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Design and Rehabilitation of Structures

EFFECTS OF NITRATE AND SULFATE ATTACKS ON MECHANICAL AND PHYSICAL PROPERTIES OF CEMENT MORTARS

تأثير مادتي نترات الأمونيوم وكبريتات الماغنيسيوم على الخواص الميكانيكية والفيزيائية للملاط الإسمنتي

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ABSTRACT

Concrete structures are exposed to aggressive aqueous environments in very varied situations, and the range of aggressive species is wide. The understanding of the mechanisms of degradation of cementitious materials by these aggressive media is an essential step toward the development of concrete to perform well in these environments and toward increase of the service life or the safety of the structures.

The main purpose of the research is to investigate the effects of ammonium nitrate and magnesium sulfate on mechanical and physical properties of cement mortar. The mechanical and physical properties investigated are compressive strength, porosity and unit weight.

The mortar specimens were immersed in ammonium nitrate and magnesium sulfate solutions with 5% (50g/L), 20% (200g/L) and 50% (500g/L) concentrations. Test specimens were prepared by placing the cement-based material into $5 \times 5 \times 5$ cm molds. After 28 days curing of specimens in distilled water, some of the specimens were immersed in ammonium nitrate and some of them were immersed in magnesium sulfate solutions until 10, 20, 40 and 60 days before testing.

Test results showed that the compressive strength decreased when the mortar specimens was treated with ammonium nitrate solutions and as the concentration of ammonium nitrate and exposure period increase, the reduction in compressive strength increase clearly. It is also found that the porosity of mortar specimens increase while the unit weight of specimens decrease when the specimens exposed to ammonium nitrate solutions.

For specimens immersed in magnesium sulfate solutions, a decrease in compressive strength is found through the conducted experiments as well as the loss in strength increase as the concentration of magnesium sulfate and immersion period increase. The results also showed that porosity and unit weight of specimens were not largely clear, however, for several concentrations of magnesium sulfate there was an increase in porosity and a decrease in unit weight.

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الملخص

تتعرض المنشآت الخرسانية للعديد من العوامل البيئية الخطيرة و التي تؤثر سلبا على المادة الإسمنتية والتي تشكل المكون الأساسي للخرسانة ، وبالتالي فهم آلية عمل هذه البيئات وكيفية تأثيرها على الخرسانة ، تعتبر خطوة مهمة في اتجاه تطوير الخرسانة للعمل في مثل هذه البيئات ، وبالتالي زيادة المدة التشغيلية للمنشأ وزيادة عوامل الأمان والتقليل من عمليات الصيانة للمنشأ.

إن الهدف الرئيسي والمنشود من هذا البحث هو دراسة تأثير مادة نترات الأمونيوم وكبريتات الماغنيسيوم على الخواص الميكانيكية والفيزيائية للملاط الإسمنتي (اسمنت + رمل + ماء). الخصائص الميكانيكية والفيزيائية للملاط الإسمنتي التي تم دراستها هي قوة الضغط ، المسامية ، ووحدة الوزن. العينات من الملاط الإسمنتي تم غمرها في محاليل من نترات الأمونيوم وكبريتات الماغنيسيوم بتراكيز 5% و 20% و 50%. العينات تم تحضيرها من خلال صب مادة الملاط في قوالب حديدية بأبعاد 5 × 5 × 5 سم . بعد 28 يوم من معالجة العينات في مياه مقطرة ، تم وضعها في أحواض تحتوي على محاليل من مادة نترات الأمونيوم ومادة كبريتات الماغنيسيوم لمدة 10 ، 20 ، 40 ، 60 يوم وذلك قيل القيام بالاختبارات اللازمة.

بينت النتائج أن هناك انخفاض في قوة الضغط للملاط الإسمنتي عند تعريض العينات إلى محاليل نترات الأمونيوم وكذلك أظهرت النتائج أنه كلما زاد التركيز وفترة الغمر في محاليل نترات الأمونيوم ، يزداد الانخفاض في القوة الضاغطة للملاط الإسمنتي.
كذلك وجد أن المسامية للعينات تزداد بينما وحدة الوزن تقل عند التعرض لمحاليل نترات الأمونيوم.

اما بالنسبة للعينات التي تم غمرها في محاليل كبريتات الماغنيسيوم ، فقد أظهرت النتائج أن هناك انخفاض في القوة الضاغطة للملاط الإسمنتي وكذلك بينت النتائج أنه كلما زاد التركيز وفترة التعرض لمادة كبريتات الماغنيسيوم ، زاد الفقد في القوة الضاغطة.
أما بالنسبة للمسامية ووحدة الوزن للعينات التي تم غمرها في محاليل كبريتات الماغنيسيوم ، لم تكن النتائج واضحة بالقدر الكافي ، إلا أنه وجد هناك زيادة في المسامية وانخفاض في وحدة الوزن ولكن بشكل قليل.

DEDICATIONS

I would like to dedicate this work to my family specially my mother and my father who loved and raised me, to my brothers and sisters and to my friends for their sacrifice and endless support.

ACKNOWLEDGMENT

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LIST OF ABBREVIATIONS

NH$_4$NO$_3$: Ammonium Nitrate.

MgSO$_4$: Magnesium Sulfate.

w/c: Water-cement ratio.

IUG: Islamic University of Gaza.

ASTM: American Society of Testing Materials.

WHO: World Health Organization.

VPV: Volume of permeable voids.

W$_1$: The weight of leached samples was measured after rinsing in water tank for ten days.

W$_2$: The weight was measured after drying of samples in an oven at a moderate temperature of 60°C.

f$_c$/f$_{c,28}$: Compressive strength of cement mortar after immersion in aggressive solutions to initial compressive strength after 28 days of curing in distilled water.

CH: Calcium hydroxide.

C-S-H: Calcium silicate hydrate.

Chapter 1

Introduction

CHAPTER 1- INTRODUCTION
1.1 General Background

Concrete and cement-based materials are the most widely used building materials globally which is employed in a wide variety of applications on the ground, underground, and under sea level **(RILEM, 2013) and (Wong et. al, 2013).** Durability, compressive strength, impermeability, abrasion resistance, and resistance to environment attacks are important properties of concrete **(Wong et. al, 2013).**

However, many of the environments to which concrete is exposed are highly aggressive due to various chemical or biological components, and the demands made on concrete to perform in such environments are likely to grow substantially in years to come as the built infrastructure expands and environmental pollution increases. These environments are often aqueous in nature, comprising natural environments such as soft waters, sea waters or ground waters, or man-made such as industrial environments, and treated water or wastewater and polluted environments **(RILEM, 2013)**.

In such environments, concrete is subjected to processes of degradation involving ion addition and exchange reactions, leading to breakdown of the matrix microstructure and weakening of the material. Ultimately, the external aggressive species progress and reach the reinforcement, leading to the destruction of the structures. Sometimes this can be extremely rapid and serious such as in acidic environments, while in other cases degradation of the concrete matrix occurs over long periods **(RILEM, 2013)**. Factors that affect the susceptibility of concrete to damage include chemical composition of its ingredients and physical factors such as porosity, density and permeability at the time of its exposure to corrosive agents **(Wong et. al, 2013).**

The chemical composition of the hydrated phases (calcium silicate hydrate (C-S-H), calcium hydroxide ($Ca(OH)_2$), calcium sulfoaluminate hydrate (ettringite) and monosulfoaluminate for hydrated Portland cement) and their proportions inside the matrix – which depend mainly on the composition of the binder– mostly determine the chemical stability of the matrix **(RILEM, 2013)**.

However, the scale of the problem means that the consequences are severe. A lots of money are spent every year on the restoration of the concrete on structures and manufactured elements deteriorated by different types of degradation **(Girardi, 2009)**.

The understanding of the mechanisms of degradation of cementitious matrices by these aggressive environments is an essential step toward the development of concrete that performs well in these environments and toward the increase of the service life or the safety of the structures and facilities.

1.2 Problem Statement

Groundwater is considered as the main source of drinking water in the Gaza strip. Nitrate and sulfate pollution to groundwater and aquifer has become a progressively serious problem to the whole life system in the area **(Shaheen, 2007)**. It was found that the groundwater of Gaza Strip has been greatly polluted by high concentrations of nitrate and sulfate which reached in some areas to 700 and 1000 mg/L respectively. Actually these concentrations exceed the WHO standards of 50 mg/L for nitrate and 250 mg/L for sulfate **(Shomar, Abu Fakher & Yahya, 2010).** In addition, the production plants of nitrate and sulfate suffer a lot from corrosion by these materials produced inside them. Therefore, there is a great need to study the influence of nitrate and sulfate on the concrete elements.

This research presents an experimental investigation of the effects of ammonium nitrate and magnesium sulfate on mechanical and physical properties of cement mortars.

1.3 Aim and Objectives

The main aim of this work is to study the effects of ammonium nitrate and magnesium sulfate on mechanical and physical properties of cement mortars. In order to achieve the overall aim of this study, the following objectives were carried out:

1. Investigate the effect of several ammonium nitrate concentrations on cement mortars at different ages in terms of mechanical and physical properties.
2. Investigate the influence of several magnesium sulfate concentrations on cement mortars at different ages in terms of mechanical physical properties.
3. Identify the relationship between the nitrate and sulfate concentrations and the behavior of the cement mortars.

1.4 Methodology

The following tasks were done to achieve the objectives of this research:

1. Conducting a literature review about nitrate and sulfate attack and their effects on concrete and cement mortar.
2. Preparing of materials for laboratory testing and executing the testing program.
3. Preparing the mix design and samples.
4. Preparing the ammonium nitrate and magnesium sulfate solutions at different three concentrations (5 % (50g/L), 20 % (200g/L) and 50 % (500g/L)).
5. After the samples were immersed in ammonium nitrate and magnesium sulfate solutions at different periods, each series were finally dried in an oven at a moderate temperature of 60 °C.
6. The following tests on samples were executed after 10, 20, 40 and 60 days after 28 days of curing:
   - Compressive strength test.
   - Unit weight of hardened cement mortar.
   - Porosity test.
7. Test results and data analysis.
8. Conclusions and the recommendations of the research work based on the experimental program results and data analysis.

1.5 Thesis Layout

This thesis is consisted of five chapters organized as follows:

Chapter 1 (Introduction)
This chapter gives a general background about concrete, cement-based materials and aggressive environments. It also contains research problem, aim and objectives of research, the methodology used to achieve the research objectives and describes the structure of the research.

Chapter 2 (Literature Review)
This chapter presents the chemical composition, cement hydration and hydration chemistry of Ordinary Portland Cement. In addition, this chapter discusses durability, permeability and deterioration of concrete and illustrates the process of nitrate and sulfate attacks. It also gives a general overview of relevant previous researches concerning the effects of nitrate and sulfate attacks on concrete and cement mortars.

Chapter 3 (Materials and Experimental Program)
This chapter outlines the materials were used in this research, their proportions, testing program and equipment were used in the testing procedures.

Chapter 4 (Test Results and Discussion)
This chapter explains and discusses the results of the tests that were performed on cement mortar cubes subjected to several concentrations of ammonium nitrate and magnesium sulfate solutions.

Chapter 5 (Conclusions and Recommendations)
This chapter includes the concluded remarks, main conclusions and recommendations drawn from this research.

Chapter 2

Literature Review

CHAPTER 2- LITERATURE REVIEW
2.1 Introduction

This chapter presents the chemical composition, cement hydration and hydration chemistry of Ordinary Portland Cement. In addition, this chapter discusses the durability of concrete and presents the main factors affecting on durability of concrete. It also presents the permeability and porosity of concrete and their role in durability. Furthermore, it displays the main factors that cause deterioration of concrete and discusses the processes of degradation due to corrosion, change in pH value, nitrate and sulfate attacks where these parameters related to this study. Finally, this chapter exhibits previous studies on magnesium sulfate and ammonium nitrate attacks.

2.2 Chemical Composition of Ordinary Portland Cement

In general, cement is described as a material used to bind the mineral fragments called aggregates. The cement paste acts as glue which makes a cohesive mass with all the aggregates (**IRICEN, 2007**). The manufacture of portland cement is very simple and relies on the use of abundant raw materials. The raw materials used in the production of Portland Cement are:

- Limestone (calcium carbonate) is the most common source of calcium oxide. Other forms of calcium oxide carbonate such as chalk, shell deposits and calcareous mud are also used.
- Clay or silts is used as a source of iron bearing aluminosilicates.
- Other materials such as shale and argillaceous rocks are used as a source of silica (**Mindess, Young & Darwin, 2002).**

Portland cement is produced by grinding limestone to a fine powder and mixing it with washed clays in the proportion of approximately two parts of limestone with one part of clay. The mixture is fed to the top of a rotating inclined kiln where fuel is fed at the bottom giving a temperature gradient along the kiln as shown in Figure (2.1).

Four distinct processes take place in the kiln:
1. **Evaporation**: In the top part of the kiln the water is evaporated.
2. **Calcinations:** The clay and limestone are decomposed through loss of bound water and carbon dioxide and thus the mixture is changed into reactive materials.
3. **Clinkering:** At the hottest part of the kiln the aluminum and iron containing compounds melt and bind the other materials to form the lumps of the clinker. The clinker consists of dark gray porous nodules of 6 to 50 mm diameter.

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4. **Cooling:** A small amount of gypsum is added to the clinker after cooling to retard setting and to prevent flash set.

The final process is that the clinker and gypsum are ground and then stored in silos until ready for distribution **(Mindess, Young & Darwin, 2002).**
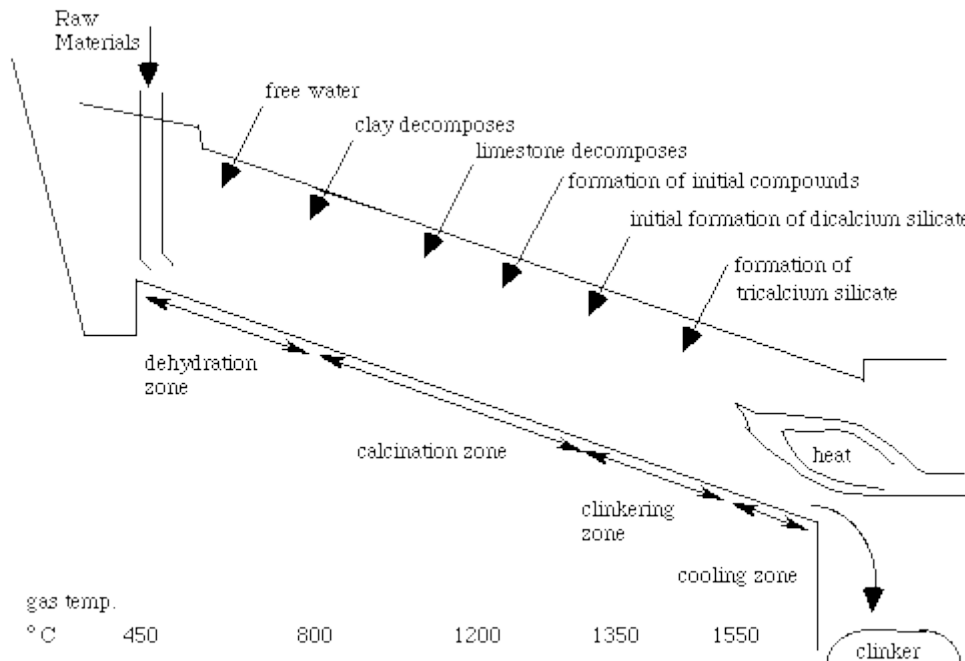
Figure 2.1: Schematic diagram of rotary kiln. (Source: (MAST, 1995))

The chemical composition of Portland cement varies from plant to plant and with the composition of the raw materials. The typical oxide composition of ordinary Portland cement is given in Table (2.1). Table (2.2) includes the compound composition of ordinary Portland cement.

Table 2.1: Oxide composition of ordinary Portland cement.
(Source: (Mindess, Young & Darwin, 2002))

Common Name	Chemical Name	Chemical Formula	Short Hand Notation	Weight Percent
Lime	Calcium oxide	CaO	C	$60 - 70$
Silica	Silicon dioxide	SiO_2	S	$17 - 25$
Alumina	Aluminum trioxide	Al_2O_3	A	$3 - 8$
Ferric oxide	Iron trioxide	Fe_2O_3	F	$0.5 - 6$
Magnesia	Magnesium oxide	MgO	M	$0.1 - 4$
Sulfur trioxide	Sulfur trioxide	SO_3	$\bar{S}$	$1 - 3$
Alkalis	Sodium and potassium oxides	Na_2O and K_2O	N and K	$0.5 - 1.3$
Carbon Dioxide	Carbon dioxide	CO_2	$\bar{C}$	0
Water	Hydrogen Oxide	H_2O	H	0

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Table 2 .2: Compound composition of ordinary Portland cement.
(Source: (Mindess, Young & Darwin, 2002) & (Newman & Choo, 2003))

Common Name	Chemical Name	Short Hand Notation	Weight Percent
Alite	Tricalcium silicate	C_3S	55
Belite	Dicalcium silicate	C_2S	18
Aluminate	Tricalcium aluminates	C_3A	10
Ferrite	Tetracalcium aluminoferrite	C_4AF	8
Gypsum	Calcium sulfate dehydrate	$C\bar{S}H_2$	6

2.3 Cement Hydration

Hydration of cement is the chemical reactions that occur when cement is mixed with water producing new materials causing hardening of concrete. These reactions liberate heat and require time to reach full hydration. The hydration characteristics of the cement compounds are summarized in Table (2.3).

Table 2. 3: Characteristics of hydration of the cement compounds.
(Source: (Mindess, Young & Darwin, 2002))

Compounds	Reaction Rate	Amount of Heat Liberated	Contribution to Cement	
			Strength	Heat Liberation
C_3S	Moderate	Moderate	High	High
C_2S	Slow	Low	Low initially, high later	Low
$C_3A + C\bar{S}H_2$	Fast	Very high	Low	Very high
$C_4AF + C\bar{S}H_2$	Moderate	Moderate	Low	Moderate

Clearly, the calcium silicates (C_3S and C_2S) provide most of the strength developed by Portland cement. C_3S provides most of the early strength in the first three to four weeks and both C_3S and C_2S contribute equally to ultimate strength (**Mindess, Young & Darwin, 2002).**

2.4 Hydration Chemistry

An adequate understanding of the chemistry of hydration is necessary for a full appreciation of the properties of cements and concretes. Hydration of cement involves chemical and physical processes between water and cement that influence the characteristics of the hardened concrete. The reactions result in an increase in solid volume on the expense of water volume and the rate of reactions increased with increased temperature **(Rikard, 2013).**

It is assumed that the hydration of each compound occurs independently of the others that are present in Portland cement. This assumption is not completely true but it is a reasonable approximation to understanding how cement hydrates. The hydration of each compound is as follows:

1. Calcium Silicates

$$2C_3S \qquad\qquad + 6H \quad \rightarrow C_3S_2H_8 + 3CH$$
Tricalcium silicate + Water → C-S-H + Calcium hydroxide

$$2C_2S \qquad\qquad + 4H \quad \rightarrow C_3S_2H_8 + CH$$
Dicalcium silicate + Water → C-S-H + Calcium hydroxide
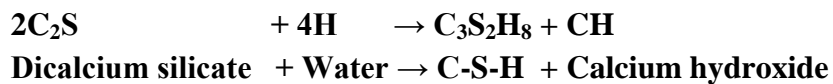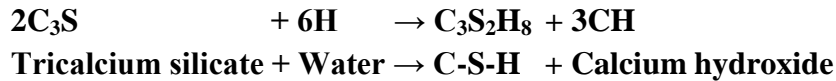
Both C_3S and C_2S react with water to produce an amorphous calcium silicate hydrate known as C-S-H gel and calcium hydroxide (CH). C-S-H is a poorly crystalline material comprising 50 to 60 % of the volume of the cement paste and thus dominates its behavior. C-S-H forms a coat around the cement grain of a spiny appearance (Figure (2.2)) which presents a physical barrier for the hydration of the inside part of the grain **(IRICEN, 2007) and (Rikard, 2013).**

Calcium hydroxide is a well crystalline material comprising 20 to 25 % of the cement paste volume. Calcium hydroxide grows within the capillary pore space (Figure (2.2)) and stops growing in a particular direction when it meets an obstacle **(Rikard, 2013).**
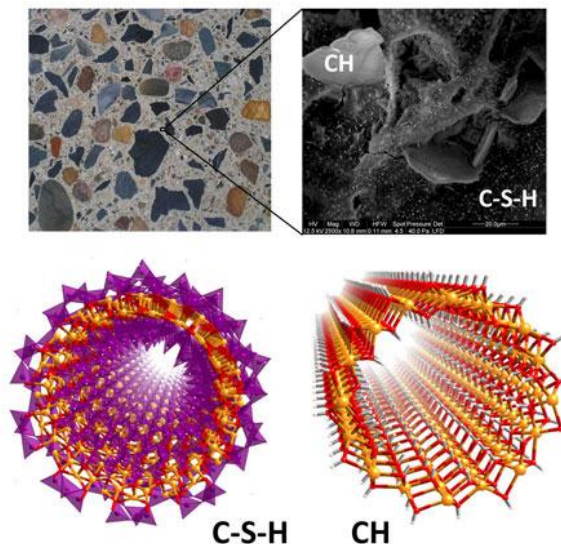
Figure 2.2: C-S-H and CH in hydrated cement paste. (Source: (Berger, 2012))

2. Tricalcium Aluminates

$$C_3A \qquad\qquad + 3C\bar{S}H_2 \quad + 26H \quad \rightarrow \quad C_6A\bar{S}_3H_{32}$$

Tricalcium aluminates   + Gypsum + Water → Ettringate
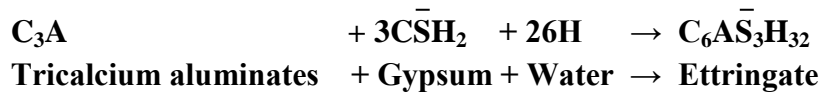
Calcium sulfoaluminate hydrate is commonly called ettringate. Ettringate is a stable hydration product only while there is an ample supply of sulfate available. If the sulfate is all consumed before the C_3A has completely hydrated, then the developed ettringate reacts once again with C_3A and water producing another form of calcium sulfoaluminates hydrate called monosulfoaluminate containing less sulfate **(Rikard, 2013):**

$$C_6A\bar{S}_3H_{32} + 2C_3A \qquad\qquad + 4H \quad \rightarrow 3C_4A\bar{S}H_{12}$$

Ettringate + Tricalcium aluminates + Water → Monosulfoaluminates

3. Ferrite

$$C_4AF \; + 3C\bar{S}H_2 \quad\; + 21H \quad \rightarrow C_6(A,F)\bar{S}_3H_{32} + (A,F)H_3$$

Ferrite + Gypsum   + Water → Ettringate   + amorphous
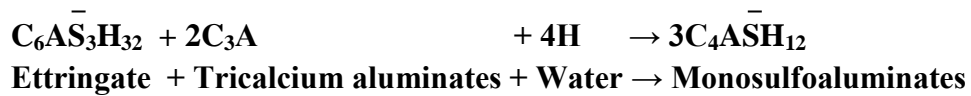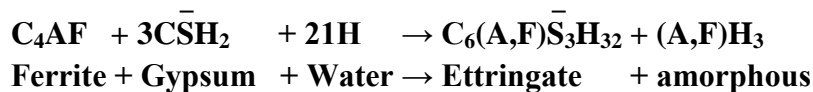
Where the amorphous is hydrous oxides of iron or alumina.

As can be seen in above reaction, C_4AF forms similar products to C_3A. The calcium sulfoaluminates (ettringate) are a relatively minor constituent of cement paste making up only 10 to 15 % by solid volume. Ettringate is seen as long slender needles (Figure (2.3)) growing into the capillary pores between cement grains **(Rikard, 2013).**
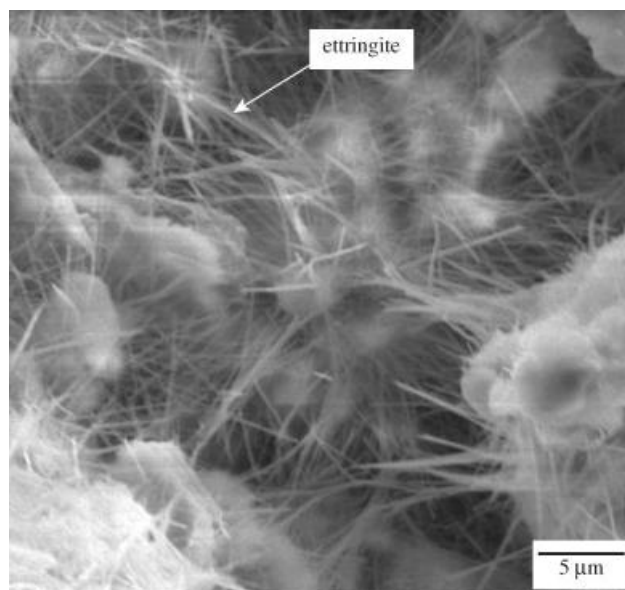
Figure 2. 3: Formation of ettringate within hydrated cement paste.
(Source: (Gemelli, Cruz & Camargo, 2004))

2.5 Durability of Concrete

The durability of concrete is one of its most important properties because it is essential that concrete should be capable of withstanding the conditions for which it has been designed throughout the life of a structure (**Neville & Brooks, 2010**). Concrete is a durable material and could have maintenance free for decades if it was designed and produced with good quality control for the environment to which it will be exposed (**Mindess, Young, & Darwin, 2002**). Based on BS 8110, a durable concrete element is one that is designed and constructed to protect embedded metal from corrosion and to perform satisfactory in working environment for life time of the structure.

The factors influence on durability of concrete include:
- Cover to embedded metal.
- Environment.
- Type of cement and cement content.
- Type of aggregate.
- w/c ratio.
- Workmanship to obtain full compaction and efficient curing (**Mindess, Young, & Darwin, 2002**).

2.6 Permeability of Concrete

The permeability of concrete plays an important role in durability because it controls the rate of entry of moisture that may contain aggressive chemicals. The permeability of concrete is related to the porosity of cement paste. However, cracking at the interface between aggregate and paste may also influence the permeability. The w/c ratio influences the permeability of concrete. As a matter of fact, the w/c ratio has the largest influence on durability of concrete. As the w/c ratio decreases, the porosity of the paste decreases and the concrete becomes more impermeable as shown in Figure (2.4) (**Mindess, Young, & Darwin, 2002**).
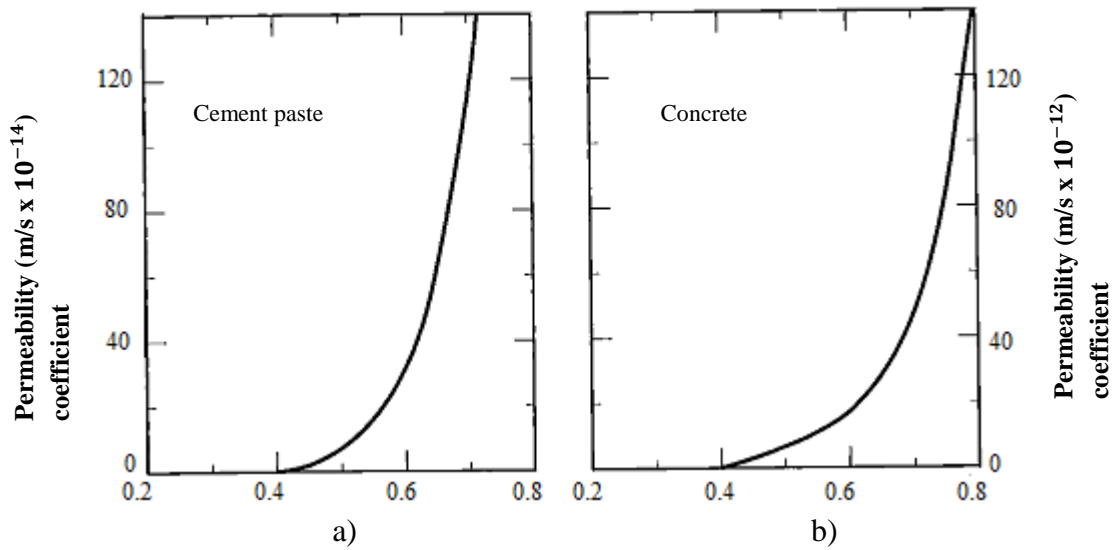
Figure 2. 4: Influence of w/c ratio on permeability of a) cement paste and b) concrete.

The w/c ratio has a dual role to play in concrete durability since a lower w/c ratio increases the strength of concrete and hence improves its resistance to cracking from the internal stresses that may be generated by adverse reactions.

The permeability of concrete can be measured by determining the rate of flow through a concrete slab. The flow of water through cement paste can be determined based on D'Arcy's law as follows:

$$v = K_p \frac{h}{x}$$

Where v is the flow rate, h is the head of water, x is the thickness of specimen and K_p is the permeability coefficient. K_p is not a constant for cement paste, being dependent on the w/c ratio and the age of the paste as can be seen in Table (2.4).

Table 2.4: Effect of age of cement paste on Kp (w/c ratio = 0.51).
(Source: (Mindess, Young, & Darwin, 2002))

Age (days)	K_p (m/s)	Notes
Fresh paste	10^{-5}	Independent of w/c ratio
1	10^{-8}	Capillary pores interconnected
3	10^{-9}	
7	10^{-11}	
14	10^{-12}	
28	10^{-13}	
100	10^{-16}	Capillary pores discontinuous (maximum hydration)
240	10^{-18}	

In a mature cement paste, K_p has a very low value even though the total porosity is high. Thus, it can be concluded that water does not easily move through very small gel pores and that permeability is controlled by an interconnecting network of capillary pores. As hydration proceeds, the capillary network becomes increasingly

tortuous as interconnected pores are blocked by the formation of C-S-H. This is accompanied by a continuous decrease in K_p and the time at which complete discontinuity of the capillary pores occurs is a function of the w/c ratio as shown in Table (2.5) (**Mindess, Young, & Darwin, 2002**).

Table 2.5: Curing time required to produce discontinuous capillary system.
(Source: (Mindess, Young, & Darwin, 2002))

w/c ratio	Curing time (days)
0.40	3
0.45	7
0.50	28
0.60	180
0.70	365
> 0.7	Not possible

In concretes with a w/c ratio greater than 0.7, complete discontinuity of capillary pores can never be achieved even with continuous moist curing and concretes will have relatively high permeability. Even after the capillary pores have been completely isolated by regions of C-S-H, K_p continuous to decrease by several more orders of magnitude. This is due not only to an increase in thickness of C-S-H between capillaries but also to the fact that calcium hydroxide continuous to grow within the residual capillary pores, thus forming impermeable regions.

2.7 Deterioration of Concrete

Concrete may deteriorate due to factors related to bad performance of paste, aggregate or reinforcement and can be due to either chemical or physical attacks as shown in Table (2.6). Deterioration is a long term problem that it is difficult to predict based on short term assessment and testing. It is noted that deterioration of concrete may be initiated due to one factor however, other factors will contribute to the problem. For example, high w/c ratio may result in shrinkage cracks that in turn increase the environment effect causing corrosion to reinforcement (**Mindess, Young, & Darwin, 2002**).

Table 2.6: Chemical and physical attack. (Source: (Mindess, Young, & Darwin, 2002))

Type	Adverse action	Affected component
Physical attack	Frost attack	Paste and aggregate
	Wetting and drying	Paste
	Temperature change	Paste and aggregate
	Wear and abrasion	Paste and aggregate
Chemical attack	Leaching and efflorescence	Paste
	Sulfate attack	Paste
	Alkali aggregate reaction	Aggregate
	Acids and alkalis	Paste
	Corrosion of metals	Reinforcement

2.7.1 Mechanism of Corrosion

Corrosion of reinforcement is well known to be the major cause of durability problems in reinforced concrete structures (**Newman & Choo, 2003**). Fortunately, concrete provides an ideal protective environment to steel from corrosion. Due to high initial alkalinity, an extremely thin passive film of ferric oxide (Fe_2O_3) is automatically formed on the surface of steel. This layer though extremely thin, effectively protects the steel from corrosion. But unfortunately this layer is effective as long as the surrounding remain alkaline. Therefore, if it is possible to keep the environment alkaline, the corrosion of steel can effectively be prevented and the durability of structure can be ensured (**IRICEN, 2007**). However, if the concrete is permeable to the extent that carbonation reaches the concrete in contact with the steel or soluble chlorides can penetrate to the reinforcement, and water and oxygen are present, then corrosion of reinforcement will take place (**Neville & Brooks, 2010**). If the passive ferric oxide film on steel is destroyed, anodic and cathodic areas will set up as shown in Figure (2.5).
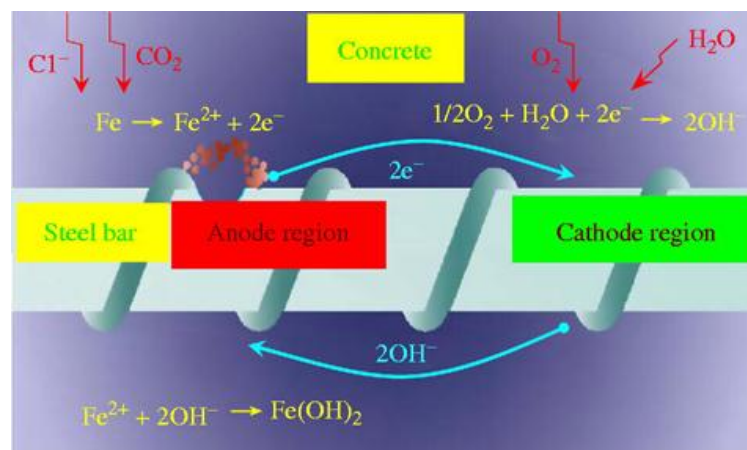
Figure 2. 5: Corrosion of concete reinforcing steel. (Source: (Qiao, Xiao & Sun, 2011))

The anode reaction is as follows:

$$Fe \rightarrow Fe^{2+} + 2e^-$$
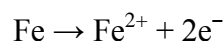
The negatively charged free electrons e^- will migrate toward the cathode where they are combined with water and oxygen to form hydroxyl ions $(OH)^-$ as follows:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$
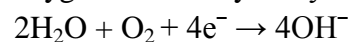
Then $(OH)^-$ ions will diffuse toward the anode and combine with ferrous ions (Fe^{2+}) to form ferrous hydroxide and this is converted by further oxidation to hydrated ferric oxide (rust) as follows:

$$Fe^{2+} + 2(HO)^- \rightarrow Fe(OH)_2 \text{ (ferrous hydroxide)}$$

$$2Fe(OH)_2 \xrightarrow{O_2, H_2O} Fe_2O_3.nH_2O \text{ (hydrated ferric oxide (rust))}$$
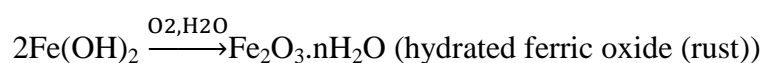
It can be concluded from above that corrosion of steel can be prevented if the concrete is sufficiently impermeable so as to keep air, water and other agents out of its reach (**IRICEN, 2007**).

2.7.2 Process of Change in pH Value
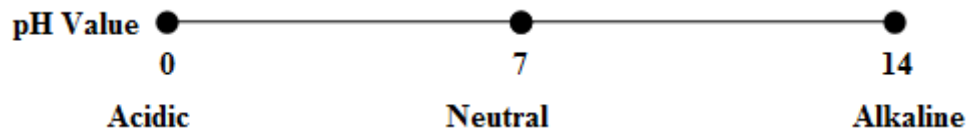
Initially cement in the hydrated form is alkaline in nature due to production of abundance of $Ca(OH)_2$ which is sufficient to maintain a high pH value in the range 12-13. But due to permeability in the concrete, this alkalinity is either destroyed due to carbonation or neutralized by acidic medium caused by varies agents. Consequently the pH value of concrete falls below the value 11.5 which is the value below which the corrosion process in the reinforcement starts. The atmospheric agents which are responsible for reduction in pH value are CO_2, Cl^- and SO_3 in presence oxygen and water (see Figure (2.6)). These agents penetrate the hydrated concrete and neutralize the alkaline medium bringing the pH value down **(IRICEN, 2007)**.
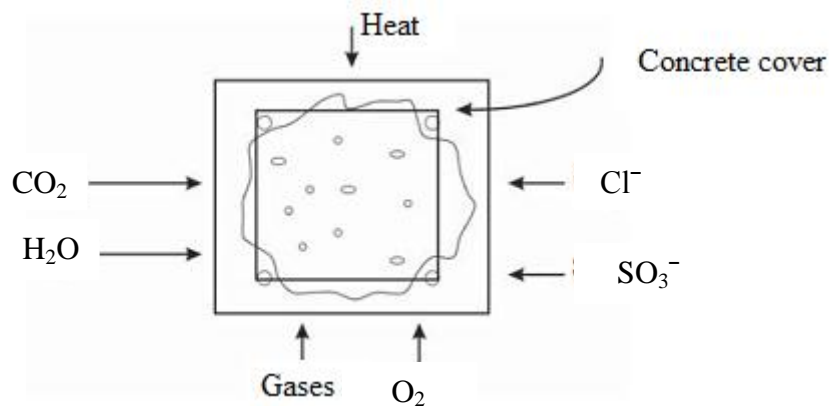
Figure 2.6: Atmospheric agents attacking concrete. (Source: (IRICEN, 2007))

2.7.3 Mechanism of Ammonium Nitrate Attack

Ammonium nitrate solutions are very corrosive to cementitious materials, which leads to dissolution of cement-based materials according to the following reactions:

$$Ca(OH)_2 + 2NH_4NO_3 \rightarrow Ca(NO_3)_2 + 2NH_3 + 2H_2O$$

$$(CaO)_3(SiO_2)_2(H_2O)_8 + 4NH_4NO_3 \rightarrow 2Ca(NO_3)_2 + 4NH_3 + (CaO)(SiO_2)_2(H_2O)_6 + 4H_2O$$
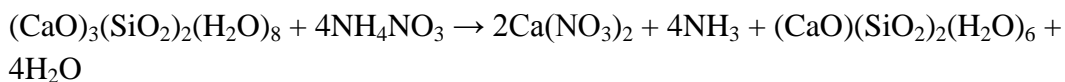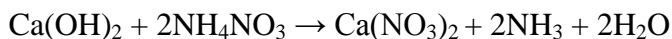
The above reactions yield calcium nitrate $Ca(NO_3)_2$ and ammonia NH_3, both of which are easily water soluble and therefore these reactions cause the dissolution of calcium hydroxide $(Ca(OH)_2)$ and calcium silicate hydrate (C-S-H). This calcium leaching in turn leads to the degradation of mechanical properties of the cement paste. Consequently, steel reinforcement corrosion may occur at an accelerated rate **(Wong et. al, 2003).**

2.7.4 Mechanism of Magnesium Sulfate Attack

Sulfate attack includes a rather complex processes related to the presence and content of C_3A. The major cause of sulfate attack is the sulfoaluminate corrosion in which ettringite (calcium sulfoaluminate hydrate) is formed again from monosulfoaluminate if an external source of sulfate is present as follows:

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \text{ (ettringite)}$$
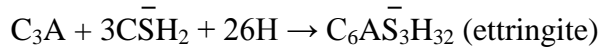
If sulfate is consumed before the complete hydration of C_3A, ettringite transforms to another form of calcium sulfoaluminate called monosulfoaluminate:

$$C_6A\bar{S}_3H_{32} + 2C_3A + 4H \rightarrow 3C_4A\bar{S}H_{12} \text{ (monosulfoaluminate)}$$

The monosulfoaluminate will in turn transform once again to ettringite when concrete is brought into contact with new source of sulfate ions from external environment:

$$C_4A\bar{S}H_{12} + 2C\bar{S}H_2 + 16H \rightarrow C_6A\bar{S}_3H_{32} \text{ (ettringite)}$$
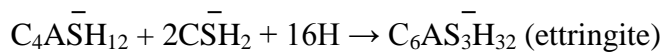
Sulfate attack results in cracking of concrete since it is associated with increase in solid volume, causing a volume expansion within the paste that generates high internal stresses and ultimately leads to cracking (**Mindess, Young, & Darwin, 2002**).

Magnesium sulfate can be even more aggressive other types of sulfates because the presence of magnesium ions may cause additional corrosive reactions that cause decomposition of both C-S-H and calcium sulfoaluminates ($C_4A\bar{S}H_{12}$) as follows:

$$C_3\bar{S}_2H_3 + 3M\bar{S} \rightarrow 3C\bar{S}H_2 + 3MH + 2\bar{S}H$$

$$C_4A\bar{S}H_{12} + 3M\bar{S} \rightarrow 4C\bar{S}H_2 + 3MH + AH_3$$
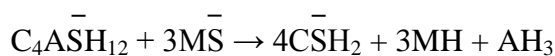
These latter reactions lead to the destruction of the hydration products that constitute the backbone of the cement paste and form the binder of cement mortar. At the same time, magnesium sulfate ($M\bar{S}$) react with portlandite (CH) and converts it to brucite (MH):

$$CH + M\bar{S} \rightarrow C\bar{S}H_2 + MH$$
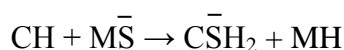
Precipitation of MH also increases the rate of gypsum corrosion and decreases the pH of the pore solution (**Mindess, Young, & Darwin, 2002**).

2.8 Previous Studies on Ammonium Nitrate Attack

Several investigations have been conducted to study the effects of ammonium nitrate on mechanical properties of cement based materials, the below studies explain that.

(Wong et. al, 2013) studied the effects of aggressive ammonium nitrate on durability properties of concrete using sandstone and granite aggregates. They aimed to investigate the durability properties of concrete being exposed to ammonium nitrate solution. To determine the durability properties, tests conducted were water absorption, volume of permeable voids (VPV) and sorptivity test. Other tests such as compressive strength test, pH measurement and degradation depth measurement were also determined.

In their investigation, experiments were conducted on two types of concretes with different proportions. The leaching process was achieved by the use of 20% concentration solution of ammonium nitrate. The specimens were cured for 3, 7, 28, 56, and 90 days respectively in the water tank for normal curing method. After 28 days curing of specimens, some of the specimens were partially immersed in ammonium nitrate solution with concentration of 20% until 56 day and 90 day (include curing age) before testing. After analysis of the results, a decrease in compressive strength and an increase in porosity were found through the conducted experiments. Apart from that, the experimental data showed that pH value decreases with increased leaching time while the degradation depth of concrete increases with leaching time.

(Escadeillas, 2013) investigated the performance of cement-based materials in aggressive aqueous environments: ammonium nitrate attack on cementitious materials. It was indicated that ammonium nitrate solutions produce rapid decalcification of cement due to the high solubility of its calcium salts and degradation reactions related to ammonium nitrate solutions are swift and severe. The results also showed that external stresses on the specimens can significantly accelerate the chemical attack. In addition, this research showed that the influencing of nitrate attack on concrete depends on the following parameters: initial strength of materials, composition of cementitious materials and initial concentration of ammonium nitrate solution.

(Schneider & Chen, 2005) investigated deterioration of high-performance concrete subjected to attack by the combination of ammonium nitrate solution and flexure stress. The behavior of ordinary concrete and high strength concrete under a combinative effect of stress and chemical corrosion was studied in this work. The concrete specimens were immersed in a variety of chemical solutions including 10%, 5%, 1% and 0.1% ammonium nitrate and simultaneously subjected to different flexural loads with load levels of 30%, 40% and 50% of their initial flexure strengths. The influences of the concentration of solutions, quality class of the

concretes and load level of applied flexural stress on the strength of concretes were investigated. The relationships between life-time of the concrete and concentration of the solution, relative strength of the concrete and penetration depth of the ammonium nitrate solutions were determined.

The results showed that a high strength of concrete, a lower load level and concentration of the aggressive solution lead to a higher resistance against stress corrosion attacks. In addition, it is concluded that the life-time of the concretes decreases significantly with an increase in concentration of the ammonium nitrate solution and a higher concentration of the solutions led to a deeper penetration of the aggressive ions after a certain period of immersion.

(Carde & Francois, 1997) presented the effect of the leaching process of cement based materials on their mechanical and physical properties. In order to characterize this effect, they performed experiments on cement paste samples. The leaching process was achieved by the use of a 50% concentrate solution of ammonium nitrate. Both compression tests and water porosity tests were conducted on micro-cylinder samples (10, 12, 14 and 20 mm of diameter) because of the slow kinetics of degradation due to the leaching. Both mechanical tests and water porosity tests showed that there is a linear variation of the loss of strength and the increase in porosity in relation to the ratio of degraded area over total area of the sample. Furthermore, it is indicated that the dissolution of calcium hydroxide is the essential parameter governing both decrease in strength and increase in porosity.

(Bellego, Gerard & Cabot, 2000) focused on coupled chemo-mechanical effects on concrete structures subjected to aggressive water inducing calcium leaching. Experimental investigations on mortar bending beams were discussed. For this study, an ammonium nitrate solution NH_4NO_3 has been selected at a concentration of 480 g/L and kept at $30^{o}C$. Experimental results indicated that the stiffness of mortar decreases, along with its strength, as the chemical attack progresses. Also due to leaching, the brittleness of the structures is increased and the fracture energy decreases.

(Agostini et. al, 2007) investigated experimental study of accelerated leaching on hollow cylinders of mortar. Two mortars, differencing mainly in their initial porosity, were degraded by the use of a chemically accelerated process with ammonium nitrate solution. The aggressive solution was a 6-M ammonium nitrate solution (480 g/l). The leaching effects were evaluated by studying variations in mechanical and hydraulic properties. The total process of degradation was carried out in three steps: 4, 8 and 16 days. The test results showed that the increase in porosity and the loss in volumetric mass roughly depend on the estimated cement paste proportion of each mortar. It is also found that a permeability increase of more than two orders of magnitude and a loss in strength and elastic modulus of more than 85% were observed for both mortars.

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(Nguyen et. al, 2007) studied concrete behavior under chemical and mechanical degradations. Experimental investigations were described where the effects of the calcium leaching process of concrete on its mechanical properties were highlighted. The calcium leaching and mechanical tests on cement paste, mortar and concrete samples were presented. The specimens are immersed into a 6mol/l ammonium nitrate solution. To quantify the leaching evolution, the degradation depth was then measured at certain time intervals (36, 57, 105, 152, 163, 197, 274 and 547 days for the case of concrete) by means of a phenolphthalein solution. The experimental results showed the chemical degradation of the cement-based material and the important role of aggregate in the calcium leaching process of concrete. They also concluded that there is a strong coupling between the calcium leaching and the mechanical behavior; as leaching grows, a loss of stiffness and of strength were observed.

(Kamali, Moranville & Leclercq, 2008) discussed the material and environmental parameter effects on the leaching of cement pastes. Four parameters were investigated: type of cement (Portland cement, silica fume cement, slag cement, ternary cement with slag and fly ash); water-to-cement ratio (0.5, 0.4, 0.25), temperature (26°C, 72°C, 85°C) and chemical composition of the leaching solution (pure water, mineralized water, ammonium nitrate solution). The tested specimens were prisms of 20 mm width, 20 mm height and 30 mm length, and the aggressive solution was a 480 g/L ammonium nitrate solution. The experimental results showed that the leaching of the different pastes in ammonium nitrate solution whether at room temperature or 85°C was characterized by the presence of an easily identified leached zone. The results clearly showed that the leaching process increases significantly with the water-to-cement ratio and temperature for the different cements with and without mineral additions. However these additions strongly decrease the leaching kinetics. This decrease depends on the type and amount of the mineral addition.

(Segura et. al, 2013) studied the decalcification of cement mortars: characterization and modeling. A thorough microstructural characterization of a set of cement mortars (made with three w/c ratios and five different cement types), degraded by the ammonium nitrate method were studied in this research. Both destructive and ultrasonic non-destructive techniques were used to characterize the samples. The results showed that the initial calcium content of the samples plays a dominant role in both the advance of the degradation process and the degradation grade of the samples.

2.9 Previous Studies on Magnesium Sulfate Attack

Several researches have been conducted to study the effects of magnesium sulfate on mechanical properties of cement based materials as follow:

(Senhadji et. al, 2010) investigated the compressive strength and visual change of mortar specimens subjected to severe sulfate attack and cured at 5°C and 23°C. Specimens were immersed in magnesium sulfate solutions with 5% (50g/L) of concentration for periods of up to 360 days. Mortars and pastes were mixed and cast as 50×50×50 mm3 prisms for compressive strength measurement. Prior to the compressive strength tests, cubic mortar specimens were thoroughly visually investigated, and signs of deterioration, e.g. cracking, spalling, and delamination, were checked. The compressive strength of the mortar cubes was measured after 28, 150, 240, and 360 days of 5% magnesium sulfate exposure.

Experimental results indicated that the first sign of attack was the deterioration of the corners, followed by cracking along the edges. Progressively, expansion and spalling took place on the surface of the specimens. The reduction in the compressive strength values of mortar specimens immersed in sulfate solutions under various conditions were also observed.

(Santhanam, Cohen, & Olek, 2002) studied the effects of concentration and temperature of sodium and magnesium sulfate solutions on the expansion of cement mortars. ASTM Type I PC mortars were immersed in sodium and magnesium sulfate solutions at five different concentrations and four different temperatures. The temperatures of storage were 5, 21, 30, and 38°C. Five different concentrations were evaluated for each type of solution that had an equivalent SO_3 content of 25,000, 12,500, 6250, 3125, and 1562 ppm (parts per million, or milligrams per liter). The length of 5×16×80 mm mortar prisms was measured periodically. According to the results, an increase in the temperature, or in the concentration of the magnesium sulfate solution results in an increase in the rate of expansion. The rate of diffusion of sulfate ions within specimens increases with the time of immersion, and, hence, the rate of expansion also continuously increases. Furthermore, it is observed that an increase in temperature or concentration causes the rate of diffusion to increase.

(Tosun, 2012) discussed the effect of C_3A content on sulfate durability of Portland limestone cement mortars. Cements with two different C_3A contents (4.6%, 11.2%) have been used. Limestone incorporation ratios were 5%, 10%, 20% and 40%, respectively. Standard mortar samples of 50×50×50 mm cubes and 25×25×285 mm prisms have been prepared. After 1 months of water curing, samples have been exposed to different sulfate solutions (Na_2SO_4 and $MgSO_4$) with 20% (200g/L) of concentration and temperatures (5 and 20°C) for a period of 6 months. During this period length changes were monitored and compressive strength values have been determined at 3 and 6 months intervals of sulfate exposure.

Test results showed that increasing C_3A content propagate the deterioration rate of limestone blended cement mortars exposed to both Na_2SO_4 and $MgSO_4$ solutions. This situation is more significant at higher limestone replacement ratios and low temperatures. It was also concluded that while the expansion increases were more

significant for samples exposed to Na_2SO_4 solution, compressive strength decreases were more indicative in the case of $MgSO_4$ solution exposure due to direct damage of the C-S-H structure besides, formation of thaumasite (a calcium-carbonate-silicate-hydrate which attacks the C-S-H matrix and causes loss of integrity of the concrete) and gypsum.

(**Türker et. al, 1997**) presented the effects of magnesium sulfate concentration on the sulfate resistance of mortars with and without silica fume. An investigation was carried out on the resistance of mortars to magnesium sulfate attack. Experiments were carried out on Portland cement (PC) and Portland cement-silica fume (PC-SF) mortars. Mortars were immersed in magnesium sulfate solutions after 28 days of lime-saturated water curing. Concentrations were 1900, 13000 and 52000 mg/L as SO_4^{-2} solutions. A number of physical and mechanical properties were determined at different periods of exposure up to 300 days.

The results indicated that for the first 28 days of exposure, some improvements of mortar properties in magnesium sulfate environment were observed. This is the early stage of sulfate attack. Thereafter, negative changes of the properties indicate a transition stage. Deterioration process of mortars was retarded by the presence of silica fume. After the transition stage, negative changes of physical properties accelerate, indicating the later stage. Compressive and flexural strength properties showed different response to magnesium sulfate attack at later stage. Only in 52000 mg/L concentration, all the measured properties showed clear negative changes.

(**Kumar & Kameswara, 1994**) studied the effect of sulfates on the setting time of cement and strength of concrete. The quantities of sodium sulfate (Na_2SO_4), calcium sulfate ($CaSO_4$), ammonium sulfate (($NH_4)_2SO_4$) and magnesium sulfate ($MgSO_4$) added to the water for making the sulfate solution with sulfate concentration (SO_4^{--}) equal to 1000, 3000, 5000 and 10000 ppm. They concluded that concrete exposed to sulfate attack, loses compressive strength and this loss increases as a function of sulfate concentration and age of exposure. In addition, the effect of different sulfate solutions on compressive strength of concrete was not equally severe. The effect of magnesium sulfate was found to be the most severe.

(**Justnes, 2003**) investigated sulfate attack on mortar with limestone filler. Experiments were performed where mortars with 20% limestone are stored in 5% magnesium sulfate solution saturated with gypsum at 5°C. Mortars were mixed and cast as 40 mm×40 mm×160 mm prisms. The prisms were cured at 90% relative humidity and 20 °C for 28 days prior to storage in magnesium sulfate solution. Length change, flexural strength and compressive strength are measured periodically for a year. The results showed that there was mass loss, expansion and strength reduction during months of exposure.

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Chapter 3

Constituent Materials and Experimental Program

CHAPTER 3- CONSTITUENT MATERIALS AND EXPERIMENTAL PROGRAM

3.1 Introduction

This chapter comprises the experimental program and the constituent materials used to study the influence of ammonium nitrate and magnesium sulfate solutions on cement mortar. Preparing of several concentrations of ammonium nitrate and magnesium sulfate are presented. The mixing, casting and curing procedures are also discussed in this chapter.

The laboratory investigations consisted of testing hardened cement mortar properties. The tests for hardened cement mortar include compression tests, porosity and unit weight tests. These tests are performed at different periods of exposure to aggressive solutions.

The properties of several constituent materials used in this work are also discussed such as moisture content, unit weight, specific gravity and the grain size distribution. The test procedures, details and equipment used to assess mortar properties are illustrated in the following sections.

3.2 Experimental Program

This study investigates the effects of aggressive environments on cement mortar properties. This experiment utilized ammonium nitrate and magnesium sulfate as aggressive solutions. The following parameters were chosen to demonstrate degradation effects:
- Compressive strength.
- Porosity.
- Unit weight.

Ammonium nitrate and magnesium sulfate solutions with the following concentrations were used to investigate their effects on the mortar:
- 5% (50g/L)
- 20% (200g/L)
- 50% (500g/L)

In addition, some samples were immersed in distilled water as control samples.

Test specimens were prepared by placing the cement-based material into $5 \times 5 \times 5$ cm molds. After 24 hours, the specimens were demolded and placed in a water tank at room temperature for 28 days. After 28 days curing of specimens, some of the specimens were immersed in ammonium nitrate and some of them were immersed in magnesium sulfate solutions until 10, 20, 40 and 60 days before testing. Each series of samples were finally dried in an oven. Such drying is necessary to carry out porosity and loss of mass measurements.

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The test program to be deployed in order to achieve the objectives of this research is shown in Figure (3.1).
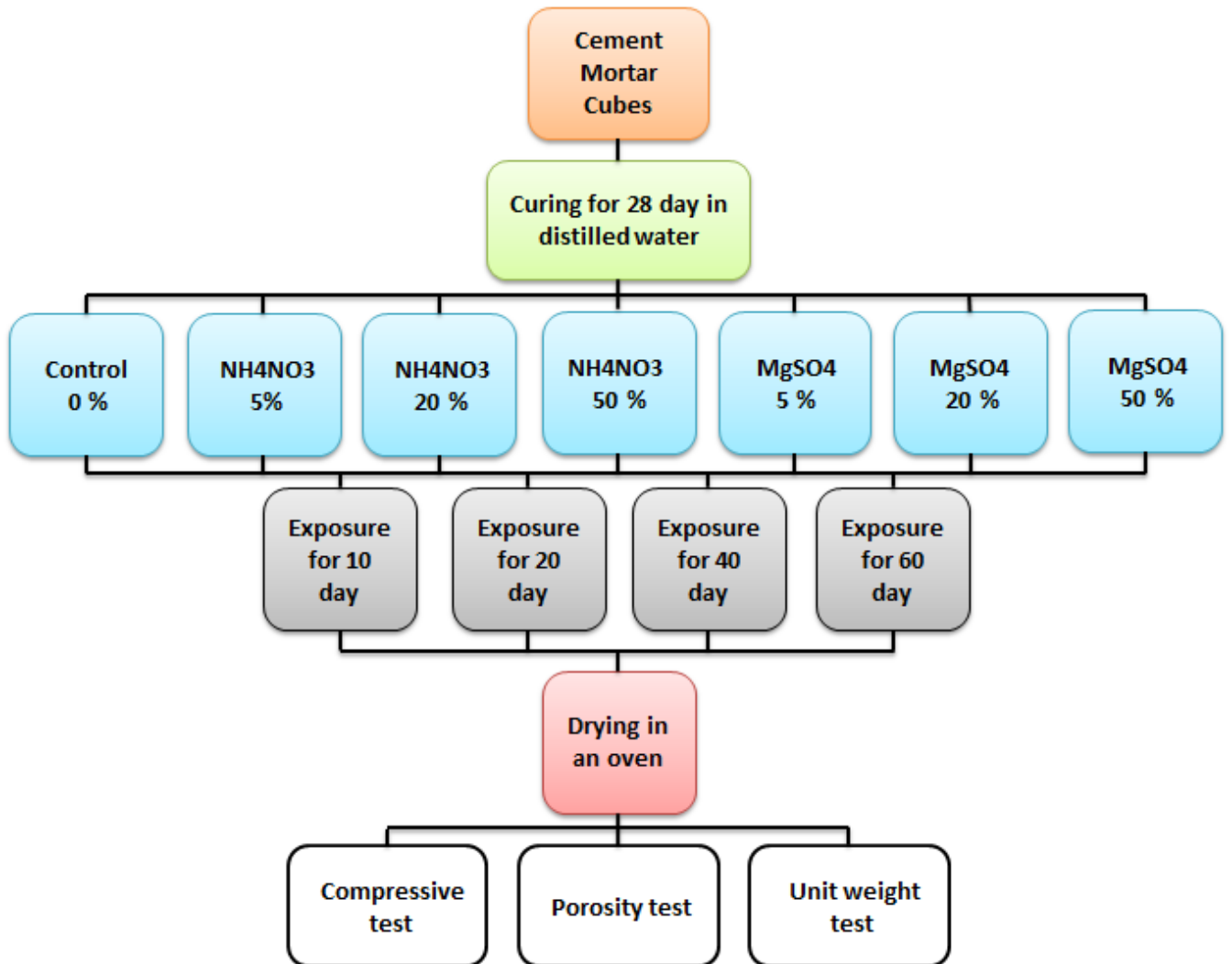
Figure 3.1: Experimental program steps chart.

3.3 Characteristics of Constituent Materials of Mortar

It is very important to know the properties and characteristics of constituent materials of mortar, as we know, mortar is a composite material made up of several different materials such as fine aggregate, cement and water. Therefore, it is necessary to work out tests on these components, and that to know the unique characteristics and their impacts on properties of mortar.

The necessary tests are conducted in the laboratory of materials and soil in the Islamic University and in accordance with ASTM "American Society for Testing and Materials".

3.3.1 Cement

In this research Arish ordinary Portland cement CEM I 52.5 N produced in Egypt was used. The cement met the requirements of ASTM C 150 specifications. The results of physical and mechanical analyses of the cement are summarized in Table (3.1) along with the requirements of relevant ASTM specifications for comparison purposes.

Table 3. 1: Cement characteristics according to the manufacture sheets.

Test type		Ordinary Portland cement	
		Results	**ASTM C 150**
Setting time (Vicat test) hr min	Initial	126	Not less than 45 min
	Final	155	Not more than 375 min
Mortar compressive strength (MPa)	3 Days	---	Min. 12 MPa
	7 Days	---	Min. 19 MPa
	28 Days	57	No limit
Fineness (cm^2/gm)		3020	Min. 2800
Normal consistency (%)		27	No limit

3.3.2 Fine Aggregate

Local dune sand was used as fine aggregate. The specific gravity and absorption of the fine aggregates are typically 2.6 and 0.57%, respectively, and the maximum sieve size for the fine aggregate is 600 μ. These tests were done according to ASTM C128.

3.3.3 Water

Distilled water without any salts and chemicals was used in mixing, curing and preparing different aggressive solutions. The water source was the soil and material lab at IUG (Islamic University of Gaza).

3.4 Preparing of Aggressive Solutions
3.4.1 Preparing of Ammonium Nitrate Concentrations

Several quantities of ammonium nitrate were added to water for making the nitrate solutions with several concentrations. Figure (3.2) shows three tanks with 5%, 20% and 50% concentrations of ammonium nitrate.

Figure 3.2: Ammonium nitrate concentrations.

3.4.2 Preparing of Magnesium Sulfate Concentrations

In order to prepare magnesium sulfate solutions with several concentrations, quantities of magnesium sulfate in solid state were added to water until reaching the required concentrations. Figure (3.3) presents several basins with 5%, 20% and 50% concentrations of magnesium sulfate.

Figure 3.3: Magnesium sulfate concentrations.

3.4 Mix Proportions

The specimens prepared for this study are based on the requirements of ASTM C109. The water/cement (w/c) ratio is fixed at 0.45 for all specimens in this study. The cement/sand ratio is set at 1:2.5.

3.5 Mixing, Casting and Curing procedures

The mortar mixture were made according to the previous mix design, after the required amounts of all constituent material are weighed properly and then they are mixed. A mechanical mixer was used in the mixing process shown in Figure (3.4).

Figure 3.4: Mechanical mixer.

The mixing procedure as the following steps:
- Place all the mixing water in the bowl.
- Add the cement to the water, then start the mixer and mix at the low speed (140 ± 5 revolution/ minute) for (30 second).
- Add the entire quantity of sand slowly over a (30 second) period , while mixing at slow speed.
- Stop the mixer, change to medium speed, (285 ± 10 revolution/ minute) and mix for 30 second.

- Stop the mixer and let the mortar stand for 1.5 min. During the first (15 second) of this interval, quickly scrape down into the batch any mortar that may have collected on the side of the bowl.
- Finish by mixing for (1minute) at medium speed.

In this study, test specimens were prepared by placing the cement-based material into $5 \times 5 \times 5$ cm steel moulds as shown in Figure (3.5). The casting procedure as the following:

- Paint the cube by oil to prevent mortar sticking on the corner of cube.
- Place a layer of mortar about 25 mm (half the depth of the mold) in all the cube specimens.
- Tamp the mortar in each cube by using tamping rod 32 times (4x8), about 4 rounds, each round to be at right angles to the other.
- When the tamping of the first layer in all cubes is completed, fill the moulds with the remaining mortar and tamp as specified for the first layer.
- Cut off the mortar to a plane surface with a straight edge.
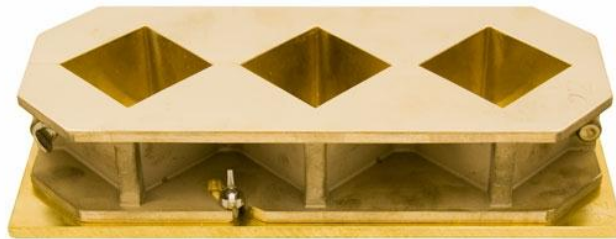
Figure 3.5: The specimens moulds.

After casting all moulds, specimens were left undisturbed for 24 hours in a moist room and then demoulded. The specimens were cured for 28 days in the water tank for normal curing method as shown in Figure (3.6). The total number of specimens were used in this research equals 120 samples.

Figure 3.6: Curing of specimens in water tanks.

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3.6 Testing of Specimens

Before conducting the following tests, **(Cheng, Chao, & Lin, 2013)** recommended that the specimens after each period of immersion are moved into distilled water soaking for 10 days before testing in order to allow for soluble materials due to degradation process to flow out from specimen (see Figure (3.7)).

Figure 3.7: Rinsing of samples before testing.

3.6.1 Compression Test

This study conducted compressive strength tests in accordance with ASTM C109 at 10, 20, 40 and 60 days after immersion of $5 \times 5 \times 5$ cm cubes in ammonium nitrate and magnesium sulfate solutions. Before doing the tests, the specimens were dried in an oven. Therefore, the dried state is a reference state which was chosen in order to compare intact and degraded material.

The compressive strength machine in Soil and Material Laboratory at IUG was used for determining the compressive loads carried by mortar specimen cubes as shown in Figure (3.8). The specimens were placed on a testing machine with a rate of 1 kgf/cm^2 of pressure per second to execute the uniaxial compression test.

The cubes are placed in the testing machine so that the load is applied to opposite sides as cast and not to the top and bottom as cast. Therefore, the bearing faces of the specimen are sufficiently plane as to require no capping. The compressive strength of the specimen σ_{comp} is calculated by dividing the maximum load carried by the cube specimen during the test by the cross sectional area of the specimen.

$$\sigma_{comp} = \frac{P}{A}$$

At least three cubes were tested for each period and the mean value of the specimens was considered as the compressive strength of the experiment.

Figure 3.8: Compressive strength machine.

3.6.2 Unit Weight Test

The weight of samples were measured after drying in an oven (see Figure (3.9) and Figure (3.10)) at a moderate temperature of 60°C for at least 48 hours (**Agostini et. al, 2007**). Higher temperatures increase the rate of hydration and lead to micro-cracking induced by shrinkage and differential strains between cement paste and aggregates. This drying is necessary to know the loss of mass due to degradation effects.

Unit weight (γ) is the weight per unit volume:

$$\gamma = \frac{W}{V}$$

Figure 3.9: Drying of samples in an oven.

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Figure 3.10: Weight of samples.

3.6.3 Porosity Test

Porosity was deduced from the difference between saturated and dried sample weight. In order to calculate the porosity ratio (%), the weight of leached samples was measured after rinsing in water tank for ten days (W_1). The weight was also measured after drying of samples in an oven at a moderate temperature of 60°C (W_2). Therefore,

$$\% \, Porosity = \frac{W_1 - W_2}{W_2} \times 100\%$$

Chapter 4

Test Results and Discussion

CHAPTER 4- TEST RESULTS AND DISCUSSION
4.1 Introduction

This chapter presents and discusses the results of the tests that were performed in order to study effects of ammonium nitrate and magnesium sulfate with several concentrations on cement mortar specimens at different ages of exposure. The results were observed from compressive strength, porosity and unit weight tests. These tests were performed at the Materials and Soil Laboratory at the Islamic University of Gaza.

4.2 Effects of Ammonium Nitrate on Cement Mortar
4.2.1 Compressive Strength Test Results

The test results of the compressive strength of cement mortar subjected to attack of ammonium nitrate solutions with several concentrations are shown in Table (4.1). Table (4.2) shows the reduction percent in compressive strength of cement mortar immersed in 5%, 20% and 50% of ammonium nitrate concentrations at 10, 20, 40 and 60 days.

Table 4. 1: Effects of ammonium nitrate on compressive strength of cement mortar at different ages.

Test	Time of immersion (days)	Concentration of NH_4NO_3			
		0%	5%	20%	50%
Compressive strength (MPa)	0	47	47	47	47
	10	48	46	44	37
	20	51	44	38	33
	40	55	38	31	23
	60	55	36	27	21

Table 4. 2: Reduction percent of compressive strength of cement mortar exposed to 5%, 20% and 50% ammonium nitrate at different ages.

	Time of immersion (days)	Concentration of NH_4NO_3		
		5%	20%	50%
Reduction in compressive strength (%)	0	0	0	0
	10	2	6	21
	20	6	19	30
	40	19	34	51
	60	23	43	55

The effects of ammonium nitrate on compressive strength of cement mortar at different ages as well as the relative strength ($f_c/f_{c,28}$) (compressive strength of cement mortar after immersion in aggressive solutions to initial compressive strength after 28 days of curing in distilled water) of the cement mortar stored in water and in

5%, 20% and 50% ammonium nitrate solutions are represented graphically versus time in Figures (4.1) and (4.2) respectively.

Figures (4.1) and (4.2) show that at 0% concentration of ammonium nitrate, the compressive strength increased from 47 MPa to 55 MPa after 60 days. This shows that the compressive strength increased by about 17% of its initial strength after 28 days of curing. It is also observed that several nitrate solutions affect the compressive strength of cement mortar differently. At 5% concentration of ammonium nitrate, the compressive strength of cement mortar specimens decreased from 47 MPa to 36 MPa after 60 days of exposure. This shows that the compressive strength reduced by 23%. The concentration of ammonium nitrate at 20%, the strength decreased to 38 MPa at the age of 20 days whereby there was a loss of 19% in strength compared to the initial strength. It continued to decrease until 27 MPa at the age of 60 days, leading to reduction of 43% compared to those treated in pure water.

The strength of the cement mortar immersed in 50% ammonium nitrate solution decreased clearly. At 20 and 60 days of exposure, the compressive strength reduced to 30 MPa and 55 MPa respectively. This indicates that the loss of strength at the age of 20 days was about 21% while for cement mortar at the age of 60 days, the reduction in strength was 55%.

It is found true that the compressive strength decreased when the mortar specimens was treated with ammonium nitrate solutions and as the nitrate concentration increase, the loss in compressive strength increase significantly at all ages.
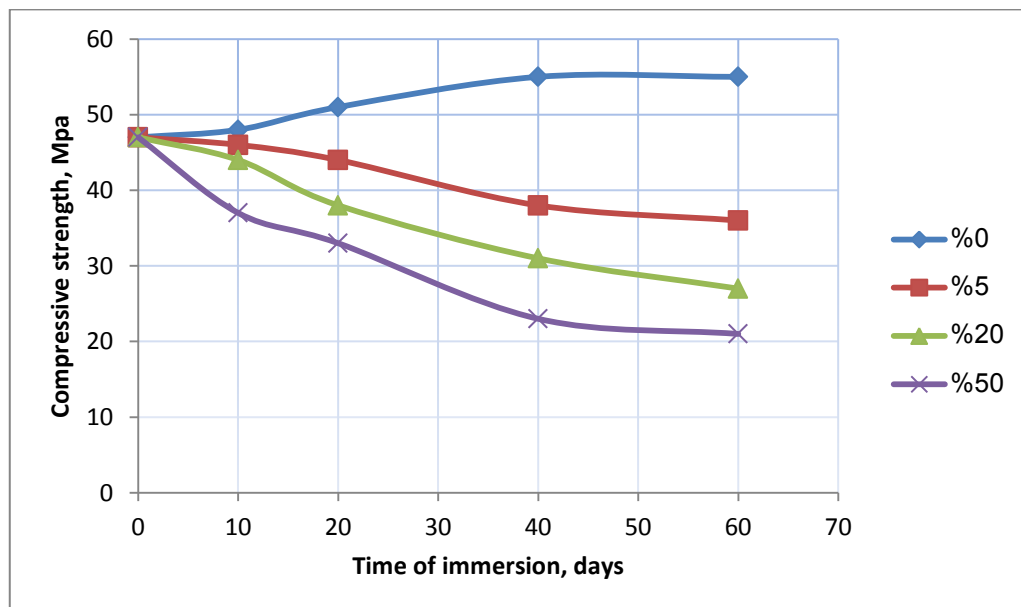
Figure 4.1: Effects of ammonium nitrate on compressive strength of cement mortar at different ages.
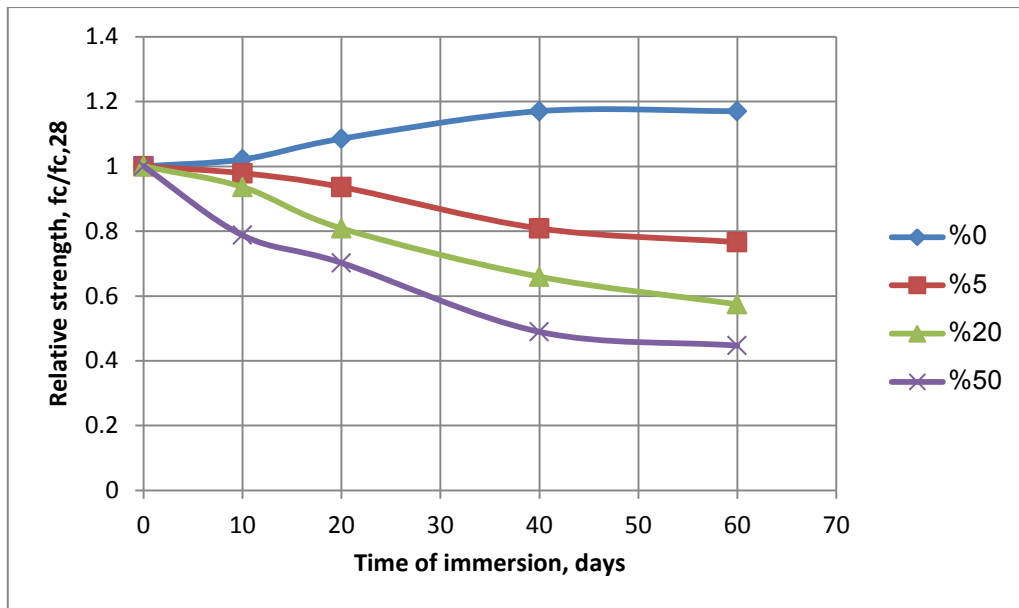
Figure 4.2: Relative strength of the cement mortar in water and in 5%, 20% and 50% NH$_4$NO$_3$ solutions.

The reduction in the compressive strength of mortar specimens exposed to 5%, 20% and 50% ammonium nitrate after 60 days is shown in Figure (4.3).
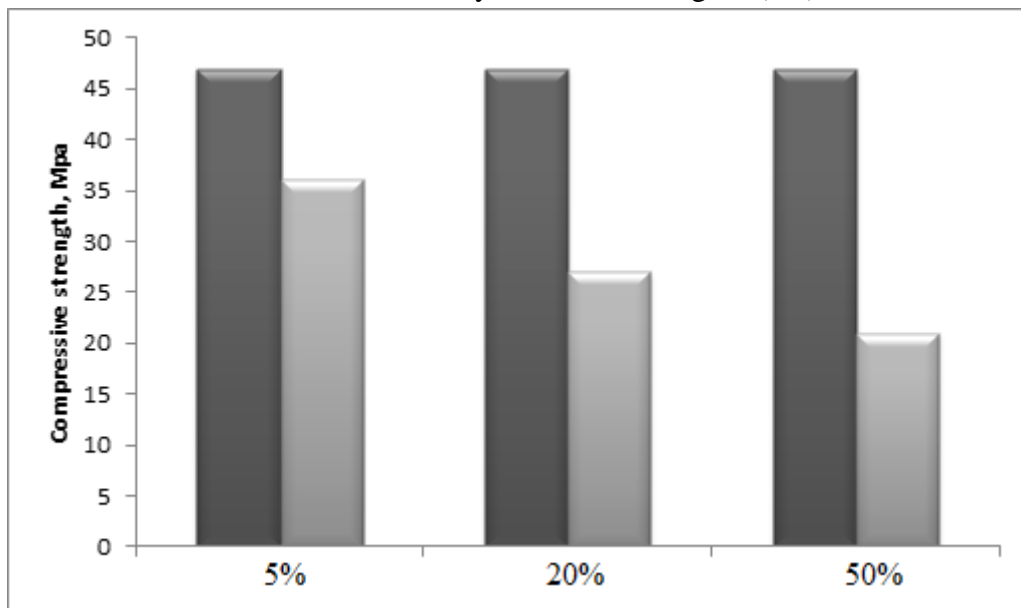
Figure 4. 3: The reduction in the compressive strength of mortar specimens exposed to 5%, 20% and 50% NH$_4$NO$_3$ after 60 days.

The loss of strength was essentially due to the removal of calcium hydroxide (CH) and progressive decalcification of C-S-H. Chemical attack by ammonium nitrate leads to a very soluble calcium nitrate salt and ammonia (NH$_3$) emanation and this produces voids or pores within cement mortar. These voids weaken the strength of mortar. This agrees with the results obtained by **(Wong et. al, 2013) and (Escadeillas, 2013)** in their studies.

4.2.2 Porosity Test Results

The test results of the porosity of cement mortar subjected to attack of ammonium nitrate solutions with several concentrations is shown in Table (4.3). The effects of ammonium nitrate on porosity of cement mortar at different ages stored in water and in 5%, 20% and 50% ammonium nitrate solutions are represented graphically versus time in Figure (4.4).

Table 4.3: Effects of different concentrations of ammonium nitrate on porosity of cement mortar at different ages.

Test	Time of immersion (days)	Concentration of NH$_4$NO$_3$			
		0%	**5%**	**20%**	**50%**
Porosity (%)	**0**	5.1	5.1	5.1	5.1
	10	5.1	5.2	5.4	6.4
	20	5.0	5.6	6.5	9.5
	40	4.8	6	8.2	12
	60	4.8	6.4	9	16

From Figure (4.4), It is observed that at several nitrate solutions, the porosity of cement mortar is significantly affected. At 5% concentration of ammonium nitrate, the porosity of cement mortar increased from 5.1% to 6.4% after 60 days. For the concentration of ammonium nitrate at 20%, the porosity increased by 3.9% of its initial porosity after 60 days of exposure while for 50% ammonium nitrate solution, the porosity increased from 5.1% to 16% after 60 days and this shows that there is a considerable increase in porosity at high concentrations of ammonium nitrate.

The test results indicated that the porosity increased when the cement mortar specimens was treated with ammonium nitrate solutions and with the immersion period.
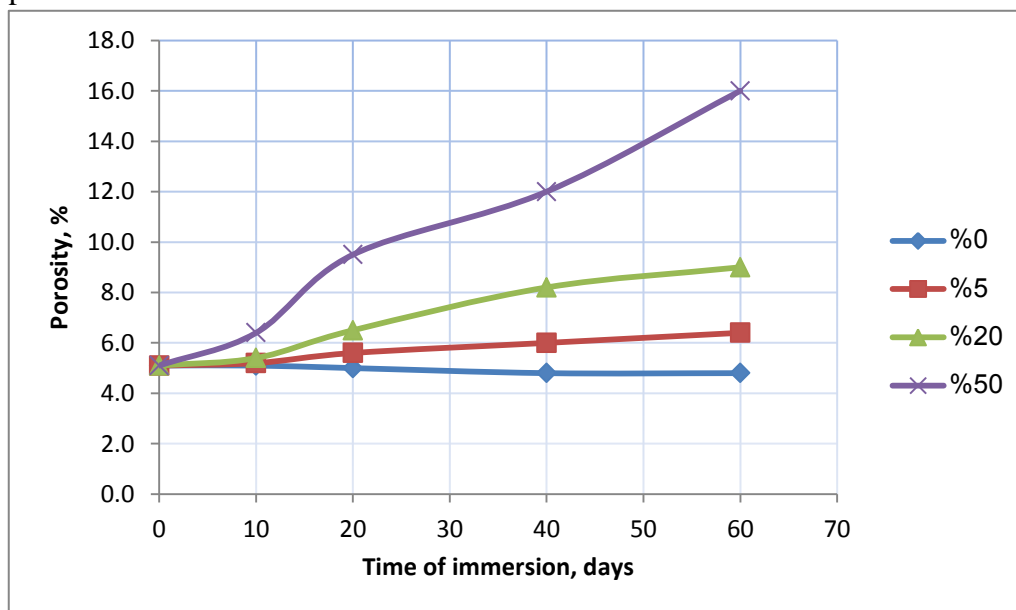
Figure 4.4: Effects of different concentrations of ammonium nitrate on porosity of cement mortar at different ages.

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The porosity of cement mortar specimens immersed in ammonium nitrate was higher than those cured in water. This can be attributed to the removal of calcium hydroxide (CH) and a progressive decalcification of C-S-H. This introduces more voids within mortar, increases the porosity of mortar and causing the mortar to become more permeable. This finding agrees with the results obtained by **(Wong et. al, 2013) and (Agostini et. al, 2007)** in their studies.

4.2.3 Unit Weight Test Results

The test results of the unit weight of cement mortar subjected to attack of ammonium nitrate solutions with several concentrations is shown in Table (4.4). The effects of ammonium nitrate on unit weight of cement mortar at different ages stored in water and in 5%, 20% and 50% ammonium nitrate solutions are represented graphically versus time in Figure (4.5).

Table 4.4: Effects of different concentrations of ammonium nitrate on unit weight of cement mortar at differrent ages.

Test	Time of immersion (days)	Concentration of NH_4NO_3			
		0%	**5%**	**20%**	**50%**
Unit weight (g/cm^3)	**0**	2.18	2.18	2.18	2.18
	10	2.18	2.18	2.16	2.14
	20	2.19	2.16	2.13	2.10
	40	2.19	2.14	2.09	2.04
	60	2.18	2.12	2.04	1.99

Figure (4.5) indicated that at several nitrate solutions, the unit weight of cement mortar is moderately affected. For the concentration of ammonium nitrate 5%, the unit weight decreased from 2.18 g/cm^3 to 2.12 g/cm^3 while the unit weight decreased from 2.18 g/cm^3 to 2.04 g/cm^3 for 20% concentration of ammonium nitrate after 60 days of immersion. The unit weight of cement mortar immersed in 50% ammonium nitrate solution was reduced by 0.19 g/cm^3 after 60 days of exposure. This shows that the loss in the unit weight was about 9% of its initial unit weight.

From the obtained test results, It can be said that the unit weight decreased when the mortar specimens was immersed in ammonium nitrate solutions.
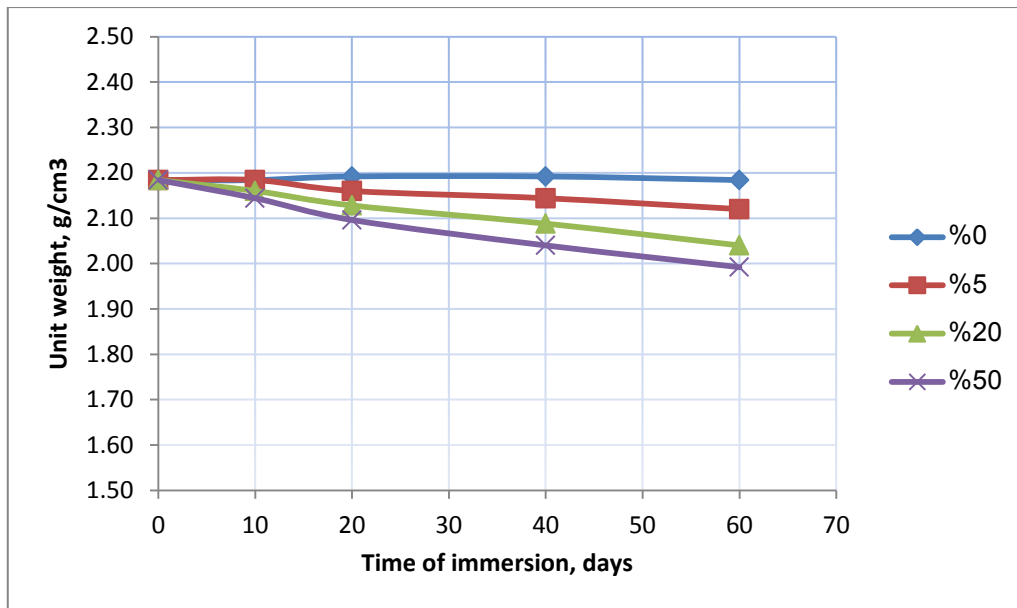
Figure 4. 5: Effects of different concentrations of ammonium nitrate on unit weight of cement mortar at differrent ages.

Removal of calcium hydroxide (CH), decalcification of C-S-H and increases of porosity of cement mortar due to expose to ammonium nitrate solution, this results in the modification of microstructure of mortar specimens causing a decrease in unit weight. This met with the results obtained by **(Wong et. al, 2013) and (Agostini et. al, 2007)** in their studies.

4.3 Effects of Magnesium Sulfate on Cement Mortar
4.3.1 Compressive Strength Test Results

Table (4.5) shows the test results for the compressive strength of cement mortar subjected to attack of magnesium sulfate solutions with different concentrations. The reduction percent in compressive strength of cement mortar immersed in 5%, 20% and 50% of magnesium sulfate concentrations at 10, 20, 40 and 60 days is shown in Table (4.6).

Table 4. 5: Effects of magnesium sulfate on compressive strength of cement mortar at different ages.

Test	Time of immersion (days)	Concentration of $MgSO_4$			
		0%	**5%**	**20%**	**50%**
Compressive strength (MPa)	**0**	47	47	47	47
	10	48	46	45	42
	20	51	45	38	32
	40	55	42	30	23
	60	55	39	28	20

Table 4.6: Reduction percent of compressive strength of cement mortar exposed to 5%, 20% and 50% of magnesium sulfate at different ages.

Reduction in compressive strength (%)	Time of immersion (days)	Concentration of MgSO$_4$		
		5%	20%	50%
	0	0	0	0
	10	2	4	11
	20	4	19	32
	40	11	36	51
	60	17	40	57

Effects of magnesium sulfate on compressive strength of cement mortar at different ages as well as the relative strength ($f_c/f_{c,28}$) of the cement mortar stored in water and in 5%, 20% and 50% magnesium sulfate solutions are represented graphically versus time in Figures (4.6) and (4.7) respectively.

As shown in Figures (4.6) and (4.7) at the concentration of ammonium nitrate 0%, the compressive strength increased from 47 MPa to 55 MPa after 60 days. This shows that the compressive strength increased by about 17% of its initial strength after 28 days of curing. It is also showed that several sulfate solutions affect the compressive strength of cement mortar differently. For 5% concentration of magnesium sulfate, the compressive strength of cement mortar specimens decreased from 47 MPa to 39 MPa after 60 days of exposure. This shows that the compressive strength reduced by almost 17%. The concentration of magnesium sulfate at 20%, the strength decreased to 38 MPa at the age of 20 days wherein there was a loss of 19% in strength compared to initial strength. It continued to decrease until 28 MPa at the age of 60 days, leading to difference of 40% compared to those treated in water.

The strength of the cement mortar immersed in 50% magnesium sulfate solution decreased significantly. After 20 and 60 days of exposure, the compressive strength reduced to 32 MPa and 20 MPa respectively. This shows that the percentage loss of strength at the age of 20 days was about 32% while for cement mortar at the age of 60 days, the reduction in strength was 57 %.

It can be concluded that the compressive strength decreased when the mortar specimens was immersed in magnesium sulfate solutions and the higher sulfate concentration and immersion period, the higher loss in compressive strength at all ages.
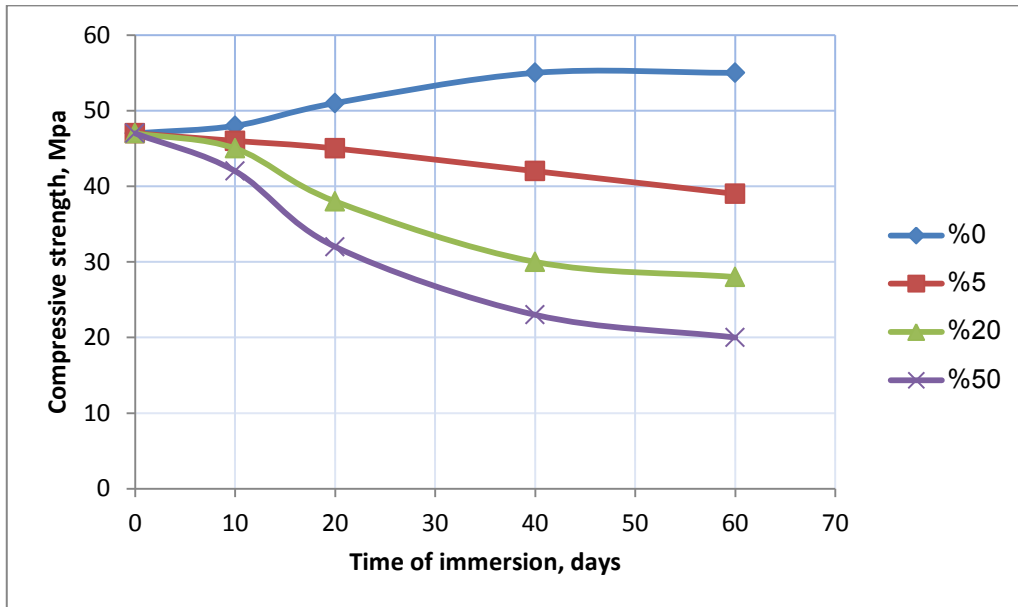
Figure 4.6: Effects magnesium sulfate on compressive strength of cement mortar at different ages.
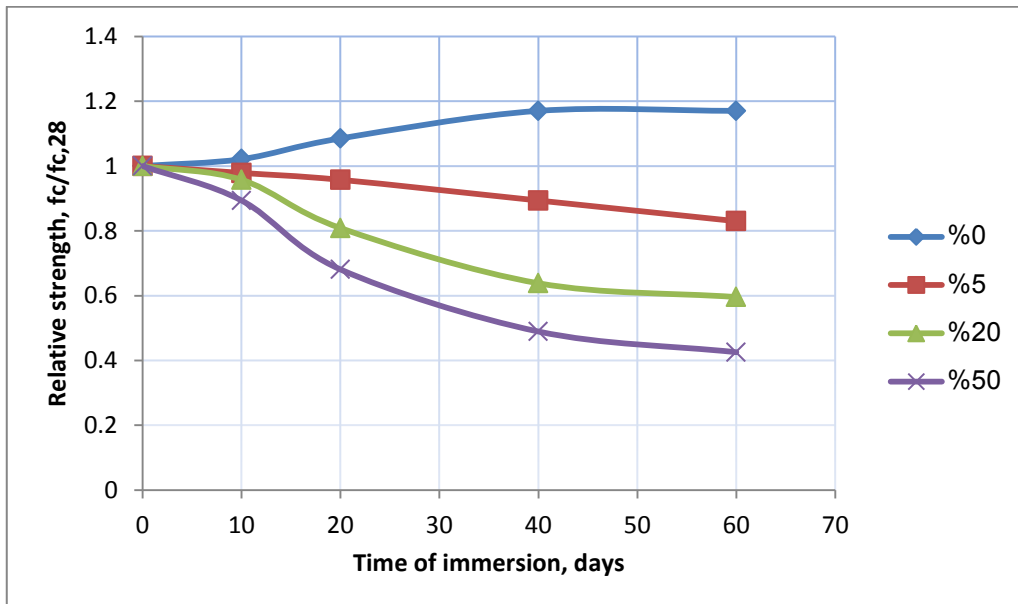
Figure 4. 7: Relative strength of the cement mortar in water and in 5%, 20% and 50% MgSO$_4$ solutions

The reduction in the compressive strength of mortar specimens exposed to 5%, 20% and 50% magnesium sulfate after 60 days is shown in Figure (5.8).
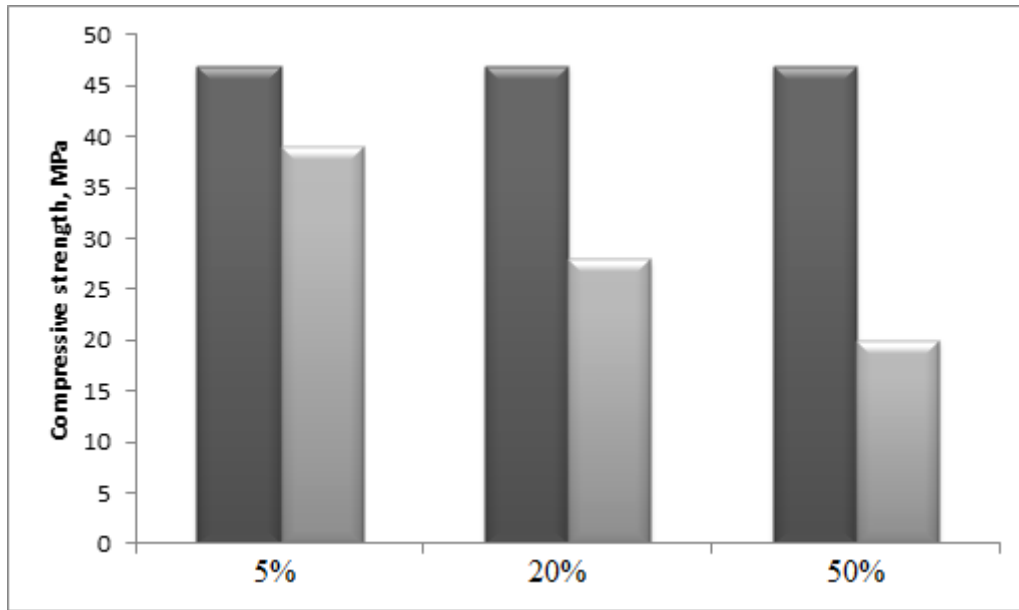
Figure 4. 8: The reduction in the compressive strength of mortar specimens exposed to 5%, 20% and 50% MgSO$_4$ after 60 days.

Sulfate attack by magnesium sulfate causes cracking and expansion of cement mortar as a whole, as well as disintegration of cement paste. It also involve consumption of portlandite (CH), decalcification of C-S-H structure and formation of gypsum. All these factors propagate the deterioration of cement mortar and lead to loss in compressive strength. This agrees with the results obtained by (**Tosun, 2012**) **and** (**Mindess, Young, & Darwin, 2002**) in their studies.

4.3.2 Porosity Test Results

The test results of the porosity of cement mortar subjected to attack of magnesium sulfate solutions with several concentrations is shown in Table (5.7). The effects of magnesium sulfate on porosity of cement mortar at different ages stored in water and in 5%, 20% and 50% magnesium sulfate solutions are represented graphically versus time in Figure (4.9).

Table 4.7: Effects of different concentrations of magnesium sulfate on porosity of cement mortar at different ages.

Test	Time of immersion (days)	Concentration of MgSO$_4$			
		0%	**5%**	**20%**	**50%**
Porosity (%)	**0**	5.1	5.1	5.1	5.1
	10	5.1	5.1	5.1	5.3
	20	5.0	5.1	5.4	6.2
	40	4.8	5.3	5.9	6.8
	60	4.8	5.4	6.2	7.4

It is observed from Figure (4.9) that several sulfate solutions influence the porosity of cement mortar. At 5% concentration of magnesium sulfate the porosity of cement mortar increased from 5.1% to 5.4% after 60 days. For the concentration of magnesium sulfate at 20%, the porosity increased by 1.1% of its initial porosity after 60 days of exposure while for 50% magnesium sulfate solution, the porosity increased from 5.1% to 7.4% after 60 days and this shows that there is an increase in porosity by about 2.3%.

However, the test results of porosity of cement mortar immersed in several concentrations of magnesium sulfate were not largely clear as in ammonium nitrate solutions.
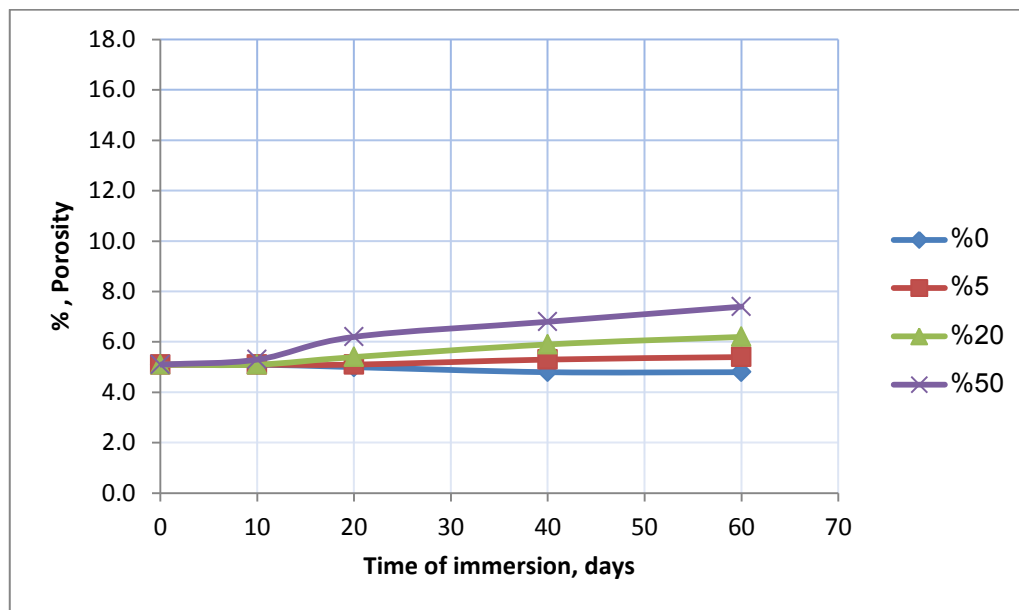
Figure 4.9: Effects of different concentrations of magnesium sulfate on porosity of cement mortar at different ages.

4.3.3 Unit Weight Test Results

Table (4.8) shows the test results for the unit weight of cement mortar subjected to attack of magnesium sulfate solutions with several concentrations. Figure (4.10) presents the effects of magnesium sulfate on unit weight of cement mortar at different ages stored in water and in 5%, 20% and 50% magnesium sulfate

Table 4 .8: Effects of different concentrations of magnesium sulfate on unit weight of cement mortar at differrent ages.

Test	Time of immersion (days)	Concentration of MgSO$_4$			
		0%	**5%**	**20%**	**50%**
Unit weight (g/cm^3)	**0**	2.18	2.18	2.18	2.18
	10	2.18	2.18	2.18	2.17
	20	2.19	2.16	2.16	2.14
	40	2.19	2.14	2.14	2.10
	60	2.18	2.14	2.12	2.08

It is observed from Figure (4.10) that for the concentration of magnesium sulfate 5%, the unit weight decreased from 2.18 g/cm^3 to 2.14 g/cm^3 while the unit weight decreased from 2.18 g/cm^3 to 2.12g/cm^3 for 20% concentration of magnesium sulfate after 60 days of immersion. The unit weight of cement mortar immersed in the 50% magnesium sulfate solution was reduced by 0.10 g/cm^3 after 60 days of exposure. This shows that the loss in the unit weight was about 5% of its initial unit weight.

From the obtained results, It can be concluded that the effects of magnesium sulfate on unit weight were not significantly clear.
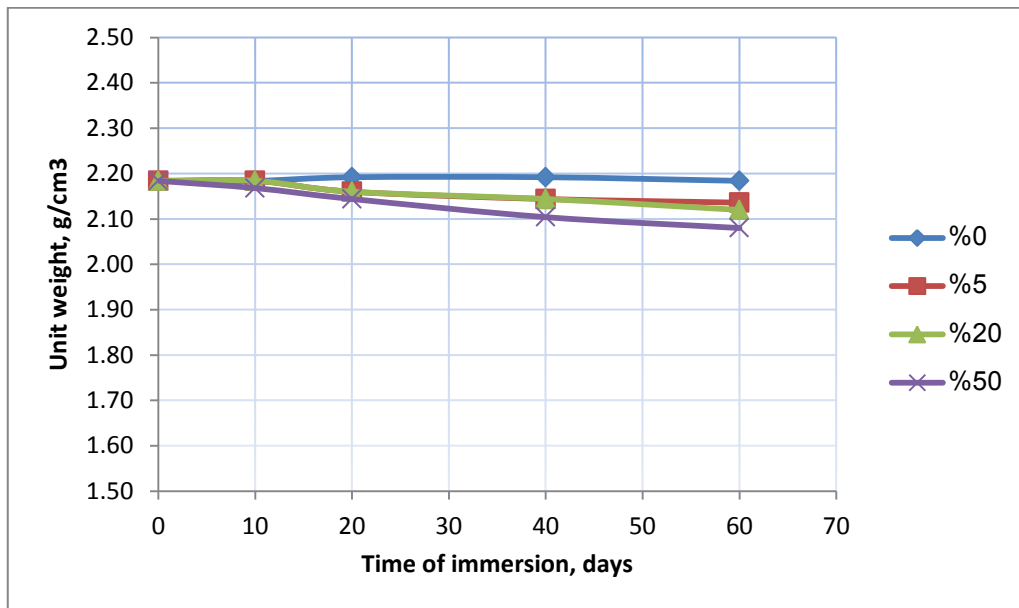
Figure 4.10: Effects of different concentrations of magnesium sulfate on unit weight of cement mortar at different ages.

Chapter 5

Conclusions and Recommendations

Chapter 5- CONCLUSIONS AND RECOMMENDATIONS
5.1 Introduction

Based on the limited experimental work carried out in the current study, the following conclusions may be drawn out and recommendations for further studies also presented in this chapter that may be taken in consideration.

5.2 Effects of Ammonium Nitrate on Cement Mortar

1. Ammonium nitrate solutions produce rapid corrosion of cement based materials due to the high solubility of its calcium salts.
2. Ammonium nitrate solutions at several concentrations affect compressive strength clearly.
3. As the concentration of ammonium nitrate increases, the loss in compressive strength increases.
4. The reduction in compressive strength increases as the exposure period to ammonium nitrate increases.
5. For 5% ammonium nitrate, the strength of cement mortar decreased by 23% after 60 days while reduced by 43% for concentration 20% ammonium nitrate at the same age.
6. For 50% ammonium nitrate, the percentage loss in compressive strength after 60 days was 55%.
7. The porosity of cement mortar increases when it expose to ammonium nitrate solutions.
8. As the concentration of ammonium nitrate and immersion period increases, the porosity increases.
9. For 5% ammonium nitrate, the porosity of cement mortar increased by 1.3% while for 20% ammonium nitrate the porosity increased by 3.9% after 60 days.
10. For concentration 50% ammonium nitrate, the increase in porosity of cement mortar was 10.9% after 60 days.
11. The unit weight of cement mortar decreases when it come in contact with ammonium nitrate solutions.
12. For 5% and 20% ammonium nitrate concentrations, the loss in the unit weight of cement mortar after 60 days was about 3% and 6% respectively.
13. The loss in the unit weight was about 9% of its initial unit weight after 60 days of exposure to 50% ammonium nitrate.

5.3 Effects of Magnesium Sulfate on Cement Mortar

1. Cement mortar deteriorates when it subjects to magnesium sulfate solutions due to expansive nature of sulfate attack which produces cracks within cement mortar as well as the presence of magnesium ions cause modification

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of both C-S-H and calcium sulfoaluminates ($C_4A\bar{S}H_{12}$) that constitute the backbone of the cement paste.

2. The deterioration of cement mortar is high at higher concentrations of magnesium sulfate.

3. Several concentrations of magnesium sulfate solutions affect compressive strength significantly.

4. At higher concentrations of magnesium sulfate, the loss in compressive strength increases rapidly.

5. The reduction in compressive strength increases as the period of contact with magnesium sulfate increases.

6. For 5% magnesium sulfate, the compressive strength of cement mortar decreased by 17% after 60 days while reduced by 40% for concentration 20% magnesium sulfate at the same age.

7. For 50% magnesium sulfate, the percentage loss in strength was 57% after 60 days.

8. The porosity and unit weight of cement mortar are not largely clear when it expose to magnesium sulfate solutions.

9. However, at higher concentration of magnesium sulfate the porosity increases while unit weight decreases.

5.4 Recommendations

The following recommendations are proposed for further research:

1. The effect of other cement mortar mix proportions such as w/c ratio and fine aggregate need to be studied.

2. The influences of other types of cement need to be investigated.

3. Other concentrations of ammonium nitrate and magnesium sulfate can be used in future studied.

4. Longer periods of exposure to ammonium nitrate and magnesium sulfate can be studied.

5. The influence of added mineral admixtures (fly ash, slag and silica fume) on the behavior of cement based materials under chemical attack need to be studied.

6. Other procedures can be used to accelerate chemical attack.

7. Other types of tests can be performed on samples such as pH measurement, degradation depth measurement, scanning electron microscopy, X-ray diffraction analysis and thermo-gravimetric analysis.

8. The effect of ammonium nitrate and magnesium sulfate on mechanical properties of concrete and reinforced concrete need to be studied.

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Appendixes

APPENDIXES

APPENDIX I : Results of cement mortar exposed to ammonium nitrate.
APPENDIX II : Results of cement mortar exposed to magnesium sulfate.

APPENDIX I : Results of Cement Mortar Exposed to Ammonium Nitrate.

❖ **Results of compressive strength test:**

For 0% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	125.00	120.00	118.00	121.00	48.40
20	50	50	50	125.00	128.00	123.00	125.33	50.13
40	50	50	50	133.00	138.00	140.00	137.00	54.80
60	50	50	50	138.00	130.00	140.00	136.00	54.40

For 5% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	113.00	120.00	118.00	117.00	46.80
20	50	50	50	100.00	113.00	115.00	109.33	43.73
40	50	50	50	90.00	90.00	100.00	93.33	37.33
60	50	50	50	88.00	90.00	85.00	87.67	35.07

For 20% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	95.00	103.00	120.00	106.00	42.40
20	50	50	50	98.00	83.00	108.00	96.33	38.53
40	50	50	50	68.00	80.00	83.00	77.00	30.80
60	50	50	50	58.00	70.00	68.00	65.33	26.13

For 50% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	93.00	100.00	90.00	94.33	37.73
20	50	50	50	78.00	80.00	95.00	84.33	33.73
40	50	50	50	68.00	50.00	58.00	58.67	23.47
60	50	50	50	48.00	63.00	45.00	52.00	20.80

❖ **Results of porosity tests:**

For 0% NH₄NO₃

Time of immersion (Days)	Weight before drying (W₁) (g)			Average W₁ (g)	Weight after drying (W₂) (g)			Average W₂ (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	291.00	286.00	284.00	287.00	277.00	271.00	271.00	273.00	5.13
20	292.00	287.00	283.00	287.33	279.00	274.00	269.00	274.00	4.87
40	290.00	289.00	284.00	287.67	278.00	274.00	270.00	274.00	4.99
60	291.00	285.00	284.00	286.67	276.00	272.00	271.00	273.00	5.01

For 5% NH₄NO₃

Time of immersion (Days)	Weight before drying (W₁) (g)			Average W₁ (g)	Weight after drying (W₂) (g)			Average W₂ (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	287.00	288.00	283.00	286.00	273.00	272.00	274.00	273.00	4.76
20	286.00	289.00	280.00	285.00	274.00	271.00	265.00	270.00	5.56
40	286.00	281.00	284.00	283.67	265.00	276.00	263.00	268.00	5.85
60	284.00	280.00	283.00	282.33	261.00	269.00	265.00	265.00	6.54

For 20% NH₄NO₃

Time of immersion (Days)	Weight before drying (W₁) (g)			Average W₁ (g)	Weight after drying (W₂) (g)			Average W₂ (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	289.00	287.00	282.00	286.00	272.00	273.00	265.00	270.00	5.93
20	282.00	280.00	289.00	283.67	264.00	263.00	271.00	266.00	6.64
40	282.00	280.00	287.00	283.00	257.00	265.00	261.00	261.00	8.43
60	283.00	277.00	274.00	278.00	261.00	254.00	252.00	255.67	8.74

For 50% NH₄NO₃

Time of immersion (Days)	Weight before drying (W₁) (g)			Average W₁ (g)	Weight after drying (W₂) (g)			Average W₂ (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	290.00	285.00	282.00	285.67	266.00	267.00	270.00	267.67	6.72
20	292.00	289.00	285.00	288.67	258.00	260.00	269.00	262.33	10.04
40	286.00	289.00	288.00	287.67	254.00	252.00	261.00	255.67	12.52
60	287.00	291.00	288.00	288.67	255.00	246.00	246.00	249.00	15.93

❖ **Results of unit weight test:**

For 0% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	277.00	271.00	271.00	273.00	2.18
20	50	50	50	279.00	274.00	269.00	274.00	2.19
40	50	50	50	278.00	274.00	270.00	274.00	2.19
60	50	50	50	276.00	272.00	271.00	273.00	2.18

For 5% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	273.00	272.00	274.00	273.00	2.18
20	50	50	50	274.00	271.00	265.00	270.00	2.16
40	50	50	50	265.00	276.00	263.00	268.00	2.14
60	50	50	50	261.00	269.00	265.00	265.00	2.12

For 20% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	272.00	273.00	265.00	270.00	2.16
20	50	50	50	264.00	263.00	271.00	266.00	2.13
40	50	50	50	257.00	265.00	261.00	261.00	2.09
60	50	50	50	261.00	254.00	252.00	255.67	2.05

For 50% NH₄NO₃

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	266.00	267.00	270.00	267.67	2.14
20	50	50	50	258.00	260.00	269.00	262.33	2.10
40	50	50	50	254.00	252.00	261.00	255.67	2.05
60	50	50	50	255.00	246.00	246.00	249.00	1.99

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APPENDIX II : Results of Cement Mortar Exposed to Magnesium Sulfate.

❖ **Results of compressive strength test:**

For 0% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	125.00	120.00	118.00	121.00	48.40
20	50	50	50	125.00	128.00	123.00	125.33	50.13
40	50	50	50	133.00	138.00	140.00	137.00	54.80
60	50	50	50	138.00	130.00	140.00	136.00	54.40

For 5% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	108.00	115.00	128.00	117.00	46.80
20	50	50	50	102.00	123.00	118.00	114.33	45.73
40	50	50	50	108.00	108.00	95.00	103.67	41.47
60	50	50	50	88.00	90.00	108.00	95.33	38.13

For 20% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	103.00	120.00	113.00	112.00	44.80
20	50	50	50	108.00	80.00	88.00	92.00	36.80
40	50	50	50	78.00	78.00	73.00	76.33	30.53
60	50	50	50	70.00	63.00	80.00	71.00	28.40

For 50% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Failure load (KN)			Average load (KN)	Average Stress (MPa)
	L	W	H	#1	#2	#3		
0	50	50	50	113.00	115.00	123.00	117.00	46.80
10	50	50	50	103.00	95.00	115.00	104.33	41.73
20	50	50	50	75.00	68.00	88.00	77.00	30.80
40	50	50	50	58.00	68.00	50.00	58.67	23.47
60	50	50	50	40.00	55.00	58.00	51.00	20.40

❖ **Results of porosity tests:**

For 0% MgSO$_4$

Time of immersion (Days)	Weight before drying (W_1) (g)			Average W_1 (g)	Weight after drying (W_2) (g)			Average W_2 (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	291.00	286.00	284.00	287.00	277.00	271.00	271.00	273.00	5.13
20	292.00	287.00	283.00	287.33	279.00	274.00	269.00	274.00	4.87
40	290.00	289.00	284.00	287.67	278.00	274.00	270.00	274.00	4.99
60	291.00	285.00	284.00	286.67	276.00	272.00	271.00	273.00	5.01

For 5% MgSO$_4$

Time of immersion (Days)	Weight before drying (W_1) (g)			Average W_1 (g)	Weight after drying (W_2) (g)			Average W_2 (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	290.00	286.00	285.00	287.00	270.00	274.00	278.00	274.00	4.74
20	288.00	280.00	284.00	284.00	269.00	270.00	272.00	270.33	5.06
40	288.00	280.00	278.00	282.00	271.00	264.00	269.00	268.00	5.22
60	279.00	282.00	282.00	281.00	265.00	268.00	268.00	267.00	5.24

For 20% MgSO$_4$

Time of immersion (Days)	Weight before drying (W_1) (g)			Average W_1 (g)	Weight after drying (W_2) (g)			Average W_2 (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	289.00	282.00	290.00	287.00	276.00	274.00	267.00	272.33	5.39
20	283.00	283.00	288.00	284.67	268.00	268.00	274.00	270.00	5.43
40	281.00	280.00	289.00	283.33	268.00	266.00	270.00	268.00	5.72
60	283.00	281.00	279.00	281.00	269.00	263.00	265.00	265.67	5.77

For 50% MgSO$_4$

Time of immersion (Days)	Weight before drying (W_1) (g)			Average W_1 (g)	Weight after drying (W_2) (g)			Average W_2 (g)	Porosity (%)
	#1	#2	#3		#1	#2	#3		
0	287.00	287.00	286.00	286.67	273.00	277.00	269.00	273.00	5.01
10	286.00	285.00	285.00	285.33	267.00	272.00	274.00	271.00	5.29
20	290.00	281.00	285.00	285.33	266.00	267.00	271.00	268.00	6.47
40	284.00	277.00	283.00	281.33	266.00	260.00	261.00	262.33	7.24
60	281.00	283.00	272.00	278.67	260.00	264.00	256.00	260.00	7.18

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❖ **Results of unit weight tests:**

For 0% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	277.00	271.00	271.00	273.00	2.18
20	50	50	50	279.00	274.00	269.00	274.00	2.19
40	50	50	50	278.00	274.00	270.00	274.00	2.19
60	50	50	50	276.00	272.00	271.00	273.00	2.18

For 5% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	270.00	274.00	278.00	274.00	2.19
20	50	50	50	269.00	270.00	272.00	270.33	2.16
40	50	50	50	271.00	264.00	269.00	268.00	2.14
60	50	50	50	265.00	268.00	268.00	267.00	2.14

For 20% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	276.00	274.00	267.00	272.33	2.18
20	50	50	50	268.00	268.00	274.00	270.00	2.16
40	50	50	50	268.00	266.00	270.00	268.00	2.14
60	50	50	50	269.00	263.00	265.00	265.67	2.13

For 50% MgSO₄

Time of immersion (Days)	Dimension of samples (mm)			Weight of sample (g)			Average weight (g)	Unit weight (g/cm³)
	L	W	H	#1	#2	#3		
0	50	50	50	273.00	277.00	269.00	273.00	2.18
10	50	50	50	267.00	272.00	274.00	271.00	2.17
20	50	50	50	266.00	267.00	271.00	268.00	2.14
40	50	50	50	266.00	260.00	261.00	262.33	2.10
60	50	50	50	260.00	264.00	256.00	260.00	2.08

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