration depths, sorptivities, and water absorption. The order of the magnitude depends mainly on the replacement level of MK, w/cm ratio, concrete age, and curing condition.

- Curing played a critical role in realizing the full potential of concrete. It is necessary to pay careful attention when using metakaolin in concrete due to the fact that the performance properties of the metakaolin-modified concretes are more sensitive to curing method adopted.

- Irrespective of w/cm ratio and replacement levels of MK, air-cured concretes exhibit lower strength and considerably higher permeability compared to the companion water cured concretes. It was observed that the strength of the plain and metakaolin-modified concretes subjected to air curing deviated up to -28% and -35% from those cured under water, respectively. The application of air curing also resulted in marked differences with respect to the water curing in terms of sorptivity, water absorption, and chloride ingress characteristics of the concretes, particularly for those made with MK.

- For all replacement levels, the MK modified concretes exhibited lower shrinkage in comparison to the plain concretes, irrespective of w/cm ratio. It is known that the drying shrinkage is influenced by many factors. The results demonstrated that the w/cm ratio was the dominating factor because both the

plain and especially the MK modified concretes with high w/cm exhibited relatively low drying shrinkage.

- With regard to the rate of drying shrinkage, it is evident that both plain and MK concretes with low w/cm ratio showed a somewhat faster development of shrinkage than those with high w/cm ratio. However, the drying shrinkage rates of the concretes had a decreasing tendency with passing drying time, particularly for the MK concretes.

- Metakaolin replacement of cement was found to be effective in improving the resistance of the concrete to the sulfate attack. The sulfate resistance of MK concrete increased with increasing the MK content. It was also observed that the drying-immersion cyclic sulfate exposure causes a worse deterioration than the continuous immersion in the sulfate solution. But in both cases, the MK modified concretes showed better performance in comparison to the plain concretes.

- According to MIP test results, the inclusion of MK into the matrix leads to a considerable reduction in the total pore volume and to a refinement of the pore structure. Curing regime to which a concrete specimen is subjected, has a substantial effect on porosity and pore structure, especially for that with MK. Less pore volume and finer pore structure are obtained when concrete is subjected to wet curing as compared with dry curing. The effect is particularly beneficial at 20% MK content, where the lowest porosity and pore diameter are achieved.

- Combine effect of the proper curing and MK inclusion resulted in further densification and pore refinement in the structure, and this brought about improved strength and durability performance. Therefore, the use of MK in the production of high performance concrete (HPC) seems advantageous. It is also noted that its use is environmentally beneficial due to the decreasing the usage of Portland cement. However, before application to construction industry, a detail cost-benefit analysis should be applied in order to optimize its use.

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APPENDIX A: Photographic Views

Figure A1 Photographic view of Portland cement and calcined kaolin (in the form of metakaolin)

Figure A2 Photographic view of shrinkage specimens

Figure A3 The humidity cabinet for the shrinkage test specimens

Figure A4 Photographic view of Na_2SO_4 solution tanks which were utilized for

a) continuous exposure b) cyclic exposure

(a)   (b)

c)

Figure A5 Photographic view of the high w/cm ratio concrete specimens subjected to 10% Na_2SO_4 solution under the circumstance of the drying-immersion cycles a) plain concrete, b) MK10 concrete, and c) MK20 concrete at the end of 180 days