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United Arab Emirates University
Deanship of Graduate Studies

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Sultan Saif R. A. AlShamsi

B. Sc. In Agriculture Sciences
Sultan Qaboos University- Oman (1993)

A Thesis
Submitted to
United Arab Emirates University
In Partial Fulfillment of the Requirements for the
Degree of Master of Science in Environmental Science

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United Arab Emirates University
2003/2004

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Abstract

The United Arab Emirates produces a large quantity of elemental sulfur from oil and gas industry. Elemental sulfur is widely used as soil treatment technique for reducing pH of alkaline soils than other techniques because it is cheaper and safer during treatment.

In this study, different designs mixes were prepared based on its content of sulfur and calcium carbonate. Different application rates of elemental sulfur (0, 1, 2, and 3%S) were added to soils having different amounts of calcium carbonates (i.e., 16.2, 21.2, 26.2, 36.2, 46.2, and 56.2% for basic mix design, and mix designs types I, II, III, IV, and V, respectively. The changes in soil pH, electrical conductivity (EC) and sulfate concentration were measured at different time intervals (0, 5, 10, 20, 40 and 80 days) and statistically analyzed. Furthermore, mineral transformations were quantified via scanning electron microscope, x-ray diffraction analysis and energy depressive x-ray techniques. Mineral transformations were further analyzed in view of possible chemical reactions and thermodynamic modeling.

The study concluded that sulfur addition for all treatments of basic mix design, mix design types I, III, IV, and V has no significant influence on pH changes but has high significance on pH changes for mix design type II as determined via statistical analysis. In this mix design, pH decreased by 1.14, 1.22, 1.27, 1.24 and 1.28 units after 5, 10, 20, 40, 80 days, respectively. For all treatment cases, sulfur addition has high influence on EC changes except for mix design type III that indicates no significance. For sulfur oxidation, similar conclusion to EC changes was reached. Furthermore, available water-soluble sulfate was highly correlated with EC. As sulfate increases, EC increases and vice versa.

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION AND PROBLEM DEVELOPMENT:

1.1.1 Sulfur Production in United Arab Emirates (UAE):

Sulfur production in the United Arab Emirates (UAE) is a by-product of the oil and gas industry. In the past, associated gas was burned off. Today, it is used to operate the production facilities, to generate electricity and for exporting.

Abu Dhabi's natural gas production has grown quickly during the last five years. Gas injection programs, for the maintenance of oil reservoirs pressure are continuing. Gas is supplied to the Natural Gas Liquefaction (NGL) plants of Abu Dhabi Gas Industries Limited (GASCO) in Asab, Bab and Bu-hasa, the ADNOC plant in Habshan, and the ADGAS LNG plant on Das Island (Abu Dhabi Gas Liquefaction Limited-ADGAS). They were enlarged during 1995-1999 and all gas supply requirements for power generation, water desalination and Abu Dhabi's other industries were satisfied.

Abu Dhabi National Oil Company (ADNOC) has put increasing emphasis on the development and uses of its natural gas resources. It is being used to meet the growing demand for power generation, water desalination, petrochemical plants and also for injection which enhances oil production. Concurrantly, an environmental priority has been given to recovering and processing the associated gas. This avoids flaring which is in line with ADNOC's zero flaring philosophy. Flaring is the process of disposing of unwanted flammable gases and vapors by combustion in the open atmosphere (ADNOC, 1995-1999).

ADNOC'S refining operations have grown steadily to keep pace with the fast development of the U.A.E. with significant improvements in both techincal fields and the field of human endeavour and excellence. Abu Dhabi Oil Refining Company (TAKREER) was established in 1999 to take over the responsibility of refining operations (ADNOC, 1995-1999). The company's areas of operation include the refining of crude oil and condensate, supply of petroleum products in compliance with domestic and international specifications, production of chlorine and related chemicals, and sulfur granulation. The ADNOC's refining capacity is over half a million barrels per day, making it one of the region's biggest operators (ADNOC, 1995-1999).

To keep pace with increasing levels of oil and gas processing, ADNOC has expanded the Sulfur Handling Terminal (SHT) at Ruwais refinery, where liquid sulfur is granulated and sold on the world market. SHT receives sulfur removed from the gaseous and liquid hydrocarbons from Ruwais and UM ANAR refineries (TAKREER), GASCO NGL plant, ATHEER Gas Processing plant, and ADGAS Das Island facility. The project was completed in early 2001, and has increased the SHT capacity from 4250 to 6250 tons/day (ADNOC, 1995-1999). In Dubai the EPCL company produces 6 tons/day of sulfur by Claus process and also Technipetrol / ENOC company produces 6 tons/day (British Sulphur Consltans, March/ April 2000).

Large quantities of sulfur are produced as a by-product during the gas liquefaction process. The UAE's natural gas reserves of roughly 212.0 trillion cubic feet (Tcf) are the world's fourth largest. Global economic factors and increased domestic consumption of electricity have provided incentives for the UAE to increase its use of natural gas. The past few years have seen the UAE embark on a massive multi-billion dollar program of investment in its gas sector, including a shift toward gas-fired power plants and gas-based industrial zones. As a result, huge amounts of sulfur has already been produced and more is being expected.

1.1.2 Sulfur and the Environment:

Due to the nature of UAE environment, which is characterized by being hot, dry, and windy, sulfur could be dispersed into air and surface water bodies. Furthermore, due to wet/dry conditions, sulfur could be oxidized into sulfuric acid, which in turn contributes to the pollution of both surface and ground water bodies. These environmental conditions contribute to the unsafe existence of the produced sulfur and pose a major risk to human health and the environment. It is obvious that there is an urgent need for developing an action plan for exploring feasible initiatives.

1.1.3 Uses of Sulfur:

Sulfur in its elemental form is recognized as an important ingredient in several agronomic applications. These include the following:

(1) an essential plant nutrient (Hilal, 1990 ; Hilal et al., 1990);

(2) an active agent for increasing crop stress resistance (Hilal et al., 1990; Shata et al. 1990);

(3) Environmentally benign pesticide; and

(4) an efficient soil amendment aid to alleviate alkalinity (Lopez, 1999; Abd-Elfattah, 1990; Hilal, 1990).

Sulfur as an essential plant nutrient has received little scientific attention. This is explained by the facts that sulfur was obviously in sufficient supply from the atmosphere, from soil and as a by-product in mineral fertilizers. However, the use of highly concentrated fertilizers containing little or no sulfur has drastically reduced the amount of sulfur supplied to soils. Recent studies have shown that adding sulfur to soil increased crop yield (Hilal, 1990; Kaplan and Orman,1998), increased drought tolerance (Hilal et al., 1990; Shata et al., 1990) and increased nitrogen efficiency and phosphorus uptake (Abdel-Samad et al., 1990; Abd-Elfattah et al. 1990; Kaplan and Orman,1998).

All of these applications are important to the national agricultural drive in the UAE. However, the fourth application alkalinity amendment is of particular significane. Soil alkalinity in the UAE demands the use of an acidifying agent to achieve the required neutrality. Sulfur is the major component to achieve this endeavour. Elemental sulfur is microbially oxidized to sulfuric acid (Wainwright, 1984), which then reacts with calcium carbonate to form gypsum (Soil Sulfur, 2003). This oxidation process is highly dependent on soil moisture, temperature, microbial activity, and the size of the elemental sulfur grain. Particle size is perhaps the most critical factor from an application and product point of view.

In general, elemental sulfur granules, in their original size (250 μm), oxidize at a very slow rate. These granules are relatively large and present soil microbes with a small specific surface area for conversion. By breaking the elemental sulfur granule into smaller sizes (45 μm), the surface area is increased which in turn increases the rate of microbial oxidation and conversion of elemental sulfur to sulfate (Hilal et al. 1990; Chapman, 1989; Neilsen et al. 1992).

1.2 OBJECTIVES:

The main objective of the thesis is to evaluate the potential use of elemental sulfur for soil treatment in the UAE.

1.3 TASKS:

To fulfill the above objective, the following tasks were conducted.

1. Literature review on sulfur oxidation in alkaline soils to know controling parameters that affect elemental sulfur use for alkaline soil treatment ;
2. Collection and analysis of sulfur samples to know it's purity level and the presence of other elements;
3. Collection and analysis of soil samples for chemical and physical properties;
4. Experimental design to evaluate the effect of calcium carbonate, elemental sulfur, and organic manure additions on soil behavior;
5. Evaluate the variations of pH, electrical conductivity, sulfur oxidiation and mineral transformation as a function of time due to the addition of the above stated parameters.

1.4 THESIS ORGANIZATION:

The thesis is organized into five chapters as detailed below:

Chapter 1: It discusses the problem development, objectives and tasks to be conducted.

Chapter 2: It discusses literature review on sulfur cycle and production, alkaline soil problems and amendment techniques and controlling parameters for elemental sulfur use as the treatment techinque.

Chapter 3: It discusses materials used and methods.

Chapter 4: It discusses the results.

Chapter 5: It discusses the summary, conclusions, and recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 SULFUR:

2.1.1 Background:

Sulfur (S) is tasteless, odourless, light yellow nonmetallic element with an atomic number of 16 and atomic weight of 32.064, is called brimstone (Sulphur, 18 March 2001). Sulfur forms are insoluble in water however the crystalline forms are soluble in carbon disulfide. Physical properties of sulphur can be changed in accordance with the temperature, pressure, and method of crust formation (Sulphur, 18 March 2001).

Sulfur has valences of two, four and six. It forms sulphides by combining with hydrogen and the metallic elements in the presence of heat such as H_2S, which is a colourless, poisonous gas with the odour of rotten eggs sulfur monochloride (S_2Cl_2) and sulfur dichloride (SCl_2) are formed when sulfur combines with chlorine. Burning sulfur in the air produces sulfur dioxide (SO_2), which is oxidized to sulfuric acid in the presence of moisture.

2.1.2 Sulfur Cycle:

The important reactions in the sulfur cycle are:

1. **Assimilative sulfate reduction:** Organic sulfhydryl groups (R-SH) are produced by reduction sulfate (SO_4^{2-}) by plant, fungi and various prokaryotes. The oxidation states of sulfur in sulfate and in R-SH are +6 and –2, respectively.
2. **Desulfuration:** Hydrogen sulfide gas can be produced (H_2S) by desulfuration of organic molecules containing sulfur. The oxidation state is -2.
3. **Oxidation of hydrogen sulfide:** Elemental sulfur (S^0) can be produced by oxidation of hydrogen sulfide, the oxidation state is 0. The photosynthetic green and purple sulfur bacteria and some chemolithotrophs can do this oxidation.
4. **Oxidation of elemental sulfur (S^0):** This is done by sulfur oxidizers and sulfate is produced.
5. **Dissimilative sulfur reduction:** Hydrogen sulfide can be produced by reduction of elemental sulfur.
6. **Dissimilative sulfate reduction:** Hydrogen sulfide can be generated from sulfate by sulfate reducers (Lecture 23 the sulfur cycle, February 2001). For more information, see sulfur cycle (Figure 2.1) (Alken Murray Corp., March 2001) and sulfur cycle (Figure 2.2) (Potash & Phosphate Institute of Canada, March 2001).

The Sulfur Cycle

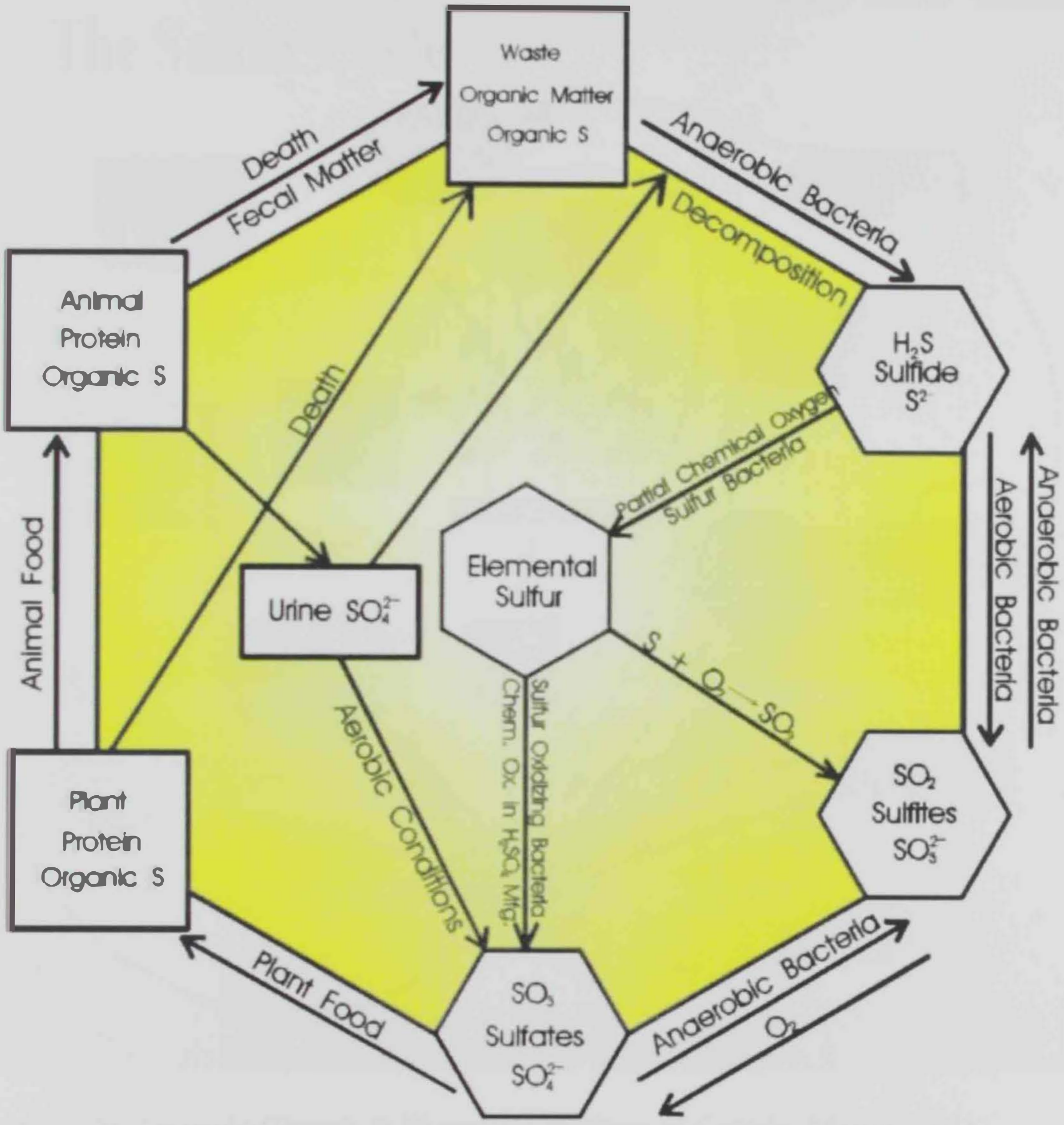

Figure 2.1: Sulfur cycle (Alken Murray Corp., March 2001)

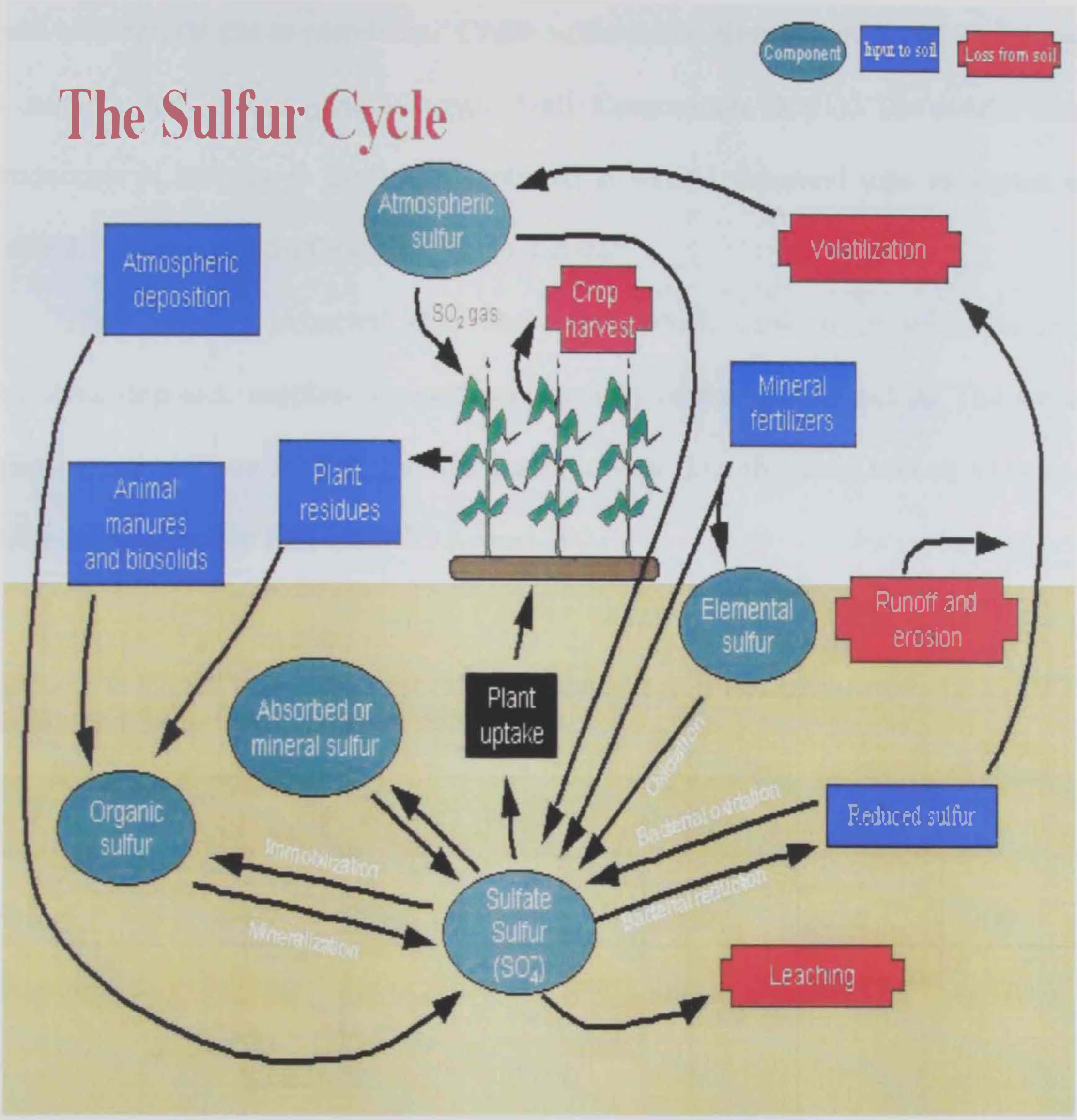

Figure 2.2: Sulfur cycle (Potash & Phosphate Institute of Canada, March 2001).

2.1.3 Sulfur Production:

2.1.3.1General:

There are two main sources of crude sulfur; natural deposition and recovery from sour natural gas or petroleum. Crude sulfur has a minimum purity of 99.5% and is suitable for various uses (Georgia Gulf Corporation, 2001). The world total production of sulphur in 2001 was recorded at 42,661 thousand tons as shown in Table 2.1 (Sulfur and Sulfuric acid, August 2002).

Free sulphur extracted from the earth, which came from sulfur bearing limestone deposits, supplies a significant quantity of the world's sulfur. The world brimstone production in 2001 by mined source was 1289 thousand tons as shown in Table 2.1 (Sulfur and Sulfuric acid, August 2002).

Table 2.1: World brimstone production (thousand tons) by source, 1996-2001 (Sulfur and Sulfuric acid, August 2002).

Year	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**
Mined	5157	4865	3422	3252	2467	1289
Recovered	32792	34442	37278	38993	40167	41372
Total	**37949**	**39307**	**40700**	**42245**	**42634**	**42661**

There are several methods to extract free sulfur from the earth. One of them is called the Frasch process, which was invented in 1891 by the American chemist

Herman Frasch and used to extract the natural sulfur deposits that may lie some 275m or more below the surface of the earth. This method is commonly used in Louisiana and Texas. In this method four concentric pipes are used. These pipes, the largest being 8 inches in diameter, are driven down into the sulfur deposits. Then water is heated under pressure to 170° C, and forced through the two outer pipes into the deposit. The water melts the sulfur. Hot air is then forced down the innermost pipe to form froth (fine bubbles) with the melted sulfur, which is forced up to the surface through the remaining pipe. Sulfur is then solidified by running into wooden bins (Sulphur, 18 March 2001).

A second source of sulfur is from petroleum refining and production of sour natural gas. This is the most important source of sulfur supply in the world. The world Brimstone production in 2001 by recovered source was 41,372 thousand tons as shown in Table 2.1 (Sulfur and Sulfuric acid, August 2002). The Arabian Gulf exported 1.2 million tons of sulfur in 2000 (Sulfur and Sulfuric acid, July 2000).

Hydrogen sulfide, which comes either from sulfur reacted with hydrogen or from sour natural gas is converted to elemental sulfur. Recovered sulfur is produced by counter-current absorption to collect the hydrogen sulfide in a solution. The gas is distilled from the solution, which is normally an alkanolamine, then burned to produce hydrogen sulfide and sulfur dioxide, which is cooled and catalyzed in a converter to produce sulfur vapor and water. The sulfur vapor is removed from the mixture by scrubbing with makeup liquid sulfur (Georgia Gulf Corporation, 2001).

2.1.3.2 Sulfur Production in ADNOC:

Sour gas, from units naphta hydrodesulfurization, kerosene hydrotreater and heavy gas oil hydrodesulfurization, is sent to the knock out drum to separate liquid hydrocarbons, which are sent to blow down. In amine absorber, H_2S is absorbed by amine, which becomes rich amine. The amine absorber produces sweet gas, which is used as fuel gas. Rich amine is heated by lean amine, which is produced by stripping rich amine through H_2S stripper. A part of lean amine is used to cool low-pressure steam. The acid gas is cooled by fin fan and then by sea cooling water. It is then sent to the reflax drum to remove a mixture of mainly water and amine, which is pumped to H_2S stripper. Finally acid gas is sent to another unit for sulfur recovery.

In this unit, the acid gas is converted to liquid sulfur by many processes. First the acid gas is sent to the knockout drum to separate liquids from it. This liquid is called acid condensate that is pumped to the oil separator vessel. A part of the acid gas is oxidized to SO_2 in furnace under thermal reaction, which reacts with H_2S to form sulfur through catalytic conversion -activate alumina. It is then cooled through waste heat boiler to heat boiler feed water. The separated gases are heated by the liquid sulfur through then they are sent to the reactor. The liquid sulfur is sent to the pots and then to the sulphur pit. Tail gas is then sent to the incinerator to be burned.

About 6000 tons/day of liquid sulfur from Habshan, Um AlNar refinery and ALRuwais refinery and also about 1000 tons/day from Das Island is unloaded by trucks and ships in underground pits. Steam is used to maintain temperature of liquid sulfur at 130°C during unloading by truck and electric coils, which is fixed around the pipes and at the bottom of the pits, during marine unloading. Then it is pumped to storage tanks. The temperature of the liquid sulfur in the storage tanks is maintained at 130°C by using steam. After that the liquid sulfur is filtered from impurities to avoid bulging the nozzles of granulation units (GX). Then it is pumped to daily pits and then to granulation units. In these units the liquid sulfur is pumped with high pressure of 18.8 bars through nozzles and also water is sprayed to form granular solid sulfur with different sizes. Air is used for cooling inside these granulation units. This operation is resulting in formation of toxic gases such as H_2S and SO_2 and also sulfur dust. In order to remove sulfur dust for recycling, wet scrubber is used in which wet sulfur dust is separated from off gases. Only clean sulfur of wet sulfur dust, which is collected in plastic drums, is sent to the remelt pit for recycling whereas the unclean sulfur is considered as waste which is collected in plastic drums and dumped in AlRuwais waste facility. Off gases is sent to incinerator. The granular sulfur is sent by conveyor belts to screen for separating small sizes, which is sent to granulation units for recycling, from normal sizes. This normal granular sulfur is sent by conveyor belts to two bulk stores, one of them has capacity of 40000 tons and the other has 110000 tons. Loading sulfur from bulk stores is done by ship loader using conveyor belts. Before ship loading, the sulfur is sprayed by dust bind chemical to avoid sulphur dust problems.

2.2 ALKALINE SOILS IN ARID LAND AND THEIR PROBLEMS:

Alkaline soils usually occur in arid regions, which has less than 625 mm of rain per year (Alkaline soils, June 2001). In these arid soils, limestone, which is calcium carbonate ($CaCO_3$), causes soil alkalinity. Some soils can contain up to 60% limestone but most arid soils contain 2- 10% limestone (Alkaline soils, June 2001).

Plant grown in alkaline soils which has a pH of more than 7.0 are less able to absorb phosphorus, iron and manganese (Earth & Table, April 2001). Also there are many problems in alkaline soils such as zinc deficiency, excess salts in some soils, iron deficiency, manganese deficiency, phosphorus is tied up by Ca and Mg, and bacterial diseases in potato (Soil Acidity and Liming, June 2001). Also alkaline soils reduce the availability of nitrogen, copper and boron (Shank, May 2001).

Previous investigation by Soaud et al. (2003) indicated that the UAE soils contain high percentage of $CaCO_3$. For example, Ras AlKhaimah's soils contain about 32- 70% $CaCO_3$.

2.3 ALKALINE SOIL AMENDMENT TECHNIQUES:

There are several types of soil amendments either organic or inorganic, which are used to improve soil physical and chemical conditions in order to increase crop production (Thorup, 2001). These amendments can be grouped into:

1. Those that used to decrease soil pH such as sulfur, sulfuric acid, calcium polysulfide, ammonium polysulfide, ferric sulfate and ammonium sulfate (Thorup, 2001);
2. Those that can be applied to improve soil tilth, e.g., organic matter; and
3. Those that are used to treat sodic soils to replace excessive sodium ions such as gypsum for non-calcareous soils and sulfur for calcareous soils (Thorup, 2001).

Elemental sulfur is the most widely used method as soil amendment because of it's economic advantages. Neilsen et al. (1992) concluded that "finely divided S is, over time (4-8 weeks), as effective as other acidulants ($FeSO_4$, $Al_2 (SO_4)$, H_2SO_4) in reducing soil pH" but elemental sulphur appeared to be best acidulant because of its gradual and effective reduction of pH and its low cost.

For the use of elemental sulfur, various environmental factors such as sulfur-oxidizing organisms, sulfur source, application rate, soil moisture and temperature, soil type, pH and time affecting elemental sulfur oxidation and use, should be evaluated.

2.4 CONTROLLING PARAMETERS FOR ELEMENTAL SULFUR USE AS THE TREATMENT TECHINQUE:

2.4.1 Elemental Sulfur Oxidizers:

Microorganisms must oxidize elemental sulfur before it is available for plant uptake. There are several types of elemental sulfur oxidizers such as autotrophic (thiobacillus) and heterotrophic bacteria. Shata et al. (1990) pronounced the positive effect of sulfur application was more evident when oxidizing bacteria, especially autotrophic bacteria, is applied to sandy and calcareous soils. Lee et al. (1990) concluded that thiobacilli have a significant role in oxidizing elemental sulfur (ES) in many New Zealand soils. Thiobacilli oxidize elemental sulfur to sulfate. Abd-Elfattah et al. (1991) showed that the percentages increased in sulphate uptake were 39.7%, 48.0% and 51.6% for treatments with bio-fertilization (Thiobacillus) and were 9.1%, 11.4% and13.7% for treatments without bio-fertilization receiving 0.5, 1.0 and 2.0 tons/sulfur/acre, respectively in clay loam soils.

Sulfur oxidizing bacteria can be found in soils without addition. Sorokin et al. (2000) isolated two sulphur-oxidizing bacteria cells of strains AL2 and AL3 (*Thiobacillus*) that could oxidize thiosulfate, sulfide, polysulfide, elemental sulfur and tetrathionate. Also he found strain AL3 more actively oxidized thiosulfate and sulphide, while strain AL2 had higher activity with tetrathionate and elemental sulfur. Also, Al Falih (1996) found both of Alkharj and Riyadh soils had the highest counts of S-oxidizing bacteria and S-oxidizing fungi that were 81 and 70x 10^3 bacteria and 77 and 68 x 10^3 fungi, respectively. Organic matter provides microflora with energy for growth and supplying carbon for the formation of new cell material. The organic fraction contains compounds of carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur and small amount of other elements. Also it is capable of supporting microbial growth for longer periods resulted in greater stimulation of elemental sulfur oxidation.

Soil organic matter is subjected to microbial decay in soils. The organic matter could be plant remains, animal tissues and excretory products which become food for the microflora in the soil. Also the cells of microorganisms which contain approximately 50% carbon provide a source of carbon for succeeding generation of the microscopic community (Alexander, 1977).

The organic constituents of plant are generally divided into six categories:

1. Cellulose (15-60%) of the dry weight;
2. Hemicelluloses (10-30%) of the dry weight;
3. Lignin (5-30%) of the plant;
4. The water-soluble fraction, in which is included simple sugars, amino acids, and aliphatic acids (5-30%) of the tissue weight;
5. Ether- and alcohol-soluble constituents, a fraction containing fats, waxes, resins, and a number of pigments; and
6. Proteins which have much of nitrogen and sulfur in their structure.

The mineral constituents of organic matter vary from (1-13%) (Alexander, 1977). The humus contains substances such as Amino acids, purines, Pyrimidines, Aromatic molecules. Uronic acids, Amino sugars, Pentose, Hexose sugars. Sugars alcohols, Methyl sugars and Aliphatic acids as shown in Table 2.2 (Alexander, 1977).

The population responding to organic carbon amendments therefore feed on: (a) the organic substrates added, (b) intermediates produced during composition, and (c) the protoplasm of microorganisms active in degradation of the organic substrates or the intermediates (Alexander, 1977).

When plant tissues are incorporated into the soil, the number of the bacteria around and within the buried materials increases rapidly. This increase in bacterial populations only occurs directly on the plant materials and reaching 10^{10} per gram in the first week while feasible counts of bacteria in the neighboring soil are not noticeably altered (Alexander, 1977). After the week, the bacteria populations begin to decline, falling to a point where the numbers are essentially the same as in unamended soil and also there is an increase followed by a decrease in the numbers of protozoa, the changes paralleling the bacteria fluctuations (Alexander, 1977).

The biotic oxidation of sulfur to sulfate includes two definitely separate steps. One of them is oxidation of sulfide to free sulfur and the second is oxidation of elemental sulfur to sulfate. The abiotic oxidation of elemental sulfur to sulfate can be written as:

$$2S + 2H_2O + 3O_2 = 2\,H_2SO_4 \qquad (\Delta G^\circ = -\,238{,}820\ \text{cal})$$

The abiotic oxidation may involve intermediates which are being indicative of microbial sulfur oxidation. These intermediates can be written in the following hypothetical case

$$S^\circ \longrightarrow S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \longrightarrow SO_3^{2-} \longrightarrow SO_4^{2-}$$

Many microorganisms can oxidize sulfur in the environment, including *Thiobacillus*, heterotrophs, the photosynthetic sulfur bacteria and the colorless, filamentous sulfur bacteria but the thiobacilli and heterotrophs play an important part in sulfur oxidation in the most agriculture soils (Wainwright, 1984).

There are many sources for organic matter such as animal manure (composed or fresh), sewage sludge, waste plant products such as Bermuda grass clippings, wheat straw and pressed sugar beet pulp. Also it could be organic amendments such as glucose, starch, cellulose, sawdust.

Cifuentes and Lindeman (1993) applied composted horse manure, fresh cow manure alone and in combination with elemental sulfur. They found that fresh manure significantly increased soil SO_4^{2-} in the field on Day 59 and approximately 22% of the added elemental sulfur was recovered as SO_4^{2-} after 270 days in the field. Also they found that the electerical coductivity (EC) was highly correlated with pH and SO_4^{2-}. They found that averaged across organic matter types and sampling dates, organic matter stimulation of elemental sulfur oxidation decreased pH values 0.24 and 0.16 units, increased soil sulfate 246 and 1455 mg/kg, and increased soil EC 0.42 and 0.48 dS/m in the laboratory and the field, respectively.

Cowell and Schoenau (1995) used sewage sludge which had total nutrient content as follows: S (5g/kg), N (9 g/kg), P (14.5 g/kg), K (3.7 g/kg) and C (98 g/kg). They concluded that elemental sulfur oxidation is stimulated by dewatered sewage sludge in incubated mixtures and when the mixtures are added to soil. They found that over 50% of elemental sulfur from these mixtures oxidized within 6 weeks, compared with about 20% oxidation of elemental sulfur applied without sewage sludge. They also concluded that acidification of the preincubation mixtures appeared to limit elemental sulfur oxidation, so that SO_4^{2-} content did not exceed 100mg S/kg. Also they found that SO_4^{2-} was rapidly released when the mixtures were added to the soil and also found that acidification was buffered by the soil. Finally they concluded that increasing the proportion of dewatered sewage sludge in the mixtures from 20% to 80% did not increase elemental sulfur oxidation.

Wainwright et al. (1986) found that the pressed sugar been (1% w/w) initially stimulated the oxidation of elemental sulfur in the soil and the concentration of thiosulfate and tetrathionate increased. Also they found that wheat straw in loam soil amended with 1% elemental sulfur stimulated the oxidation of elemental sulfur over the first 2 to 3 weeks of the incubation period.

Cifuentes and Lindeman (1993) added glucose (40% C), starch (44.4% C), cellulose (44.4% C) or sawdust (79% Lignocellulosic material and 48% C) alone and in combination with elemental sulfur. They found that addition of organic matter to the soils amended with elemental sulfur significantly decreased soil pH compared with elemental sulfur alone or organic matter alone. Cellulose or starch addition to elemental sulfur amended treatments resulted in significantly lower values than combination of glucose or sawdust during the first 5 weeks. Also they found that addition of organic matter to the soils amended with elemental sulfur significantly increased soil SO_4^{2-} compared with elemental sulfur alone or organic matter alone. Sawdust or cellulose addition to elemental sulfur amended treatments had significantly higher SO_4^{2-} levels (13.7- 7.8%) than those amended with starch or glucose after 15 days. Also they found that EC was highly correlated with pH and SO_4^{2-}.

Table 2.2: Several constituents of the organic molecules found in humus[a]

I. **Amino acids**
  - Glutamic acid
  - Alanine
  - Valine
  - Proline
  - Cystine
  - Phenylalanine

II. **Purines**
  - Guanine
  - Adenine

III. **Pyrimidines**
  - Cytosine
  - Thymine
  - Uracil

IV. **Aromatic molecules**

V. **Uronic acids**
  - Glucuronic acid
  - Galacturnoic acid

VI. **Amino sugars**
  - Glucosamine
  - N-Acetylglucosamine

VII. **Pentose sugars**
  - Xylose
  - Arabinose
  - Ribose

VIII. **Hexose sugars**
  - Glucose
  - Galactose
  - Mannose

IX. **Sugars alcohols**
  - Inositol
  - Mannitol

X. **Methyl sugars**
  - Rhamnose
  - Fucose
  - 2-0-Methyl-D-xylose
  - 2-0-Methyl-D-arabinose

XI. **Aliphatic acids**
  - Acetic acid
  - Formic acid
  - Lactic acid
  - Succinic acid

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[a] Except for the amino acids and aliphatic acids, which are found only in low concentrations, the constituents rarely exist in free form; rather they are found in polymers or other poor defined complexes.

2.4.2 Effect of Sulfur Grain Size and Application Rate:

The elemental sulphur source, the specific surface area for particles and application rate, play a major role in the effectiveness of elemental sulphur application. Hilal et al. (1990) found that application of fine sulphur was more effective than granular sulphur especially at low levels. Also, Chapman (1989) showed that the oxidation of sulphur sources of smaller particle size, which had the greater specific surface area, was greater than sulphur sources of larger particle size. Furthermore, Neilsen et al. (1992) said that "S should be finely divided and incorporated in the soil for maximum acidulation of calcareous soils". Kaplan and Orman (1998) observed that both elemental sulphur and sulphur containing waste applications 0 - 2000 kg ha^{-1} and 0 -100 tons ha^{-1} respectively decreased soil pH from 0.07 to 0.35 units for pot experiment and 0.03 to 0.5 for field experiment and also increased soil electrical conductivity after 5 weeks from 2.49 mmhos/cm to 3.74, 4.90 and 4.85 mmhos/cm for 500, 1000, 1500 and 2000 kg/ha, respectively. Many elemental products are manufactured, which differ in physical characteristics that influence their effectiveness for supplying sulphur or acidifying the soil. Slaton et al. (2001) suggested that commercial elemental sulfur had different rates of oxidation and so the knowledge of their oxidation kinetics must be known before application to the soil.

The amount of elemental sulfur applied to the soil will affect the oxidation rate. Chapman (1989) showed that the rate of sulfur oxidation was roughly proportion to the level of sulfur addition up to 200 μg S g^{-1} fresh weight but the oxidation was less than expected from this proportionality at levels of 640 μg S g^{-1}fresh weight and at 6400 μg S g^{-1}. Modaihsh et al. (1989) found that low sulfur application at 0.5% had slightly decreased the pH and increased the EC and the sulphate content, whereas higher rates of sulphur application at 1.5 and 3.0 (w/w) had little or no further effect on pH, EC or amount of sulphate. Reda and Modaihsh (1990) highly recommended the application level of 1.5% of sulphur to calcareous soil as most of it can be oxidized after (9-18 weeks).

2.4.3 Effect of Soil Temperature and Moisture:

The soil temperature is known to exert strong influences on sulfur oxidation. Janzen and Bettany (1987) observed that sulfur oxidation rate was negligible (0.4 μg $S.cm^{-2}. D^{-1}$) at $3^{\circ}C$ but sulfur oxidation rates increased at temperatures 15, 23, and $30^{\circ}C$ which were 1.4, 5.0 and 11.1 μg $S.cm^{-2}. D^{-1}$, respectively. The sulphur oxidation become slow at low temperatures whereas fast at high temperatures. Chapman (1989) indicated that the temperature had an effect on the time needed for sulphur oxidation. He also found that the time needed for 50% of the maximum oxidation of the micronized sulphur was 6-10 days at $20^{\circ}C$, 23-26 days at $7^{\circ}C$ and 36-42 days at $2^{\circ}C$. Also, Boswell et al. (1992) showed differences in soil temperatures appeared to generate differences in oxidation rates throughout New Zealand.

Temperature can affect mineralization of native soil organic sulphur and oxidation of elemental sulphur. Jaggi et al. (1999) observed that an increasing in rate of mineralization associated with increasing of temperature resulting into the highest accumulation of SO_4^{2-} -S at $36^{\circ}C$. Also, it was indicated that S° oxidation in all the three soils was highest at $36^{\circ}C$ and was fastest during initial 14 days with sharp decline for each successive 14 days period. Furthermore in all three soils, $12^{\circ}C$ had no effect or negligible on sulphur oxidation but a greater stimulatory effect on the accumulation of SO_4^{2-} was caused by each subsequent increment in temperature.

The oxidation rate of the elemental sulphur determines its effectiveness. Janzen and Bettany (1987) observed that oxidation rates and maximum rates were generally related to water potential at all temperatures. Also, it was observed that the maximum oxidation rate was at water potential near field capacity (-0.03 MPa) but not in all soils. In addition, it was reported that the maximum oxidation rates were (>-0.01 MPa) and (–0.27 MPa) in sand and clay soils, respectively.

2.4.4 Effect of Soil Type and pH:

Elemental sulphur oxidation would be affected by soil texture and by $CaCO_3$ content. Neilsen et al (1992) concluded that the magnitude of pH decreases in response to sulphur addition was highly related to the initial $CaCO_3$ content and soil texture. Alfalih (1996) reported that a large decline in pH and $CaCO_3$ content was achieved with the addition of 1% sulphur. Soil texture may affect the rate of sulphur oxidation. Zhao et al. (1996) reported that the net increases in sulphate- S as a percentage of total oxidized S were greater in the two sandy soils than in the two clayey soils.

Sulfur oxidation rate differs in alkaline, neutral and acidic soils. Jaggi et al. (1999) observed that oxidation rates of added elemental sulfur during initial 14 days period at 36°C for alkaline, neutral and acidic soils were 292, 180 and 125 μg S $cm^{-2}d^{-1}$, respectively. So the highest oxidation rates were in alkaline soil whereas the lowest were in acidic soil.

2.4.5 Effect of time:

Changing in soil pH is affected by the time with addition of elemental sulfur. However the time is affected by other environmental factors such as elemental sulfur grain size. Neilsen et al. (1992) concluded that finely divided sulphur was effective in reducing soil pH over time of 4-8 weeks. The time also depends on the temperature. Lee et al. (1990) reported that all the soils were oxidized when elemental sulphur was added for incubation period of 10 -12 weeks at 25 °C. Also, Chapman (1989) found that the time needed for 50% of the maximum oxidation of the micronized sulphur was 6-10 days at 20 °C, 23-26 days at 7 °C and 36-42 days at 2 °C. The time of sulphur oxidation rate was affected by it's application level. Reda and Modaihsh (1990) highly recommended the use of an application rate of 1.5% of sulphur to calcareous soil as most of it can be oxidized after 9-18 weeks.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS:

3.1.1 Elemental Sulfur:

Bright yellow granual elemental sulfur was collected from Al Ruwais Refinery from Sulfur Handling Terminal (SHT). A photo is shown in Figuer 3.1. Two samples (A, B) of the sulfur were taken from the same location of the process production as well as at the same time and were analyzed at the Central Laboratories Unit in the United Arab Emirates University to determine chloride as Cl^- (mg/kg) and ash (%) by using methods descriped by Horwitz (1990). Also, purity as S(%) and carbon contents (%) were determined by using Elemental Analyzer (FLASH- EA- ThermoFinnigan instrunment) by combustion method. The experimental results shown in Table 3.1 indicate that the two samples were identical in composition. Also, the amount of metals such as As, Se, Al, Ba, Cd, Cu, Ni, Pb, Zn in the samples was determined in (μg/l) by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) instrument and the method (USEPA 200.7). The chemical results are shown in Table 3.2.

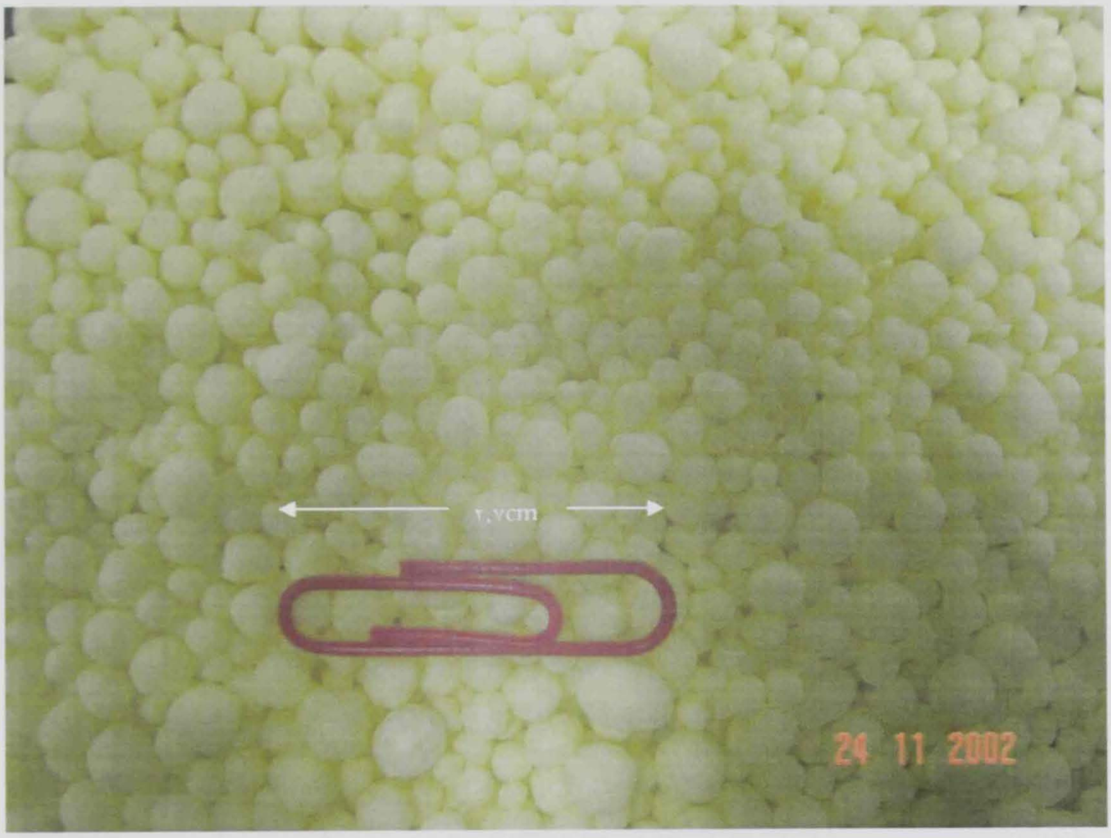

Figure 3.1: Granular elemental sulfur.

Table 3.1: Analysis of granular sulfur

Sample ID	Chloride as Cl– (mg/kg)	Carbon contents (%)	Purity as S (%)	Ash (%)
0048/S/MEWA/SULFUR-A-2001	2.50	0.40	99.90	0.04
0048/S/MEWA/SULFUR-B-2001	2.50	0.40	99.89	0.04

Table 3.2: Analysis of metals in granular sulfur

Sample ID	Asμg/l	Se μg/l	Al μg/l	Ba μg/l	Cd μg/l	Cu μg/l	Ni μg/l	Pb μg/l	Zn μg/l
0048/S/MEWA/SULFUR-A-2001	370	*< 5	76460	100	76	20	7	18	500
0048/S/MEWA/SULFUR-B-2001	360	*< 5	76590	98	74	21	7	17	498
Instrument Detection Limits	5.0	5.0	2.0	0.5	2.0	2.0	1.3	2.0	0.3

Note: * less than instrument Detection Limit (ICP-AES)

Other analysis for this sulphur was collected from Abu Dhabi Gas Liquiefacation Company Limited (ADGAS) in Das Island and shown in Table 3.3 (ADGAS, 1999).

Table 3.3: Sulfur certificate of quality (ADGAS, 1999)

TEST	**STANDARD METHOD**	**ALTERNATIVE METHOD**	**RESULT**
COLOUR (SOLID)	VISUAL	VISUAL	BRIGHT YELLOW
CARBON (PPM)	BS4113	PROCOR	37
ASH (PPM)	BS4113	PROCOR	NIL
PURITY (%Wt)	BS4113	PROCOR	99.9963
H_2S (PPM)	SNEA	R.M.P	4.8

The granular sulfur collected from AlRuwais Refinery from Sulfur Handling Terminal (SHT) was crushed and sieved by mesh (2mm). The grain size is shown in Figuer 3.2. Also, it was examined by Scanning Electrone Microscope (SEM-Jeol 5600) and the results were shown in Figures 3.3 and 3.4 at magnification levels of 3000 and 1000.

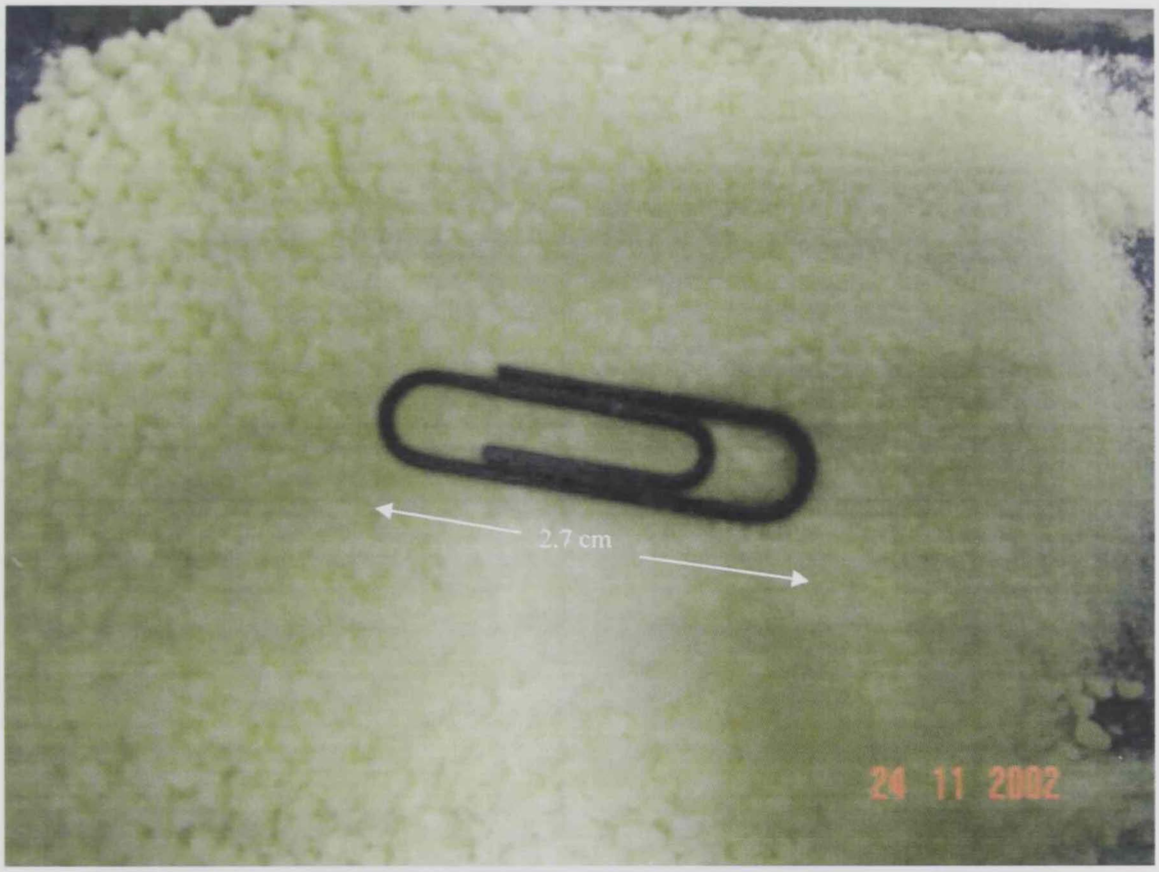

Figure 3.2: The Crushed and sieved elemental sulfur

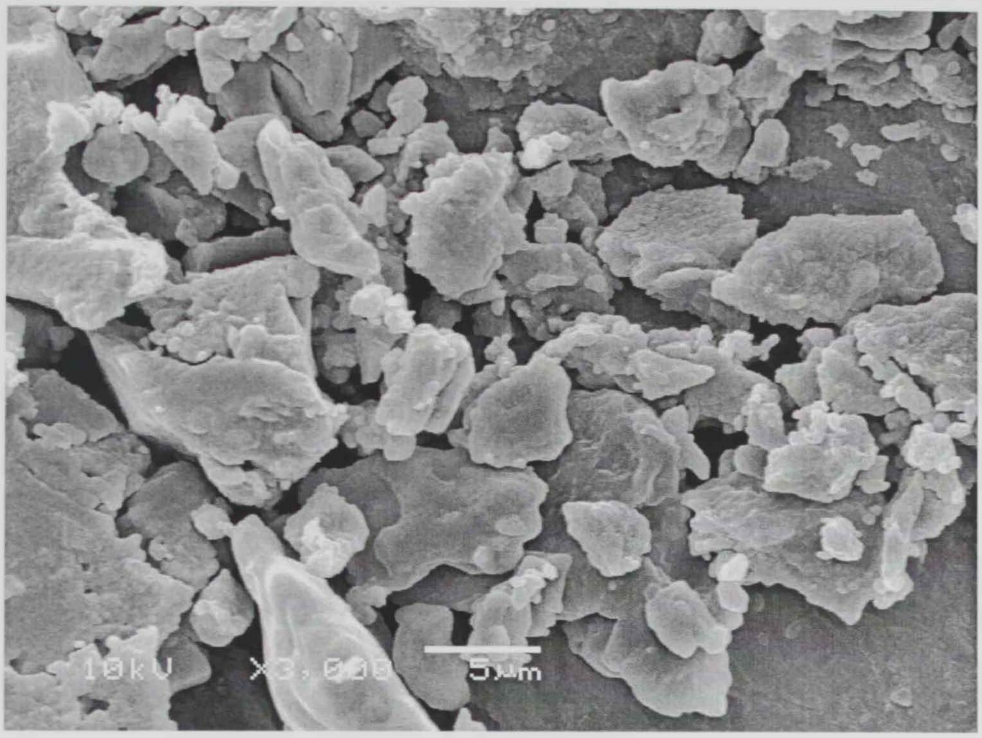

Figure 3.3: SEM image for crushed and sieved elemental sulfur.

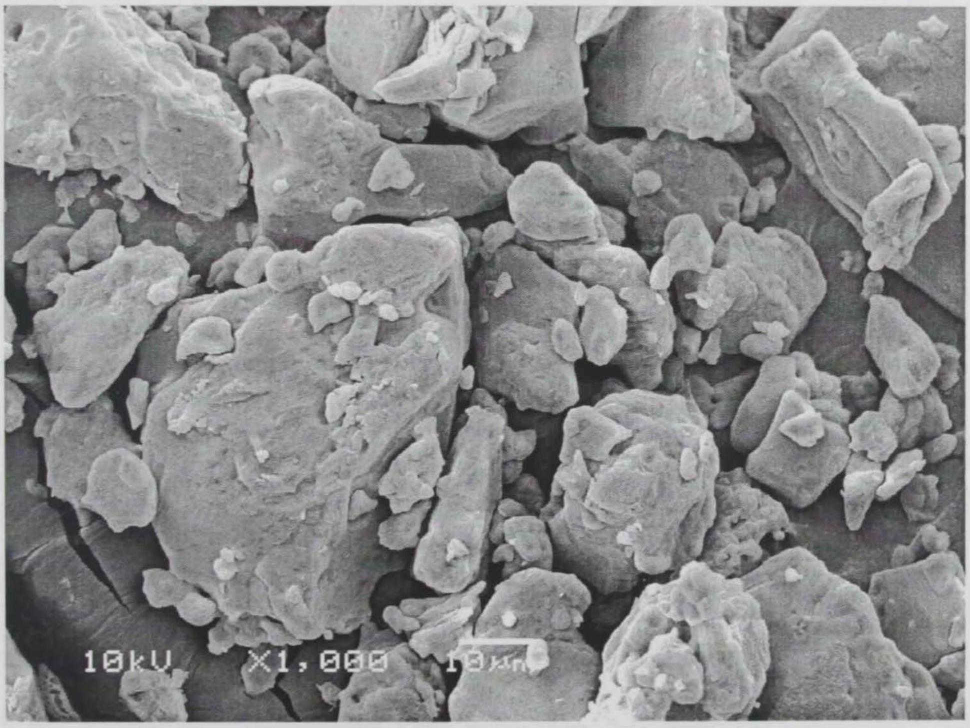

Figure 3.4: SEM image for crushed and sieved elemental sulfur

3.1.2 Soil:

The desert sand, in this investigation, was obtained from a sandy dunes quary in Al Ain area, UAE. The sand was characterized by a grain size ranging from 0.1 to 2 mm, specific gravity of 2.58. Soil pH and electrical conductivity (EC) were determined in soil water extract (1:5). The soil pH was 8.98 and EC was 42.5 µS/cm. The calcium carbonates was determined as follow: first the concentration of calcium ions in the soil was calculated by ICP, then multiplied by the ratio of atomic weight of carbonate divided by the atomic weight of calcium ions (100/40) , the resultant is then multiplied by the volume of 100ml distilled water , and the dilution factor (100). Finally, the resultant was divided by the weight of soil sample (2.5124 g). The above calculation showed that soil contains 161.8 g/kg (16.18%) $CaCO_3$.

The carbonate content in soil is consistent with previous experimental results reported by Soaud et al. (2003), which indicates that in Abu Dhabi: Agban, Al Semaih and Al Rahbah areas contain the highest range of total $CaCO_3$ (52 – 65%) , while the soils of Saih Al Khair and Um Al hesn contain the lowest range (4.3 – 15.6%). Also, most soils of Ras Al Khaimah contain high percentage of $CaCO_3$ (32 – 70%).

The major cations and the heavy metals were determined by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AESVarian-MPX-CCD) instrument. Sand soil sample of 2.51 gram of air dried and sieved soil, and then weighed and digested in a mixture of HCl and HNO_3 (3:1) in volume of 100 ml. The following elements and heavy metals Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn were determined by using (ICP-AES- Vista-MPX-CCD- Simultaneous-Axial- Varian Austriala) instrument. This instrument has detection limits for Cd, Cu, Pb, Zn, Ca, K, Mg, P, S04 and Na of 0.2, 1, 2, 0.2, 1, 1, 2, 5, 10 and 0.5 μg/l, respectively. The chemical composition of sand dunes is shown in Table 3.4. Also, total sulfur measured as sulfate, was determined by the method mentioned above, was 326 mg/kg. The SEM image for sand is shown in Figure 3.5.

Table 3.4: Chemical composition of the soil (sand dunes)

ELEMENT	**CONCENTRATION Mg/kg**	**ELEMENT**	**CONCENTRATION mg/kg**
Al	2782	Mg	1690.4
B	16	Mn	87.4
Ba	14.2	Mo	0.1
Ca	64722	Na	132.6
Cd	0.1	Ni	126.6
Co	5.7	P	63.5
Cr	39.3	Pb	1.9
Cu	3.3	Sr	138.1
Fe	7812.1	Zn	8.1
K	929.1		

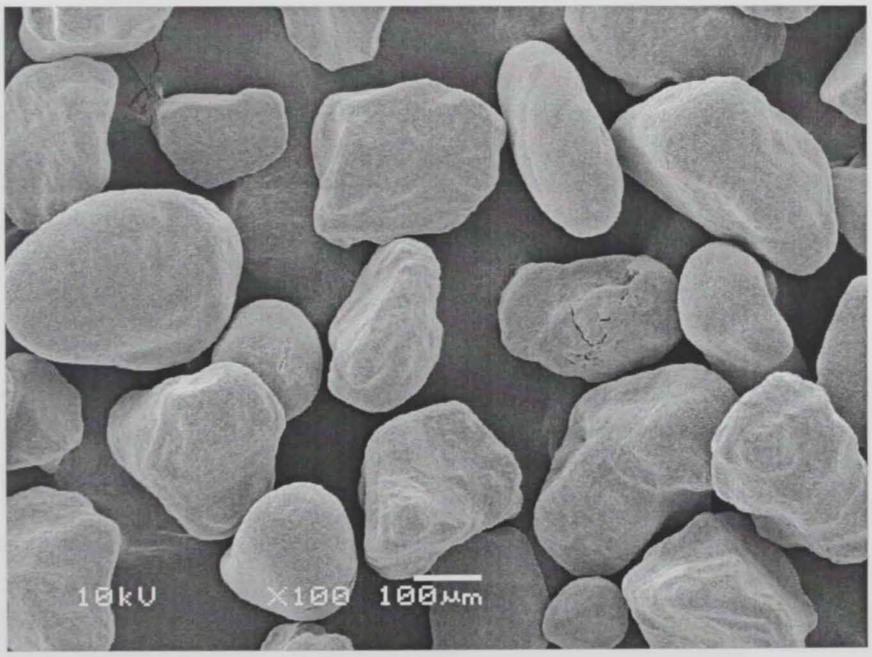

Figure 3.5: SEM image of tested dune sand.

3.1.3 Irrigation Water:

The water used through out the experiment was produced by General Utilities Units in Al Ruwais Refinery. The pH, EC and total dissolved solids (TDS) were determined in the Central Laboratories Unit in United Arab Emirates University. Also the following elements and heavy metals Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn (μg/l) were determined by using (ICP-AES) instrument. The chemical composition of the used water is shown in Table 3.5. Also, the total sulfur measured as sulfate, determined by the method mentioned above, was 13 mg/L.

Table 3.5: Chemical composition of the used irrigation water (mg/l)

ELEMENT	CONCENTRATION μg/l	ELEMENT	CONCENTRATION μg/l
Al	11.5	Mg	9994.6
B	70.6	Mn	5.8
Ba	1.2	Mo	0.1
Ca	11539	Na	53181
Cd	0.2	Ni	107.5
Co	0.1	P	27043
Cr	0.2	Pb	25.3
Cu	3.0	Sr	1060.2
Fe	1.7	Zn	753.4
K	2637.9		

3.1.4 Organic Matter:

The organic manure used was obtained from commerial stores which is generally used for agriculture purposes. It was analyzed in the Central Laboratories Unit in United Arab Emirates University to determine pH with glass electrode and it was 7.90. Also organic matter sample of 0.8422 gram was sieved, weighed, and digested in a mixture of HCl and HNO_3 (3:1) in a volume of 100 ml for metals analysis. The following elements and heavy metals (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn) were determined using (ICP-AES) instrument. The chemical composition of the organic manure used is shown in Table 3.6. Also the total sulfur measured as sulfate, determined by the method mentioned above, was 9409 mg/kg.

Table 3.6: Chemical composition of the used organic manure

ELEMENT	CONCENTRATION mg/kg	ELEMENT	CONCENTRATION mg/kg
Al	3087	Mg	3400.1
B	120.6	Mn	124.1
Ba	19.7	Mo	1.2
Ca	50768.2	Na	4818.1
Cd	0.5	Ni	12.8
Co	1.8	P	3211
Cr	11.9	Pb	3.0
Cu	41.1	Sr	125.9
Fe	3775.6	Zn	89.5
K	15084.3		

3.1.5 Calcium Carbonate:

A commercial calcium carbonate called AnalaR was used throughout the study. A sample of 0.2683 gram of calcium carbonate was weighed and digested in a mixture of HCl and HNO_3 (3:1) in a volume of 100 ml. Then, the following elements and heavy metals (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn) were determined by using (ICP-AES) instrument in the Central Laboratories Unit in United Arab Emirates University. The chemical composition of the used calcium carbonate is shown in Table 3.7. Also, the total sulfur measured as sulfate, determined by the method mentioned above, was 0.4 mg/kg. Also, the SEM image for the calcium carbonate is shown in Figure 3.6.

Table 3.7: Analysis of major cations and heavy metals in the used calcium carbonate

ELEMENT	CONCENTRATION mg/kg	ELEMENT	CONCENTRATION mg/kg
Al	12.2	Mg	101.9
B	22.5	Mn	0.3
Ba	0.7	Mo	0.2
Ca	423742.1	Na	147.6
Cd	0.04	Ni	2.4
Co	0.1	P	8.5
Cr	1.6	Pb	2.2
Cu	1.2	Sr	67.4
Fe	12.0	Zn	2.9
K	70.0		

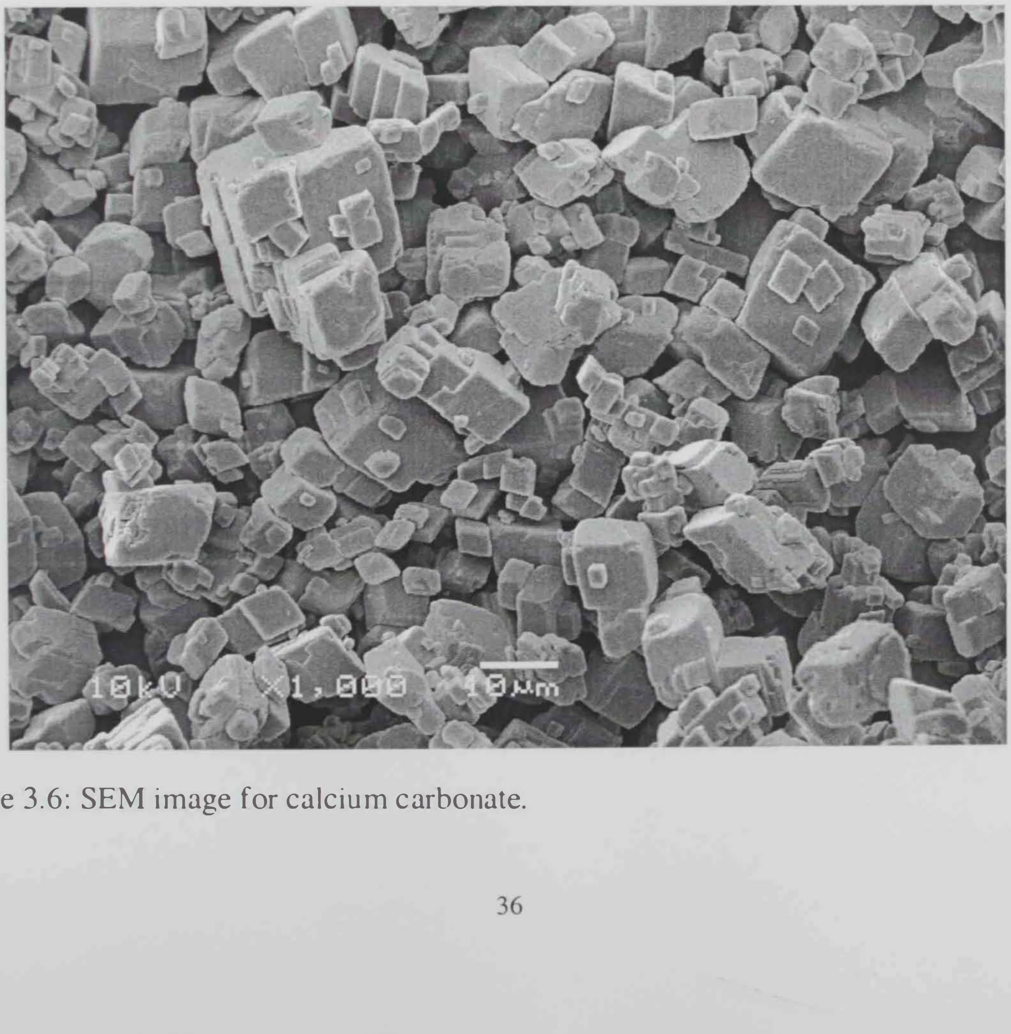

Figure 3.6: SEM image for calcium carbonate.

3.2 CONCENTRATION USED FOR TESTING:

3.2.1 Calcium Carbonate:

The calcium carbonate was added with different percentage of 0%, 5%, 10%, 20%, 30%, 40% in addition to initially $CaCO_3$% found naturally in the soil (16.2%). The resultant mixtures were identified as basic mix design, mix design type I, mix design type II, mix design type III, mix design type IV, and mix design type V. The added amounts of calcium carbonate are within the existing $CaCO_3$% naturally found in UAE soils (Soaud et al, 2003). Detailed composition of these mix designs are shown in Table 3.8.

3.2.2 Elemental Sulfur Application Rate:

Application percentge of 0%, 1%, 2% and 3% (g S°/ g soil) of crashed granular elemental sulfur (< 2mm) were added to different amount of soil as shown in Table 3.8.

3.3 SAMPLE PREPARATION:

Six mix designs, which are basic mix design, mix design type I, mix design type II, mix design type III, mix design type IV, mix design type V, were prepared by mixing different amounts of soil and calcium carbonate as detailed in Table 3.8. Each design contains 4 samples treated by addition of 0% S, 1%S, 2%S and 3%S. Also (1g) organic manure was added to each sample to form at the end samples of 100g of mixture additives as detailed in Table 3.8.

3.4 EXPERIMENTAL PROCEDURES :

Samples were prepared by mixing different amounts of soil, organic manure, sulfur and calcium carbonate as detailed in Table 3.8. Irrigation was added as required until saturation level was achieved. For each sample, the initial pH and EC were determined before adding sulfur (at 0 days) by using glass electrode with a water soil slurry (1:5). Then the six designs, which contain total of 24 samples, were placed in an oven at controlled temperature of 39 °C for 5 days. After 5 days, the 24 samples were taken for pH, EC, soluble water sulfate and mineral formation analysis. These procedures were repeated for 10, 20, 40 and 80 days. At the end, a total of 120 samples were prepared and analyzed for pH, EC, soluble water sulfate, and mineral formation analysis.

3.5 EXPERIMENTAL ANALYSIS:

At termination of each incubation period, pH and EC were determined with glass electrode with a water soil slurry (1:5) for all the samples. Also, water soluble sulfate was determined in soil water slurry (1:10) by using ICP-ASE instrument in the Central Laboratories Unit in United Arab Emirates University. Also, mineral formation was examined in all the samples by Scanning Electrone Microscope (SEM) and X-ray differaction analysis. A philips X-ray diffractometer model PW/ 1840, with Ni filter, Cu-Kα radiation (λ=1.542A°) at 40 kV, 30mA and scanning speed 0.02°/S was used. The diffraction peaks between $2\theta = 2°$ and $2\theta = 60°$ were recorded. The corresponding spacing and relative intensities were calculated and compared with the standard data.

Table 3.8 : The experiment design

	ADDED CaCO3%					
S^{O} %	**BASIC MIX DESIGN**	**MIX DESIGN TYPE I**	**MIX DESIGN TYPE II**	**MIX DESIGN TYPE III**	**MIX DESIGN TYPE IV**	**MIX DESIGN TYPE V**
0%	0%S : 0% $CaCO_3$ **1** 1 g OM :99 g sand	0%S : 5% $CaCO_3$ **5** 5g $CaCO_3$:1g OM: 94g sand	0%S : 10% $CaCO_3$ **9** 10g $CaCO_3$:1g OM: 89g sand	0%S : 20% $CaCO_3$ **13** 20g $CaCO_3$: 1g OM : 79g sand	0%S : 30% $CaCO_3$ **17** 30g $CaCO_3$: 1g OM : 69g sand	0%S : 40% $CaCO_3$ **21** 40g $CaCO_3$: 1g OM : 59g sand
1%	1%S : 0% $CaCO_3$ **2** 1g S:1g OM: 99 g sand	1%S : 5% $CaCO_3$ **6** 1g S:5g $CaCO_3$:1g OM: 93g sand	1%S : 10% $CaCO_3$ **10** 1g S:10g $CaCO_3$:1g OM : 88g sand	1%S : 20% $CaCO_3$ **14** 1g S:20g $CaCO_3$: 1g OM : 78g sand	1%S : 30% $CaCO_3$ **18** 1g S:30g $CaCO_3$: 1g OM : 68g sand	1%S : 40% $CaCO_3$ **22** 1g S:40g $CaCO_3$: 1g OM : 58g sand
2%	2%S : 0% $CaCO_3$ **3** 2g S: 1g OM: 99 g sand	2%S : 5% $CaCO_3$ **7** 2g S:5g $CaCO_3$: 1g OM: 92g sand	2%S : 10% $CaCO_3$ **11** 2g S:10g $CaCO_3$:1g OM : 87g sand	2%S : 20% $CaCO_3$ **15** 2g S:20g $CaCO_3$: 1g OM : 77g sand	2%S : 30% $CaCO_3$ **19** 2g S:30g $CaCO_3$: 1g OM : 67g sand	2%S : 40% $CaCO_3$ **23** 2g S:40g $CaCO_3$: 1g OM : 55
3%	3%S : 0% $CaCO_3$ **4** 3g S: 1g OM: 99 g sand	3%S : 5% $CaCO_3$ **8** 3g S:5g $CaCO_3$:1g OM : 91g sand	3%S : 10% $CaCO_3$ **12** 3g S:10g $CaCO_3$:1g OM : 86g sand	3%S : 20% $CaCO_3$ **16** 3g S:20g $CaCO_3$: 1g OM : 76g sand	3%S : 30% $CaCO_3$ **20** 3g S:30g $CaCO_3$: 1g OM : 66g sand	3%S : 40% $CaCO_3$ **24** 3g S:40g $CaCO_3$: 1g OM : 56g sand

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS:

3.1.1 Elemental Sulfur:

Bright yellow granual elemental sulfur was collected from Al Ruwais Refinery from Sulfur Handling Terminal (SHT). A photo is shown in Figuer 3.1. Two samples (A, B) of the sulfur were taken from the same location of the process production as well as at the same time and were analyzed at the Central Laboratories Unit in the United Arab Emirates University to determine chloride as Cl^- (mg/kg) and ash (%) by using methods descriped by Horwitz (1990). Also, purity as S(%) and carbon contents (%) were determined by using Elemental Analyzer (FLASH- EA- ThermoFinnigan instrunment) by combustion method. The experimental results shown in Table 3.1 indicate that the two samples were identical in composition. Also, the amount of metals such as As, Se, Al, Ba, Cd, Cu, Ni, Pb, Zn in the samples was determined in (μg/l) by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) instrument and the method (USEPA 200.7). The chemical results are shown in Table 3.2.

Figure 3.1: Granular elemental sulfur.

Table 3.1: Analysis of granular sulfur

Sample ID	**Chloride as Cl– (mg/kg)**	**Carbon contents (%)**	**Purity as S (%)**	**Ash (%)**
0048/S/MEWA/SULFUR-A-2001	2.50	0.40	99.90	0.04
0048/S/MEWA/SULFUR-B-2001	2.50	0.40	99.89	0.04

Table 3.2: Analysis of metals in granular sulfur

Sample ID	**Asμg/l**	**Se μg/l**	**Al μg/l**	**Ba μg/l**	**Cd μg/l**	**Cu μg/l**	**Ni μg/l**	**Pb μg/l**	**Zn μg/l**
0048/S/MEWA/SULFUR-A-2001	370	*< 5	76460	100	76	20	7	18	500
0048/S/MEWA/SULFUR-B-2001	360	*< 5	76590	98	74	21	7	17	498
Instrument Detection Limits	5.0	5.0	2.0	0.5	2.0	2.0	1.3	2.0	0.3

Note: * less than instrument Detection Limit (ICP-AES)

Other analysis for this sulphur was collected from Abu Dhabi Gas Liquiefacation Company Limited (ADGAS) in Das Island and shown in Table 3.3 (ADGAS, 1999).

Table 3.3: Sulfur certificate of quality (ADGAS, 1999)

TEST	**STANDARD METHOD**	**ALTERNATIVE METHOD**	**RESULT**
COLOUR (SOLID)	VISUAL	VISUAL	BRIGHT YELLOW
CARBON (PPM)	BS4113	PROCOR	37
ASH (PPM)	BS4113	PROCOR	NIL
PURITY (%Wt)	BS4113	PROCOR	99.9963
H_2S (PPM)	SNEA	R.M.P	4.8

The granular sulfur collected from AlRuwais Refinery from Sulfur Handling Terminal (SHT) was crushed and sieved by mesh (2mm). The grain size is shown in Figuer 3.2. Also, it was examined by Scanning Electrone Microscope (SEM-Jeol 5600) and the results were shown in Figures 3.3 and 3.4 at magnification levels of 3000 and 1000.

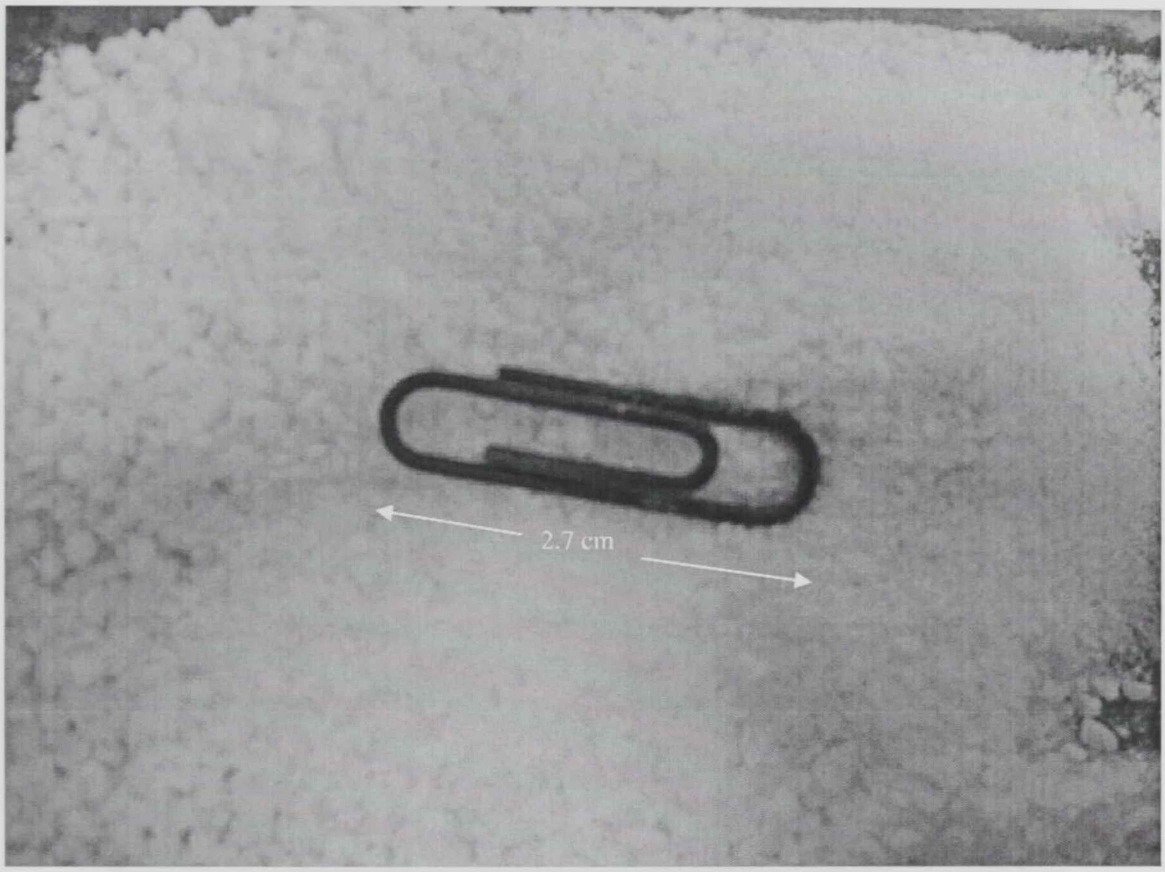

Figure 3.2: The Crushed and sieved elemental sulfur

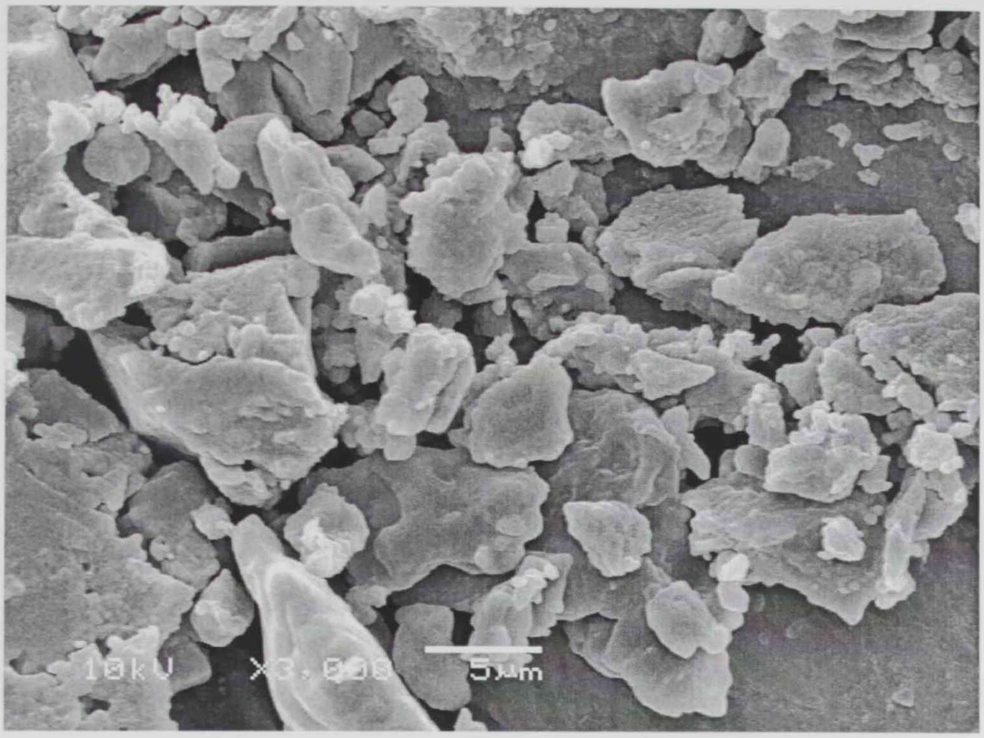

Figure 3.3: SEM image for crushed and sieved elemental sulfur.

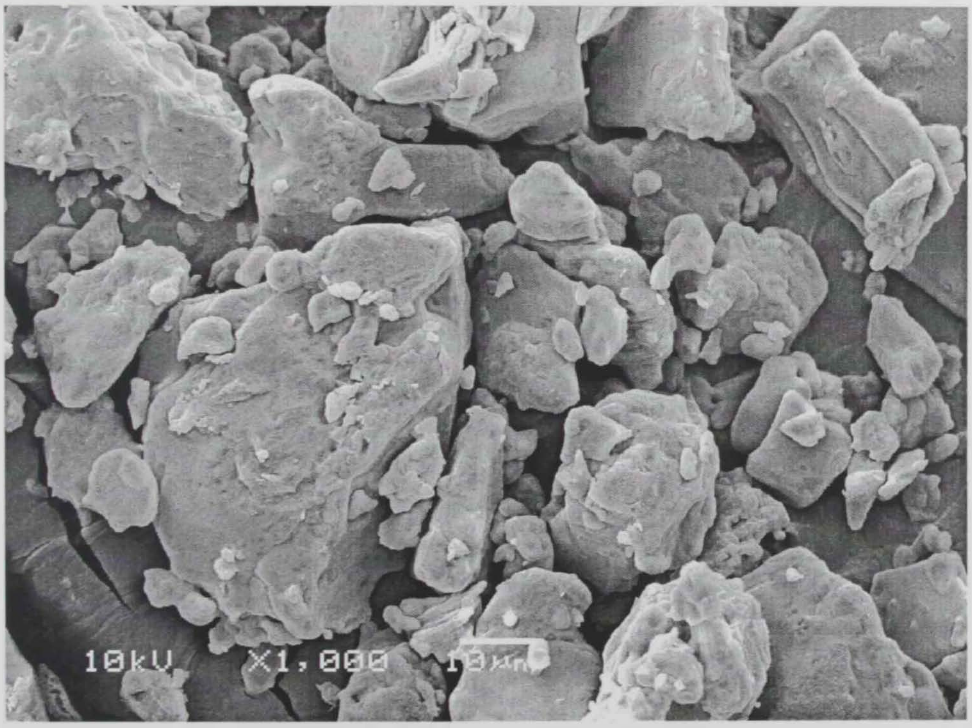

Figure 3.4: SEM image for crushed and sieved elemental sulfur

3.1.2 Soil:

The desert sand, in this investigation, was obtained from a sandy dunes quary in Al Ain area, UAE. The sand was characterized by a grain size ranging from 0.1 to 2 mm, specific gravity of 2.58. Soil pH and electrical conductivity (EC) were determined in soil water extract (1:5). The soil pH was 8.98 and EC was 42.5 μS/cm. The calcium carbonates was determined as follow: first the concentration of calcium ions in the soil was calculated by ICP, then multiplied by the ratio of atomic weight of carbonate divided by the atomic weight of calcium ions (100/40) , the resultant is then multiplied by the volume of 100ml distilled water , and the dilution factor (100). Finally, the resultant was divided by the weight of soil sample (2.5124 g). The above calculation showed that soil contains 161.8 g/kg (16.18%) $CaCO_3$.

The carbonate content in soil is consistent with previous experimental results reported by Soaud et al. (2003), which indicates that in Abu Dhabi: Agban, Al Semaih and Al Rahbah areas contain the highest range of total $CaCO_3$ (52 – 65%) , while the soils of Saih Al Khair and Um Al hesn contain the lowest range (4.3 – 15.6%). Also, most soils of Ras Al Khaimah contain high percentage of $CaCO_3$ (32 – 70%).

The major cations and the heavy metals were determined by using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AESVarian-MPX-CCD) instrument. Sand soil sample of 2.51 gram of air dried and sieved soil, and then weighed and digested in a mixture of HCl and HNO_3 (3:1) in volume of 100 ml. The following elements and heavy metals Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn were determined by using (ICP-AES- Vista-MPX-CCD- Simultaneous-Axial- Varian Austriala) instrument. This instrument has detection limits for Cd, Cu, Pb, Zn, Ca, K, Mg, P, S04 and Na of 0.2, 1, 2, 0.2, 1, 1, 2, 5, 10 and 0.5 µg/l, respectively. The chemical composition of sand dunes is shown in Table 3.4. Also, total sulfur measured as sulfate, was determined by the method mentioned above, was 326 mg/kg. The SEM image for sand is shown in Figure 3.5.

Table 3.4: Chemical composition of the soil (sand dunes)

ELEMENT	CONCENTRATION Mg/kg	ELEMENT	CONCENTRATION mg/kg
Al	2782	Mg	1690.4
B	16	Mn	87.4
Ba	14.2	Mo	0.1
Ca	64722	Na	132.6
Cd	0.1	Ni	126.6
Co	5.7	P	63.5
Cr	39.3	Pb	1.9
Cu	3.3	Sr	138.1
Fe	7812.1	Zn	8.1
K	929.1		

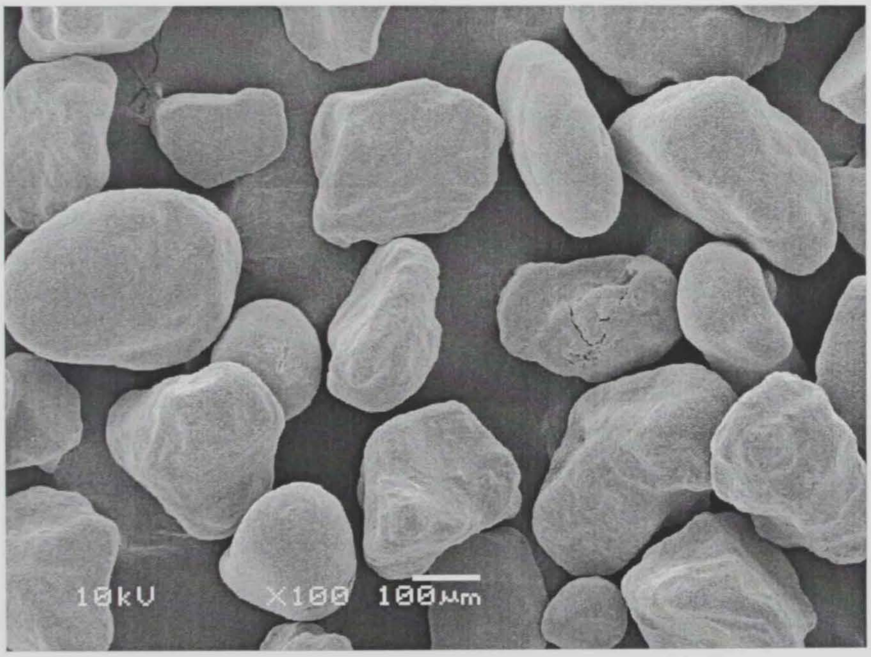

Figure 3.5: SEM image of tested dune sand.

Zn, Ca, K, Mg, P, S04 and Na of 0.2, 1, 2, 0.2, 1, 1, 2, 5, 10 and 0.5 μg/l, respectively. The chemical composition of sand dunes is shown in Table 3.4. Also, total sulfur measured as sulfate, was determined by the method mentioned above, was 326 mg/kg. The SEM image for sand is shown in Figure 3.5.

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Fe	7812.1	Zn	8.1
K	929.1		

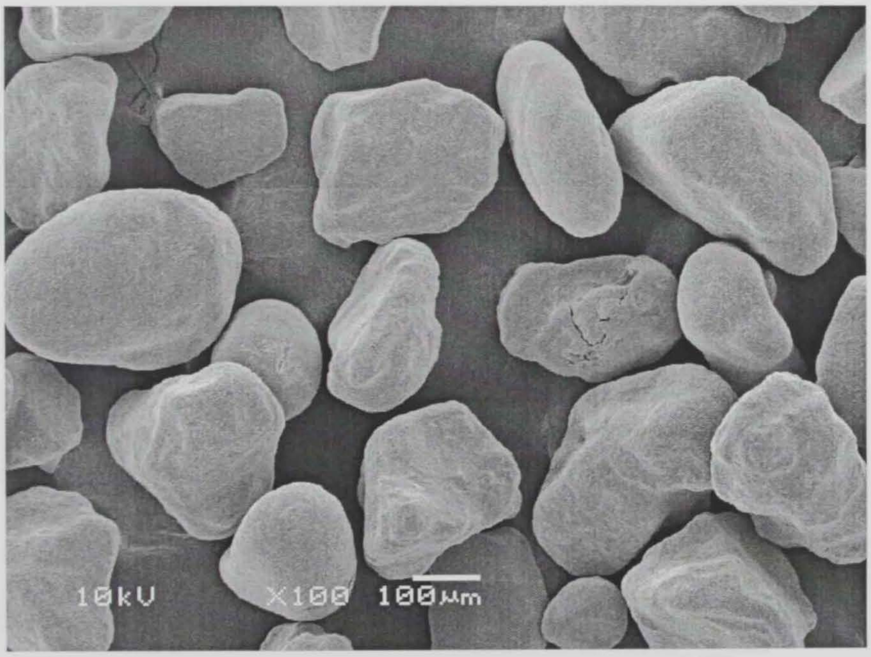


Figure 3.5: SEM image of tested dune sand.

3.1.3 Irrigation Water:

The water used through out the experiment was produced by General Utilities Units in Al Ruwais Refinery. The pH, EC and total dissolved solids (TDS) were determined in the Central Laboratories Unit in United Arab Emirates University. Also the following elements and heavy metals Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn (µg/l) were determined by using (ICP-AES) instrument. The chemical composition of the used water is shown in Table 3.5. Also, the total sulfur measured as sulfate, determined by the method mentioned above, was 13 mg/L.

Table 3.5: Chemical composition of the used irrigation water (mg/l)

ELEMENT	**CONCENTRATION µg/l**	**ELEMENT**	**CONCENTRATION µg/l**
Al	11.5	Mg	9994.6
B	70.6	Mn	5.8
Ba	1.2	Mo	0.1
Ca	11539	Na	53181
Cd	0.2	Ni	107.5
Co	0.1	P	27043
Cr	0.2	Pb	25.3
Cu	3.0	Sr	1060.2
Fe	1.7	Zn	753.4
K	2637.9		

3.1.4 Organic Matter:

The organic manure used was obtained from commerial stores which is generally used for agriculture purposes. It was analyzed in the Central Laboratories Unit in United Arab Emirates University to determine pH with glass electrode and it was 7.90. Also organic matter sample of 0.8422 gram was sieved, weighed, and digested in a mixture of HCl and HNO_3 (3:1) in a volume of 100 ml for metals analysis. The following elements and heavy metals (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn) were determined using (ICP-AES) instrument. The chemical composition of the organic manure used is shown in Table 3.6. Also the total sulfur measured as sulfate, determined by the method mentioned above, was 9409 mg/kg.

Table 3.6: Chemical composition of the used organic manure

ELEMENT	CONCENTRATION mg/kg	ELEMENT	CONCENTRATION mg/kg
Al	3087	Mg	3400.1
B	120.6	Mn	124.1
Ba	19.7	Mo	1.2
Ca	50768.2	Na	4818.1
Cd	0.5	Ni	12.8
Co	1.8	P	3211
Cr	11.9	Pb	3.0
Cu	41.1	Sr	125.9
Fe	3775.6	Zn	89.5
K	15084.3		

3.1.5 Calcium Carbonate:

A commercial calcium carbonate called AnalaR was used throughout the study. A sample of 0.2683 gram of calcium carbonate was weighed and digested in a mixture of HCl and HNO_3 (3:1) in a volume of 100 ml. Then, the following elements and heavy metals (Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sr and Zn) were determined by using (ICP-AES) instrument in the Central Laboratories Unit in United Arab Emirates University. The chemical composition of the used calcium carbonate is shown in Table 3.7. Also, the total sulfur measured as sulfate, determined by the method mentioned above, was 0.4 mg/kg. Also, the SEM image for the calcium carbonate is shown in Figure 3.6.

Table 3.7: Analysis of major cations and heavy metals in the used calcium carbonate

ELEMENT	CONCENTRATION mg/kg	ELEMENT	CONCENTRATION mg/kg
Al	12.2	Mg	101.9
B	22.5	Mn	0.3
Ba	0.7	Mo	0.2
Ca	423742.1	Na	147.6
Cd	0.04	Ni	2.4
Co	0.1	P	8.5
Cr	1.6	Pb	2.2
Cu	1.2	Sr	67.4
Fe	12.0	Zn	2.9
K	70.0		

Figure 3.6: SEM image for calcium carbonate.

3.2 CONCENTRATION USED FOR TESTING:

3.2.1 Calcium Carbonate:

The calcium carbonate was added with different percentage of 0%, 5%, 10%, 20%, 30%, 40% in addition to initially $CaCO_3$% found naturally in the soil (16.2%). The resultant mixtures were identified as basic mix design, mix design type I, mix design type II, mix design type III, mix design type IV, and mix design type V. The added amounts of calcium carbonate are within the existing $CaCO_3$% naturally found in UAE soils (Soaud et al, 2003). Detailed composition of these mix designs are shown in Table 3.8.

3.2.2 Elemental Sulfur Application Rate:

Application percentge of 0%, 1%, 2% and 3% (g S°/ g soil) of crashed granular elemental sulfur (< 2mm) were added to different amount of soil as shown in Table 3.8.

3.3 SAMPLE PREPARATION:

Six mix designs, which are basic mix design, mix design type I, mix design type II, mix design type III, mix design type IV, mix design type V, were prepared by mixing different amounts of soil and calcium carbonate as detailed in Table 3.8. Each design contains 4 samples treated by addition of 0% S, 1%S, 2%S and 3%S. Also (1g) organic manure was added to each sample to form at the end samples of 100g of mixture additives as detailed in Table 3.8.

3.4 EXPERIMENTAL PROCEDURES :

Samples were prepared by mixing different amounts of soil, organic manure, sulfur and calcium carbonate as detailed in Table 3.8. Irrigation was added as required until saturation level was achieved. For each sample, the initial pH and EC were determined before adding sulfur (at 0 days) by using glass electrode with a water soil slurry (1:5). Then the six designs, which contain total of 24 samples, were placed in an oven at controlled temperature of 39 °C for 5 days. After 5 days, the 24 samples were taken for pH, EC, soluble water sulfate and mineral formation analysis. These procedures were repeated for 10, 20, 40 and 80 days. At the end, a total of 120 samples were prepared and analyzed for pH, EC, soluble water sulfate, and mineral formation analysis.

3.5 EXPERIMENTAL ANALYSIS:

At termination of each incubation period, pH and EC were determined with glass electrode with a water soil slurry (1:5) for all the samples. Also, water soluble sulfate was determined in soil water slurry (1:10) by using ICP-ASE instrument in the Central Laboratories Unit in United Arab Emirates University. Also, mineral formation was examined in all the samples by Scanning Electrone Microscope (SEM) and X-ray differaction analysis. A philips X-ray diffractometer model PW/ 1840, with Ni filter, Cu-Kα radiation (λ=1.542A°) at 40 kV, 30mA and scanning speed 0.02°/S was used. The diffraction peaks between $2\theta = 2°$ and $2\theta = 60°$ were recorded. The corresponding spacing and relative intensities were calculated and compared with the standard data.

Table 3.8 : The experiment design

	ADDED CaCO3%					
S^0 %	**BASIC MIX DESIGN**	**MIX DESIGN TYPE I**	**MIX DESIGN TYPE II**	**MIX DESIGN TYPE III**	**MIX DESIGN TYPE IV**	**MIX DESIGN TYPE V**
0%	0%S : 0% CaCO$_3$ **1** 1 g OM :99 g sand	0%S : 5% CaCO$_3$ **5** 5g CaCO$_3$:1g OM: 94g sand	0%S : 10% CaCO$_3$ **9** 10g CaCO$_3$:1g OM: 89g sand	0%S : 20% CaCO$_3$ **13** 20g CaCO$_3$: 1g OM : 79g sand	0%S : 30% CaCO$_3$ **17** 30g CaCO$_3$: 1g OM : 69g sand	0%S : 40% CaCO$_3$ **21** 40g CaCO$_3$: 1g OM : 59g sand
1%	1%S : 0% CaCO$_3$ **2** 1g S:1g OM: 99 g sand	1%S : 5% CaCO$_3$ **6** 1g S:5g CaCO$_3$:1g OM: 93g sand	1%S : 10% CaCO$_3$ **10** 1g S:10g CaCO$_3$:1g OM : 88g sand	1%S : 20% CaCO$_3$ **14** 1g S:20g CaCO$_3$: 1g OM : 78g sand	1%S : 30% CaCO$_3$ **18** 1g S:30g CaCO$_3$: 1g OM : 68g sand	1%S : 40% CaCO$_3$ **22** 1g S:40g CaCO$_3$: 1g OM : 58g sand
2%	2%S : 0% CaCO$_3$ **3** 2g S: 1g OM: 99 g sand	2%S : 5% CaCO$_3$ **7** 2g S:5g CaCO$_3$:1g OM: 92g sand	2%S : 10% CaCO$_3$ **11** 2g S:10g CaCO$_3$:1g OM : 87g sand	2%S : 20% CaCO$_3$ **15** 2g S:20g CaCO$_3$: 1g OM : 77g sand	2%S : 30% CaCO$_3$ **19** 2g S:30g CaCO$_3$: 1g OM : 67g sand	2%S : 40% CaCO$_3$ **23** 2g S:40g CaCO$_3$: 1g OM : 55
3%	3%S : 0% CaCO$_3$ **4** 3g S: 1g OM: 99 g sand	3%S : 5% CaCO$_3$ **8** 3g S:5g CaCO$_3$:1g OM : 91g sand	3%S : 10% CaCO$_3$ **12** 3g S:10g CaCO$_3$:1g OM : 86g sand	3%S : 20% CaCO$_3$ **16** 3g S:20g CaCO$_3$: 1g OM : 76g sand	3%S : 30% CaCO$_3$ **20** 3g S:30g CaCO$_3$: 1g OM : 66g sand	3%S : 40% CaCO$_3$ **24** 3g S:40g CaCO$_3$: 1g OM : 56g sand

CHAPTER 4

RESULTS AND DISCUSSTION

4.1 THERMODYNAMIC MODELING OF POSSIBLE CHEMICAL REACTIONS:

The activity ratio diagrams for calcium bearing minerals are shown in Figure 4.1 (Mohamed et al. 1995). The Figures indicate that below pH 8, the formed minerals are gypsum [$CaSO_4$.$2H_2$], tricalcium aluminate hydrate [3CaO. Al_2O_3 .$6H_2O$], or sometimes it is referred to as C_3AH_6, dicalcium aluminate hydrate (C_2AH_8) or in chemical form [2CaO. Al_2O_3 .$8H_2O$], tetracalcium aluminate hydrate (C_4AH_{13}) or in chemical form [3CaO. Al_2O_3 .Ca $(OH)_2$.$12H_2O$], and calcium monosulfoaluminate [3CaO. Al_2O_3 .Ca SO_4 .$12H_2O$].

4.2 POSSIBLE CHEMICAL REACTION AND MINERAL FORMATION:

Let us investigate the possibility of forming the above described minerals in the sample under investigation. The possible processes could be described as follow (Mohamed et al. 1995, Mohamed, 2003):

Formation of Sulfuric Acid due to sulfur oxidation:

$$2S + 2H_2O + 3O_2 \longrightarrow 2H_2SO_4 \text{ (Sulfuric Acid)}$$

1. Formation of Gypsum and Carbonic Acid:

$$H_2SO_4 + CaCO_3 + 2H_2O \longrightarrow Ca\,SO_4.\ 2H_2O\text{(Gypsum)} + H_2CO_3 \text{ (Carbonic Acid)}$$

2. Dissolution of Calcite in Carbonic Acid:

$$CaCO_3 + H_2CO_3 \longrightarrow Ca^{2+} + 2H^+ + 2CO_3^{-2}$$

3. Formation of Secondary Gypsum:

$$Ca^{2+} + SO_4^{-2} + 2H_2O \longrightarrow Ca\,SO_4.\ 2H_2O\text{(Secondary Gypsum)}$$

4. Formation of Secondary Calcite:

$$Ca^{2+} + CO_3^{-2} \longrightarrow CaCO_3 \text{ (Calcite)}$$

5. Formation of Calcium Hydroxide:

$$Ca^{2+} + 2H_2O \longrightarrow Ca(OH)_2 \text{ (Calcium Hydroxide)} + 2H^+$$

6. Ionization of Calcium Hydroxide; pH increases:

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2(OH)^-$$

7. Formation of Tricalcium Aluminate:

$$3Ca^{2+} + 2Al\,(OH)^-_4 \longrightarrow \underset{\text{Tricalcium Aluminate }(C_3A)}{3CaO.\ Al_2O_3 + 2H_2O + 4H^+}$$

8. Formation of Tricalcium Aluminate Hydrate:

$$\underset{(C_3A)}{3CaO.\ Al_2O_3} + \underset{(6H)}{6H_2O} \longrightarrow \underset{\text{Tricalcium Aluminate Hydrate }(C_3AH_6)}{3CaO.Al_2O_3.\ 6H_2O}$$

9. Formation of Tetracalcium Aluminate Hydrate:

$$\underset{\substack{\text{Tricalcium Aluminate}\\(C_3A)}}{3CaO.\ Al_2O_3} \underset{\text{+ water}}{+} \underset{(12H)}{12H_2O} \underset{\text{+ lime}}{+} \underset{(CH)}{Ca(OH)_2} \longrightarrow \underset{\substack{\text{Tetracalcium Aluminate Hydrate}\\(C_4AH_{13})}}{3CaO.\ Al_2O_3.\ Ca(OH)_2.12H_2O.}$$

10. Formation of Calcium Monosulfoaluminate:

$$3CaO.\ Al_2O_3 + 10H_2O + CaSO_4.2H_2O \longrightarrow \underset{\text{Calcium Monosulfoaluminate}}{3CaO.\ Al_2O_3.\ CaSO_4.12H_2O.}$$

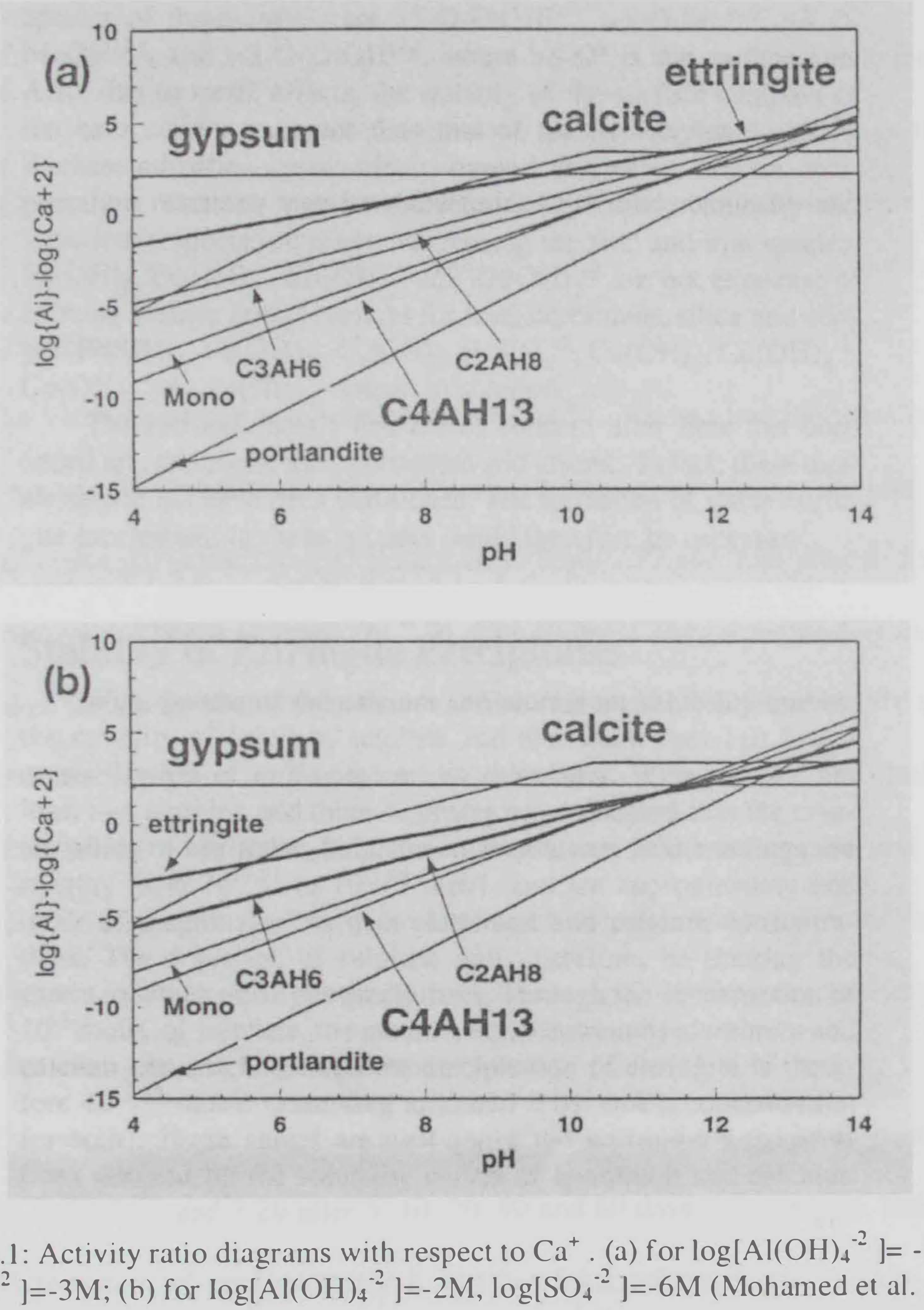


Figure 4.1: Activity ratio diagrams with respect to Ca^+ . (a) for $\log[Al(OH)_4^{-2}]$= -2M, $\log[SO_4^{-2}]$=-3M; (b) for $\log[Al(OH)_4^{-2}]$=-2M, $\log[SO_4^{-2}]$=-6M (Mohamed et al. 1995).

4.3 EFFECT OF ELEMENTAL SULFUR APPLICATION ON BASIC MIX DESIGN:

The effect of added elemental sulfur on basic mix design (without addition of $CaCO_3$) was determined by measuring the pH levels, electrical conductivity (EC) in μS/cm and water soluble SO_4^{-2} (g/kg). It should be noted that, as previously discussed, the basic mix design contained initial carbonates in the amount of 16.2% in the sand used. The variations of these parameters as a function of time are discussed below.

4.3.1 pH Variation:

The variation of pH as a function of time and sulfur addition is shown in Figure 4.2. The experimental results of pH variation of the basic mix design samples without addition of elemental sulfur reduced from 8.46 to 8.06, 7.77 and 7.69 after 5, 10 and 20 days, respectively. Then it increased to 7.96 after 40 days. Then it reduced again to 7.87 after 80 days. This is attributed to the amount of sulfur which was found mainly in added organic manure (1%) and in the sand as discussed in Chapter 3. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic matter, sand and $CaCO_3$, respectively. This means that a pH reduction of approximately 0.4 units has been achieved after 5 days and pH continued to decrease until 40 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite.

The results indicate that the addition of 1% S reduced the pH level from 8.43 to 7.23, 7.24, 6.88, 7.19 and 7.26 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1 unit has been achieved after 5 days and pH continued to decrease until 40 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite. The increase of pH after 40 and 80 days could be attributed to the formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide.

The addition of 2% S reduced the pH level from 8.41 to 7.30, 7.29, 7.15, 7.13 and 7.28 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 0.91 units has been achieved after 5 days and pH continued to decrease until 40 days.

The addition of 3% S reduced the pH level from 8.48 to 7.07, 7.39, 6.68, 7.12 and 7.27 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.41 units has been achieved after 5 days and pH continued to decrease until 40 days.

Based on both the possible chemical reactions discussed previously as well as the experimental results, the pH first reduced because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it increased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it decreased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate.

The experimental results of pH variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.120 with 3 degrees of freedom, indicating that addition of sulfur has no significance (P-value > 0.05) on the changes in pH value. Also there was a little difference in the mean as shown in Table 4.1.

Table 4.1: One-way stacked ANOVA analysis for pH results of the basic mix design samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	7.9717	7.3717	7.4267	7.3350
StDiv	0.2725	0.5375	0.4874	0.6105

4.3.2 Electrical Conductivity (EC) Variation:

The variation of EC as a function of time and sulfur addition is shown in Figure 4.3. The EC of the basic mix design samples without addition of elemental sulfur increased from 371 to 625 μS/cm after 5 days then decreased to 537 μS/cm after 10 days but increased again to 1313 μS/cm after 20 days. Then decreased again to 654 μS/cm after 40 days but increased again to 733 μS/cm after 80 days. This can be attributed to: (1) the amount of organic manure that the basic mix design sample contains (1%); (2) the amount of total sulfur measured as sulfate that the organic manure contains 9409 mg/kg, and (3) the amount of total sulfur measured as sulfate of 326, 0.4 mg/kg in sand and $CaCO_3$, respectively. Due to sulfur oxidation, pH decreased and the amount of soluble ions increased leading to an increase of EC.

The results indicate that the addition of 1%S increased EC from 375 to 2570, 3220, 1457, 1400 and 3290 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 2205 μS/cm has been achieved after 5 days and EC continued to increase after 10 days, then decreased after 20 and 40 days but increased after 80 days.

Also the addition of 2%S increased EC from 367 to 1024, 2500, 1551, 1600 and 2700 µS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 657 µS/cm has been achieved after 5 days and EC continued to increase after 10 days, then decreased after 20 and 40 days but increased after 80 days.

The addition of 3% S also increased EC from 370 to 2630, 2480, 1524, 2050 and 2630 µS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 2260 µS/cm has been achieved after 5 days and EC continued to increase after 10 days, then decreased after 20 and 40 days but increased after 80 days. The increase in soluble salts as measured by soil EC was due to dissolution of $CaCO_3$ by H_2SO_4 (Cifuentes and Lindeman, 1993).

Based on both the possible chemical reactions discussed previously as well as the experimental results, the EC first increased because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it decreased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it increased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate.

The experimental results of EC variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.004 with 3 degrees of freedom, indicating that addition of sulfur has highly significance (P-value < 0.05) on the changes in EC value. Also there was a difference in the mean as shown in Table 4.2.

Table 4.2: One-way stacked ANOVA analysis for EC results of the basic mix design samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	772.4	2387.4	1875.0	2242.8
StDiv	310.2	919.5	702.9	458.9

4.3.3 Oxidation of Elemental Sulfur:

Oxidation of elemental sulfur was evaluated based on the amount of measured water soluble sulfate. Therefore, Figure 4.4 shows the amount of water soluble sulfate as a function of time and amount of elemental sulfur added. Thus, the Figure 4.4 indicates that the addition of 1% S, 2%S and 3%S kept the amount of water soluble SO_4^{-2} higher than without addition of elemental sulfur.

In addition of 1%S, the amount of water soluble SO_4^{-2} were 8.2, 3.0, 3.7, 2.2, and 3.9 g/kg after 0, 10, 20, 40 and 80 days, respectively. It can be seen that the sulfate amount decreased from 8.2 g/kg at 0 day to 3.0 g/kg after 10 days then increased to 3.7 after 20 days but decreased again to 2.2 after 40 days. Then, it increased again after 80 days. Whereas, the amount of water soluble SO_4^{-2} in samples without addition of elemental sulfur, which were less than 1%S, were 8.2, 0.2, 0.4, 0.2 and 0.2 g/kg after 0, 10, 20, 40 and 80 days, respectively. It can be seen that the amount of sulfate reduced from 8.2 g/kg at 0 day to 0.2 g/kg after 10 days then increased to 0.4 g/kg after 20 days but decreased again to 0.2 g/kg after 40 days and remained at 0.2 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 2% S, the amount of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 3.4 g/kg after 10 days then increased to 4.5 g/kg after 20 days but decreased again to 2.5 g/kg after 40 days. Then, it decreased again to 3.3 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 3% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 3.4 g/kg after 10 days then increased to 5.2 g/kg after 20 days but decreased again to 2.8 g/kg after 40 days. Then, it increased again to 3.2 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

It can be observed that the high amount of initial water soluble SO_4^{-2} in all samples was due to addition of organic manure (1%) which had 8.17 g/kg water soluble SO_4^{-2} and sand which had 0.03 g/kg water soluble SO_4^{-2}. Also the presence of water soluble SO_4^{-2} was due to sulfur oxidation which was found mainly in the added organic manure (1%) and in the sand. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic manure, sand and $CaCO_3$ respectively. This initial amount was completely reduced after 10 days in samples without addition of elemental sulfur. Also there were variations of water soluble SO_4^{-2} between the time periods for samples treated by elemental sulfur. This could be attributed to: (1) neutralization of calcium carbonate by H_2SO_4 (Cifuentes and Lindeman, 1993) and formation of both gypsum [$CaSO_4.2H_2O$] and carbonic acid [[H_2CO_3]; (2) formation of calcium monosulfoaluminate (Mohamed and Antia, 1998; Mohamed 2003); and (3) sulfate reduction into hydrogen sulfide (H_2S) (Lecture 23, February 2001, Alken Murray Corp., March 2001, Potash & Phosphate Institute of Canada, March 2001).

The initial available sulfate in the irrigation water was completely consumed by the substrate as indicated from the results of the reference sample (0%S added). However, with the addition of sulfur, the available sulfate increased during the same period (10 days) due to possible formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it continued to increase from 10 to 20 days due to formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate. From 20 to 40 days, it decreased due to formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. From 40 to 80 days, it increased due to generation of sulfuric acid, carbonic acid and dissolution of calcite.

The experimental results of sulfate variations were further studied via the use of statistical analysis. The analysis of variance (One-way ANOVA) p- value was found to be 0.000 with 3 degrees of freedom, indicating that addition of sulfur has highly significance (P-value < 0.05) on the changes in sulfate value. Also there was a difference in the mean as shown in Table 4.3.

Table 4.3: One-way stacked ANOVA analysis for sulfate results of the basic mix design samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	0.2500	3.2000	3.4250	3.6500
StDiv	0.1000	0.7703	0.8221	1.0630

4.3.4 Mineral Formation:

To identify whether or not gypsum has been formed, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) analysis were utilized. For basic mix design all samples were examined by XRD analysis, after all time periods (5, 10, 20, 40 and 80 days). In all tested samples, the major mineral found was quartz. Also, the minor formed minerals were examined after 5, 10, 20 and 40 days. In all samples, calcite and plagioclase were found after 80 days. However, for basic mix design treated with 3%S with no addition of $CaCO_3$, calcite, plagioclase and gypsum were found. Also after 80 days, calcite, plagioclase and dolomite minerals were found in sample without addition of elemental sulfur. Calcite and plagioclase were found in basic mix design treated by 1 and 2% S as shown in Table 4.4.

The SEM results for basic mix design samples (1 – 4) after 20, 40 and 80 days are shown in Figures 4.5- to 4.7. Figures 4.5 (a) to (d) show the basic mix design images at magnification levels of X80, X3500, X1400, and X1200 after 20 days. Figures 4.6 (a) to (d) show the basic mix design images at magnification levels of X80, X2000, X3300, and X1500 after 40 days. Figures 4.7 (a) to (d) show the basic mix design images at magnification levels of X35, X1000, X500, and X1500 after 80 days. The major minerals are quartz and minor mineral are calcite and plagioclase. After 20 days, no clear gypsum was formed as shown from Figures 4.5 (a) to (d). Also, no gypsum was formed after 40 days as shown from Figures 4.6 (a) to (d). After 80 days, the micrographs shown in Figures 4.7 (a) to (d) indicate the formation of gypsum rods in basic mix design sample 4 (3%S), which is shown in Figure 4.7 (d).

Furthermore, the Energy Dispersive X-ray (EDX- 6587 Oxford) analysis was done for basic mix design sample 4 (3%S) to support the existence of minerals as shown in Figure 4.8.

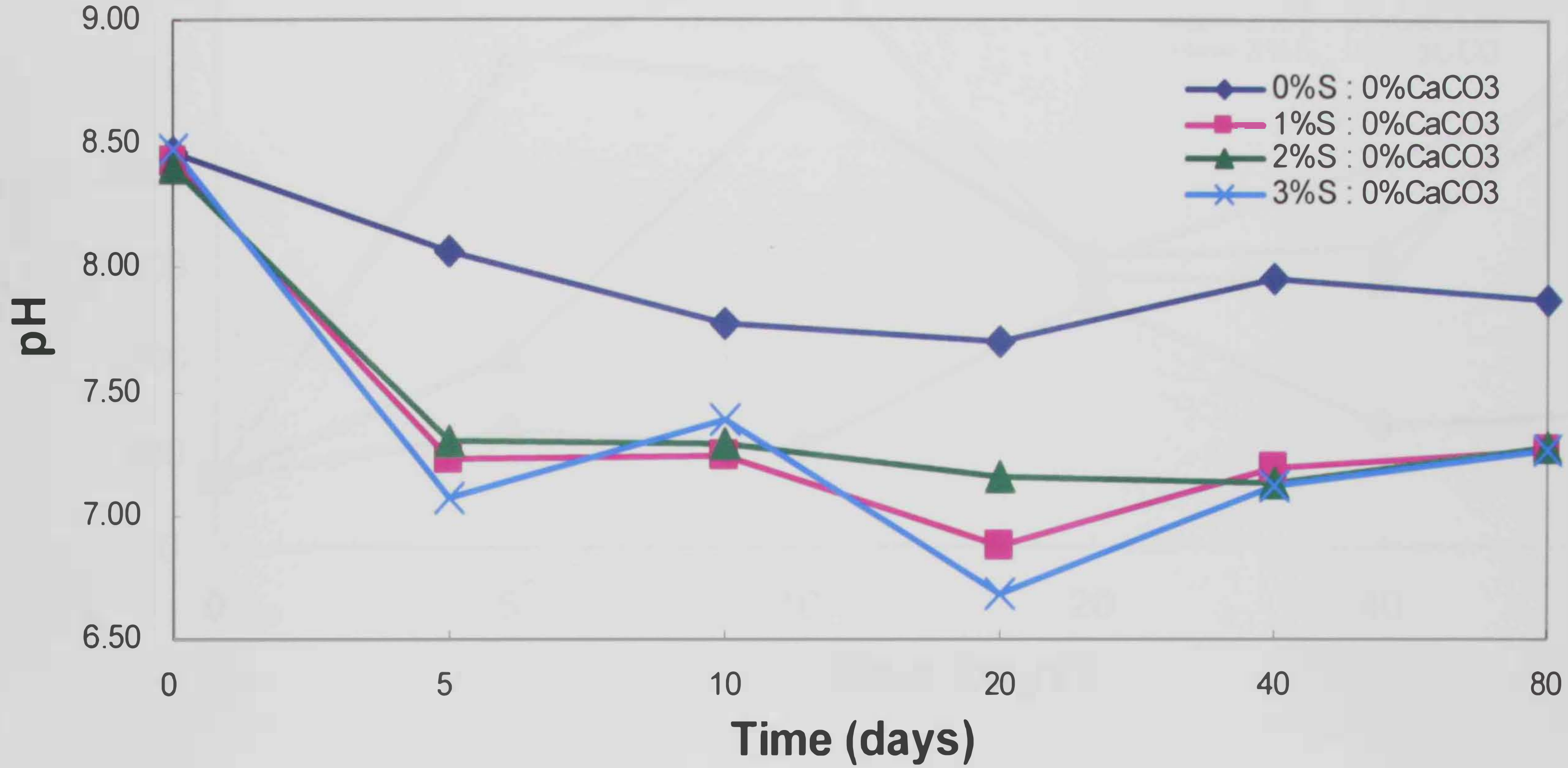


Figure 4.2: Variation of pH with Time and Amount of Added Elemental Sulfur for Basic Mix Design Samples (without addition of $CaCO_3$).

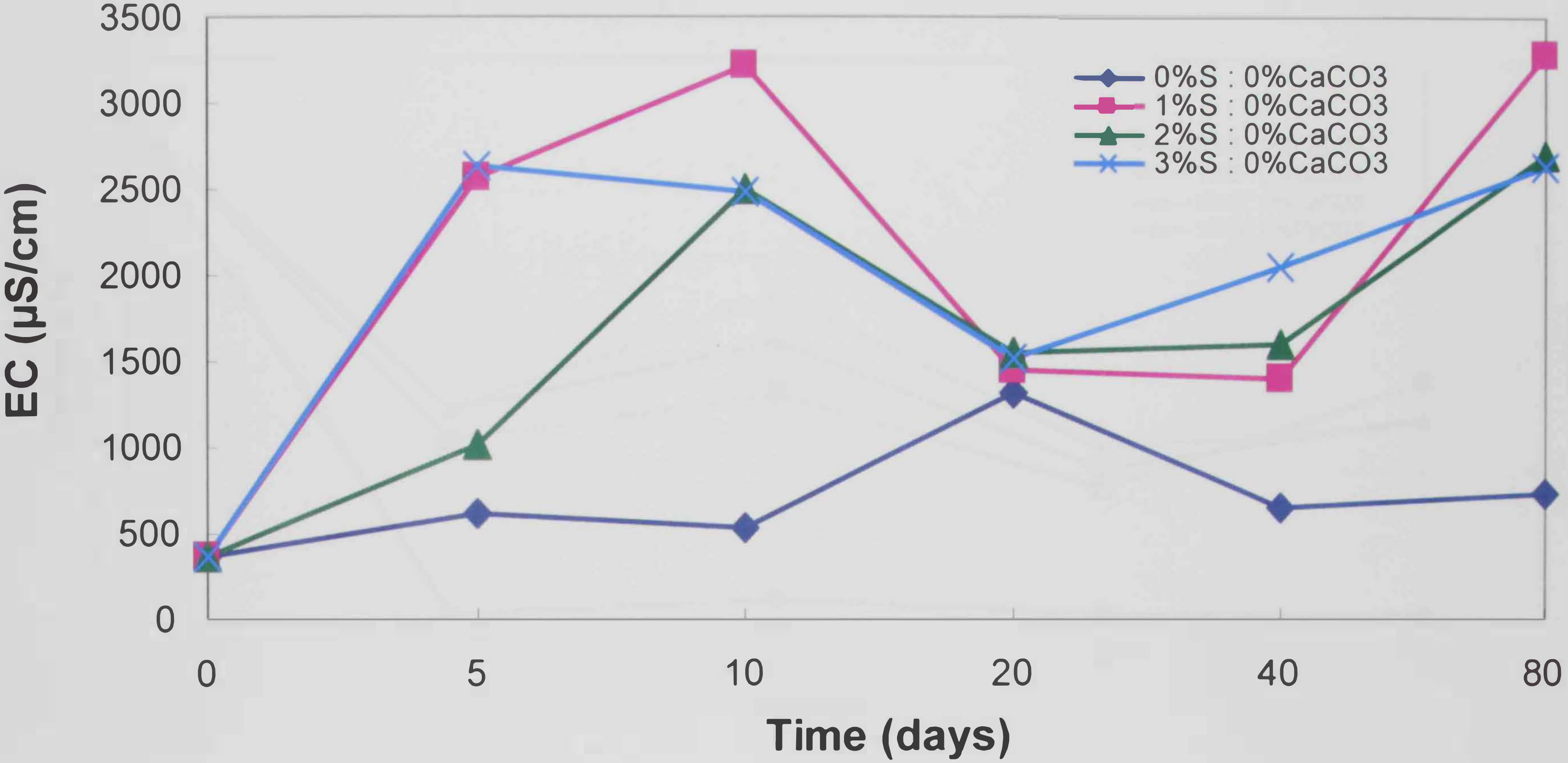


Figure 4.3: Variation of Electrical Conductivity (EC) with time and amount of added elemental sulfur for basic mix design samples (without addition of $CaCO_3$).

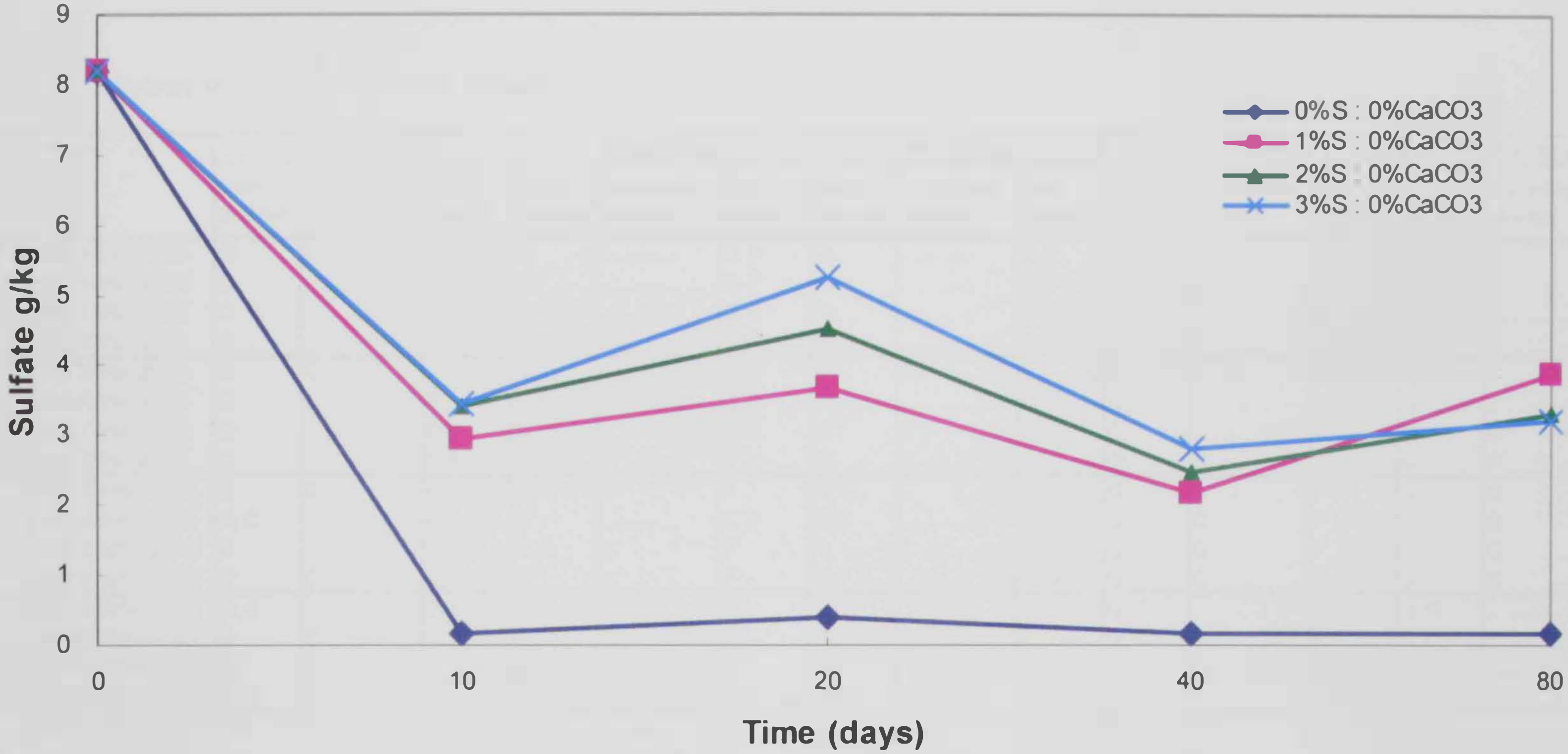
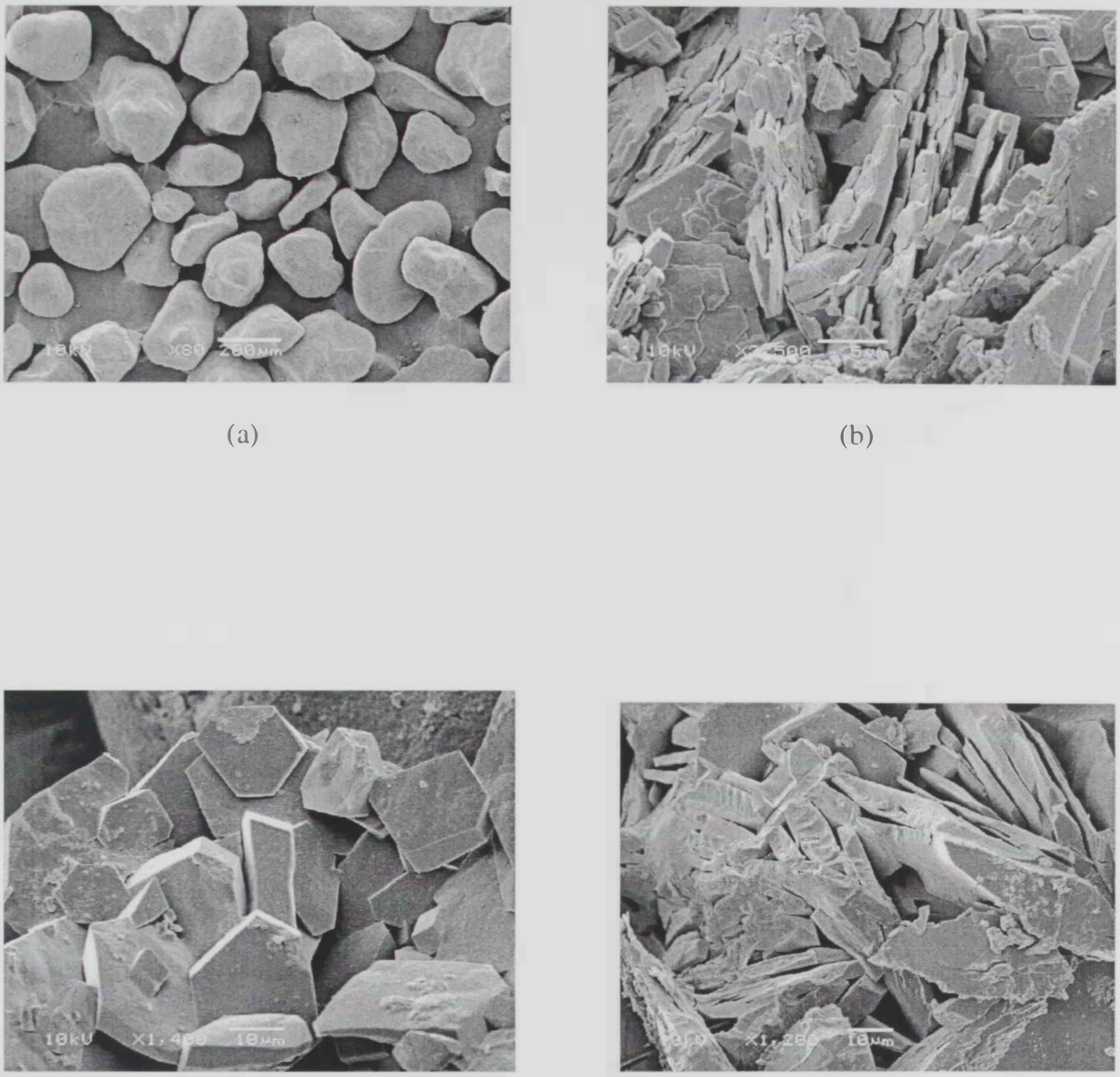


Figure 4.4: Variation of water soluble sulfate with time and amount of added elemental sulfur for basic mix design samples (without addition of $CaCO_3$).

Table 4.4: X-ray diffraction analysis for gypsum formation.

Sample No.	Design type	Sample	After 5 days			After 10 days			After 20 days			After 40 days			After 80 days		
			Major Minerals	Subordinate Minerals	Minor Minerals	Major Minerals	Subordinate Minerals	Minor Minerals	Major Minerals	Subordinate Minerals	Minor Minerals	Major Minerals	Subordinate Minerals	Minor Minerals	Major Minerals	Subordinate Minerals	Minor Minerals
1	basic	0%S X 0%CaCO3	Q	....	C, P	Q	....	C, P	Q	....	C, P	Q	....	P, C	Q	....	C, P, D
2	mix	1%S X 0%CaCO3	Q	....	C, P	Q	....	C, P	Q	....	C, P	Q	....	P, C	Q	....	C, P
3	Design	2%S X 0%CaCO3	Q	....	C, P	Q	....	C, P	Q	....	C, P	Q	....	C, P	Q	....	C, P
4		3%S X 0%CaCO3	Q	....	C, P	Q	....	C, P	Q	....	C, P	Q	....	C, P	Q	....	C, P, G
5	mix	0%S X 5%CaCO3	Q	C	P	Q	C	P	Q	C	P	Q	....	P, D	Q	....	C, P
6	Design	1%S X 5%CaCO3	Q	C	P	Q	....	C, P	Q	....	C, P	Q	....	P, C	Q	....	C, P
7	type I	2%S X 5%CaCO3	Q	....	C, P	Q	....	C, P	Q	C	P	Q	....	C, P	Q	C	P, D, G
8		3%S X 5%CaCO3	Q	....	C, P	Q	C	P	Q	C	P	Q	C	P, D	Q	P	C, G
9	mix	0%S X 10%CaCO3	Q	C	P	Q	C	P	Q	C	P	Q	C	P	Q	C	P
10	Design	1%S X 10%CaCO3	Q, C	....	P	Q	....	C, P	Q,C	....	P	Q	C	P	Q	C	P
11	type II	2%S X 10%CaCO3	Q	....	C, P	Q, C	C	P	Q	C	P	Q	C	P	Q	C	P
12		3%S X 10%CaCO3	Q	C	C, P	Q	C	P	Q,C	....	P, G	Q	C	P	Q	C	G , P
13	mix	0%S X 20%CaCO3	Q, C	....	C, P	Q, C	....	P	Q,C	....	P	Q, C	....	P	Q, C	....	P
14	Design	1%S X 20%CaCO3	Q	C	C, P	Q	C	P	Q,C	....	P	Q, C	....	P	Q, C	P	....
15	type III	2%S X 20%CaCO3	Q	C	C, P	Q, C	....	P	Q,C	....	P	Q, C	....	P	Q, C	....	....
16		3%S X 20%CaCO3	Q, C	....	C, P	Q, C	C	P	Q,C	....	P	Q, C	P	....	Q, C	....	P
17	mix	0%S X 30%CaCO3	Q, C	....	C, P	C, Q	....	P	Q,C	....	P	Q, C	....	P	Q, C	....	P
18	Design	1%S X 30%CaCO3	Q, C	....	C, P	Q, C	....	P	C, Q	....	P	Q, C	....	P	Q, C	....	P
19	type IV	2%S X 30%CaCO3	Q, C	....	C, P	Q, C	....	P	C, Q	....	P	Q, C	....	P	C, Q	....	....
20		3%S X 30%CaCO3	Q, C	....	C, P	C, Q	....	P	C, Q	....	P	Q, C	....	P	Q, C	....	....
21	mix	0%S X 40%CaCO3	Q, C	....	C, P	C, Q	....	P	C, Q	....	P	C, Q	....	P	C, Q	....	....
22	Design	1%S X 40%CaCO3	Q, C	....	C, P	C, Q	....	P	C, Q	....	P	C, Q	....	P	C, Q	....	P
23	type V	2%S X 40%CaCO3	Q, C	....	C, P	C, Q	....	P	C, Q	....	P	C, Q	....	P	C, Q	....	P
24		3%S X 40%CaCO3	Q, C	....	C, P	C, Q	....	P	C, Q	....	P	C, Q	....	P	C, Q	....	P

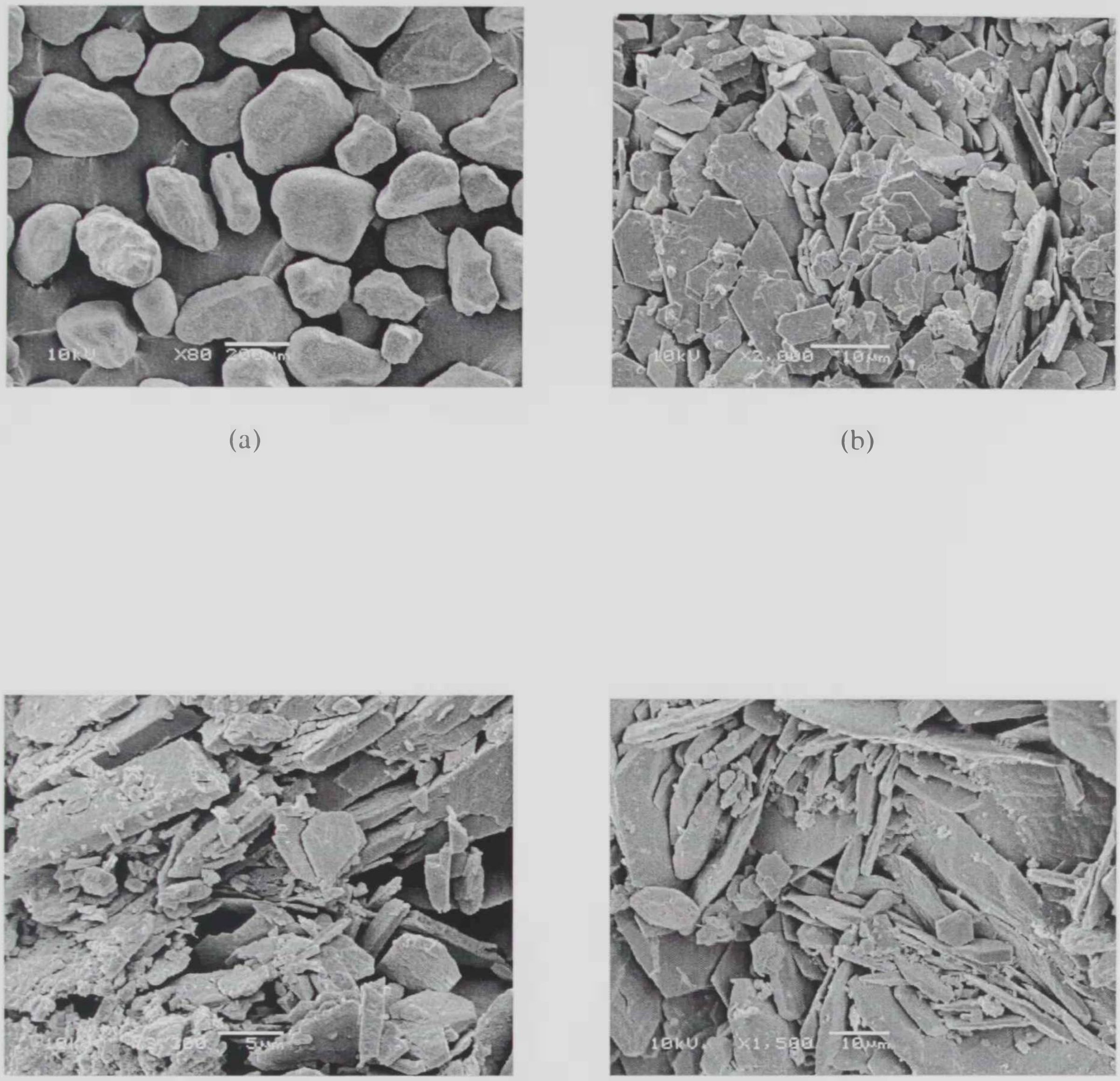
Q= Quartz, C= Calcite, D= Dolomite, G= Gypsum, P= Plagioclase



(a) (b)

(c) (d)

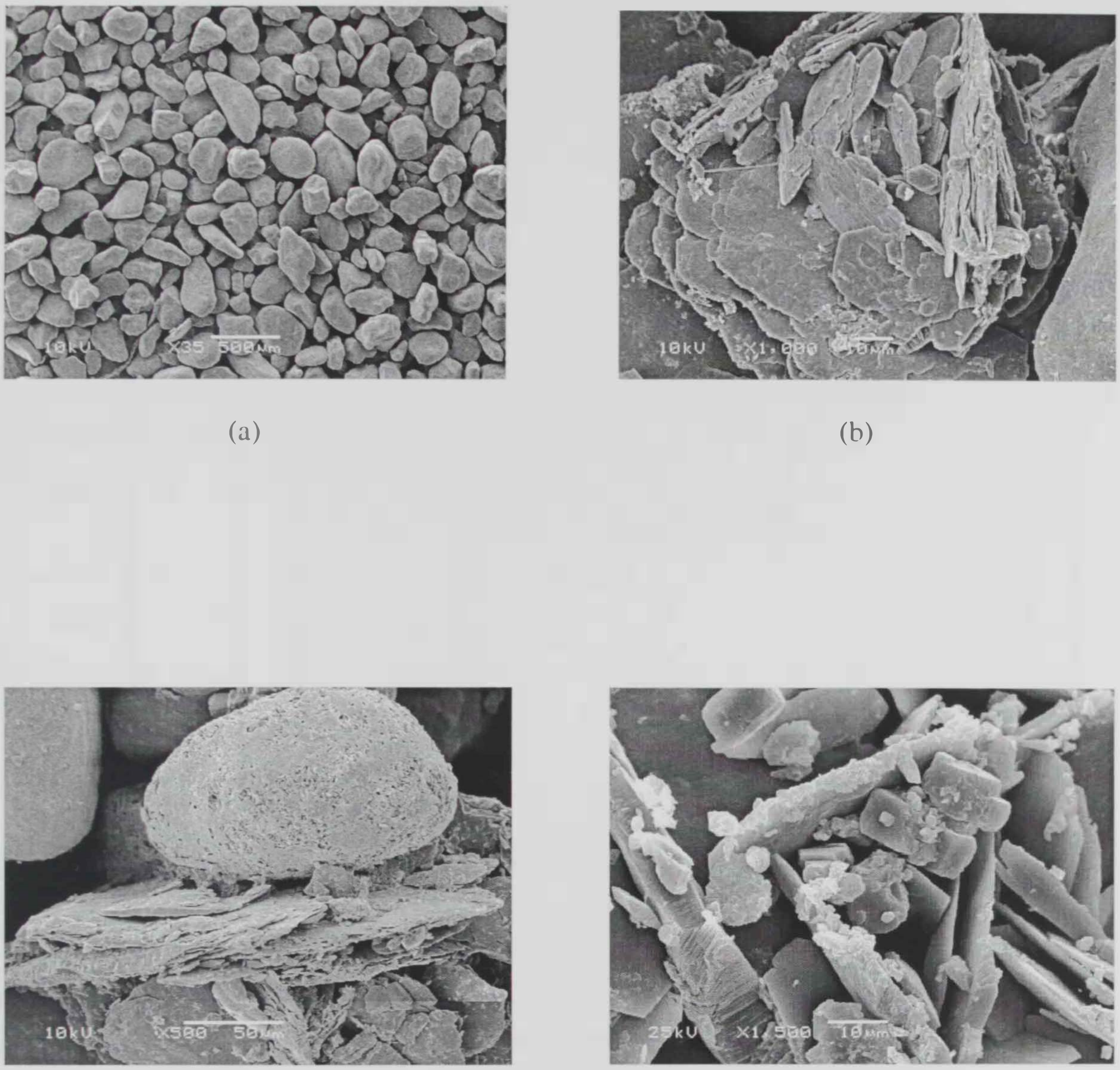
Figure 4.5: SEM micrograph for basic mix design samples after 20 days at different magnification levels and sulfur content: (a) X800: 0%S; (b) X3500: 1%S; (c) X1400: 2%S; (d) X1200: 3%S.



(a) (b)

(c) (d)

Figure 4.6: SEM micrograph for basic mix design samples after 40 days at different magnification levels and sulfur content: (a) X80: 0%S; (b) X2000: 1%S; (c) X3300: 2%S; (d) X1500: 3%S.



(a) (b)

(c) (d)

Figure 4.7: SEM micrograph for basic mix design samples after 80 days at different magnification levels and sulfur content: (a) X80: 0%S; (b) X2000: 1%S; (c) X3300: 2%S; (d) X1500: 3%S.

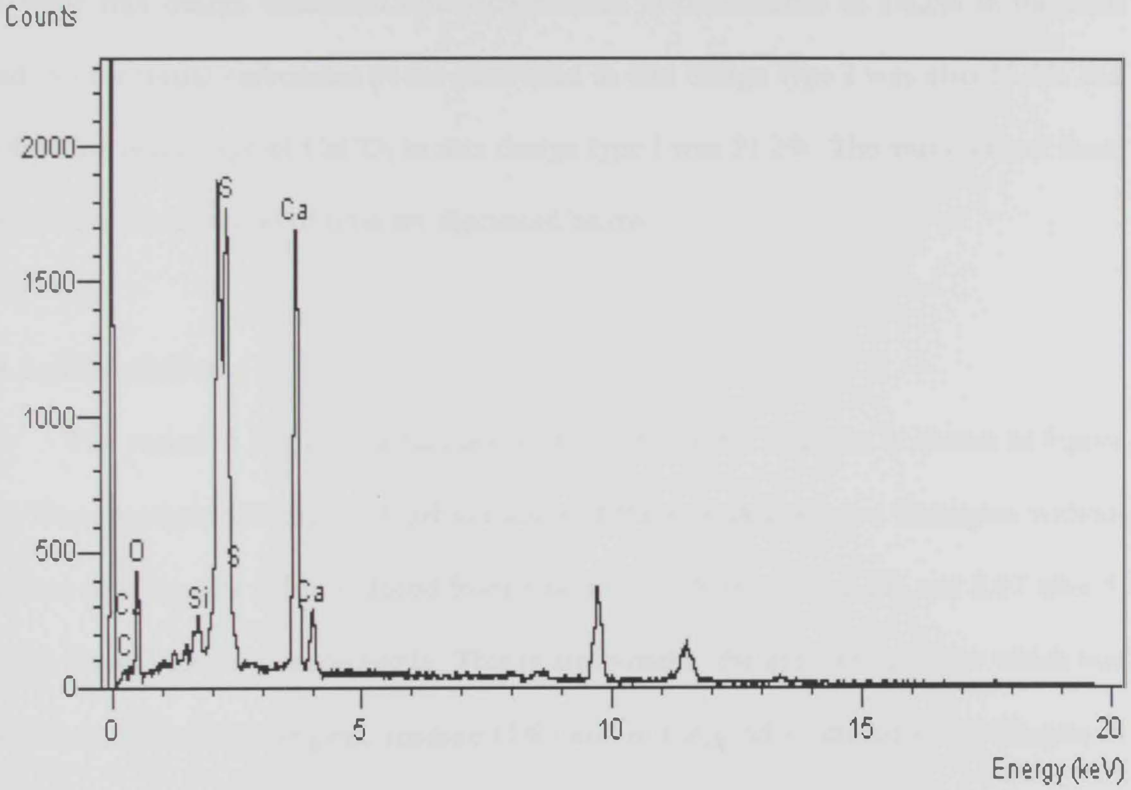


Figure 4.8: EDX graph for basic mix design sample 4 (3%S) after 80 days

4.4 EFFECT OF ELEMENTAL SULFUR APPLICATION ON MIX DESIGN TYPE I:

The effect of added elemental sulfur on mix design type I (with addition of 5% $CaCO_3$) was determined by measuring the pH levels, electrical conductivity (EC) in µS/cm and water soluble SO_4^{-2} (g/kg). It should be noted that, as previously discussed, the basic mix design contained initial carbonates in the amount of 16.2% in the used sand. So the initial carbonates in the sand used in mix design type I was also 16.2% and so the total percentage of $CaCO_3$ in mix design type I was 21.2%. The variations of these parameters as a function of time are discussed below.

4.4.1 pH Variation:

The variation of pH as a function of time and sulfur addition is shown in Figure 4.9. The experimental results of pH variation of the mix design type I samples without addition of elemental sulfur reduced from 8.66 to 8.02, 8.16, 8.07, 8.21, and 8.07 after 5, 10, 20, 40 and 80 days, respectively. This is attributed to the amount of sulfur which was found mainly in added organic manure (1%) and in the sand as discussed in Chapter 3. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic matter, sand and $CaCO_3$, respectively. This means that a pH reduction of approximately 0.59 units has been achieved after 5 days and pH continued to decrease until 80 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite.

The results indicate that the addition of 1% S reduced the pH level from 8.68 to 7.62, 7.44, 7.11, 7.44 and 7.26 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.06 units has been achieved after 5 days and pH continued to decrease until 20 days due to formation sulfuric acid, carbonic acid and dissolution of calcite. The increase of pH after 40 days could be attributed to the formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. After 80 days, pH decreased again due to formation of tricalcium aluminate (C_3A), tricalcium aluminate hydrate (C_3AH_6), tetracalcium aluminate hydrate (C_4AH_{13}) and calcium monosulfoaluminate.

The addition of 2% S reduced the pH level from 8.64 to 7.16, 7.47, 7.19, 7.40 and 7.35 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.48 units has been achieved after 5 days and pH continued to decrease until 40 days.

The addition of 3% S reduced the pH level from 8.65 to 7.69, 7.45, 7.30, 7.26 and 7.34 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 0.96 units has been achieved after 5 days and pH continued to decrease until 40 days.

Based on both the possible chemical reactions discussed previously as well as results, the pH first reduced because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it increased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it decreased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate.

The experimental results of pH variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.097 with 3 degrees of freedom, indicating that addition of sulfur has no

significance (P-value > 0.05) on the changes in pH value. Also there was a little difference in the mean as shown in Table 4.5.

Table 4.5: One – way stacked ANOVA analysis for pH results for mix design type I samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	8.1983	7.5967	7.5350	7.6156
StDiv	0.2364	0.5575	0.5545	0.5301

4.4.2 Electrical Conductivity (EC) Variation:

The variation of EC as a function of time and sulfur addition is shown in Figure 4.10. The EC of the mix design type I samples without addition of elemental sulfur increased from 348 to 522 μS/cm after 5 days then decreased to 423 and 310 μS/cm after 10 and 20 days, respectively. Then it increased to 339 and 600 μS/cm after 40 and 80 days, respectively. This can be attributed to: (1) the amount of organic manure that the mix design type I sample contains (1%); (2) the amount of total sulfur measured as sulfate that the organic manure contains 9409 mg/kg, and (3) the amount of total sulfur measured as sulfate of 326, 0.4 mg/kg in sand and $CaCO_3$, respectively. Due to sulfur oxidation, pH decreased and the amount of soluble ions increased leading to an increase of EC.

The results indicate that the addition of 1%S increased EC from 341 to 2070, 1988, 1330, 1300 and 2550 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 1729 μS/cm has been achieved after 5 days and EC then decreased after 10, 20, 40 days, but increased after 80 days.

Also the addition of 2%S increased EC from 347 to 3090, 2470, 1226, 1730 and 2630 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 2743 μS/cm has been achieved after 5 days and EC then decreased after 10, 20 and 40 days but increased after 80 days.

The addition of 3% S also increased EC from 348 to 1261, 2410, 1178, 1460 and 2650 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 913 and 2062 μS/cm has been achieved after 5 and 10 days, respectively. The EC continued to increase after 10 days, then decreased after 20 and 40 days but increased after 80 days. The increase in soluble salts as measured by soil EC was due to dissolution of $CaCO_3$ by H_2SO_4 (Cifuentes and Lindeman, 1993).

Based on both the possible chemical reactions discussed previously as well as the experimental results, the EC first increased because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it decreased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it increased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate.

The experimental results of EC variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.005 with 3 degrees of freedom, indicating that addition of sulfur has highly significance ($P\text{-value} < 0.05$) on the changes in EC value. Also there was a difference in the mean as shown in Table 4.6.

Table 4.6: One-way stacked ANOVA analysis for EC results of the mix design type I samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	438.8	1475.0	2229.2	1791.8
StDiv	122.2	877.2	744.2	686.9

4.4.3 Oxidation of Elemental Sulfur:

Oxidation of elemental sulfur was evaluated based on the amount of measured water soluble sulfate. Therefore, Figure 4.11 shows the amount of water soluble sulfate as a function of time and amount of elemental sulfur added. Thus, the Figure indicates that the addition of 1% S, 2%S and 3%S kept the amount of water soluble SO_4^{-2} higher than without addition of elemental sulfur.

In addition of 1%S, the amount of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 2.4 g/kg after 10 days then increased to 2.8 g/kg after 20 days but decreased again to 1.5 g/kg after 40 days then increased again to 2.6 g/kg after 80 days. Whereas, the amount of water soluble SO_4^{-2} in samples without addition of elemental sulfur decreased from 8.2 g/kg at 0 day to 0.1 g/kg after 10 days then increased to 0.3 g/kg after 20 days but decreased again to 0.1 g/kg after 40 days then remained at 0.1 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 2%S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 2.9 g/kg after 10 days then increased to 3.3 g/kg after 20 days but decreased again to 2.1 g/kg after 40 days then increased again to 3.1 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 3% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 at 0 days to 3.4 g/kg after 10 days then increased to 5.2 g/kg after 20 days but decreased again to 2.8 g/kg after 40 days. Then, it increased again to 3.2 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

It can be observed that the high amount of initial water soluble SO_4^{-2} in all samples was due to addition of organic manure (1%) which had 8.17 g/kg water soluble SO_4^{-2} and sand which had 0.03 g/kg water soluble SO_4^{-2}. Also the presence of water soluble SO_4^{-2} was due to sulfur oxidation which was found mainly in the added organic manure (1%) and in the sand. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic manure, sand and $CaCO_3$ respectively. This initial amount was completely reduced after 10 days in samples without addition of elemental sulfur. Also there were variations of water soluble SO_4^{-2} between the time periods for samples treated by elemental sulfur. This could be attributed to: (1) neutralization of calcium carbonate by H_2SO_4 (Cifuentes and Lindeman, 1993) and formation of both gypsum [$CaSO_4.2H_2O$] and carbonic acid [[H_2CO_3]; (2) formation of calcium monosulfoaluminate (Mohamed

and Antia, 1998; Mohamed 2003); and (3) sulfate reduction into hydrogen sulfide (H_2S) (Lecture 23, February 2001, Alken Murray Corp., March 2001, Potash & Phosphate Institute of Canada, March 2001).

The initial available sulfate in the irrigation water was completely consumed by the substrate as indicated from the results of the reference sample (0%S added). However, with the addition of sulfur, the available sulfate increased during the same period (10 days) due to possible formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it continued to increase from 10 to 20 days due to formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate. From 20 to 40 days, it decreased due to formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. From 40 to 80 days, it increased due to generation of sulfuric acid, carbonic acid and dissolution of calcite.

The experimental results of sulfate variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.000 with 3 degrees of freedom, indicating that addition of sulfur has highly significance (P-value < 0.05) on the changes in sulfate value. Also there was a difference in the mean as shown in Table 4.7.

Table 4.7: One-way stacked ANOVA analysis for sulfate results of the mix design type I samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	0.1500	2.3250	2.8500	2.9500
StDiv	0.1000	0.5737	0.5260	0.8185

4.4.4 Mineral Formation:

To identify whether or not gypsum has been formed, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) analysis were utilized. For mix design type I all samples were examined by XRD analysis, after all time periods (5, 10, 20, 40 and 80 days). In all tested samples, the major mineral found was quartz. Also the minor formed minerals were examined after 5, 10, 20 and 40 days. In all samples, calcite and plagioclase were found after 5, 10, 20 days but after 40 days dolomite was found. After 80 days, for mix design type I treated with 2 and 2% S, calcite, plagioclase, dolomite and gypsum were found as shown in Table 4.4.

The SEM results for mix design type I samples (5 – 8) after 20, 40 and 80 days are shown in Figures 4.12- 4.14. Figures 4.12 (a) to (d) show the mix design type I images at magnification levels of X2300, X1500, X2000, and X1500 after 20 days. Figures 4.13 (a) to (d) show the mix design type I images at magnification levels of X1800, X1600, X2200, and X1800 after 40 days. Figures 4.14 (a) to (d) show the mix design type I images at magnification levels of X35, X2500, X3300, and X5000 after 80 days. The major minerals are quartz and minor mineral are calcite and plagioclase. After 20 days, no clear gypsum was formed as shown from Figures 4.12 (a) to (d). Also, no gypsum was formed after 40 days as shown from Figures 4.13 (a) to (d). After 80 days, the micrographs shown in Figures 4.14 (a) to (d) indicate the formation of gypsum rods in mix design type I samples 7 (2%S) and 8 (3%S), which are shown in Figures 4.14 (c) and (d).

Furthermore, the Energy Dispersive X-ray (EDX) analysis was done for mix design type I samples 7 and 8 after 80 days to support the existence of minerals as shown in Figures 4.15 and 4.16, respectively.

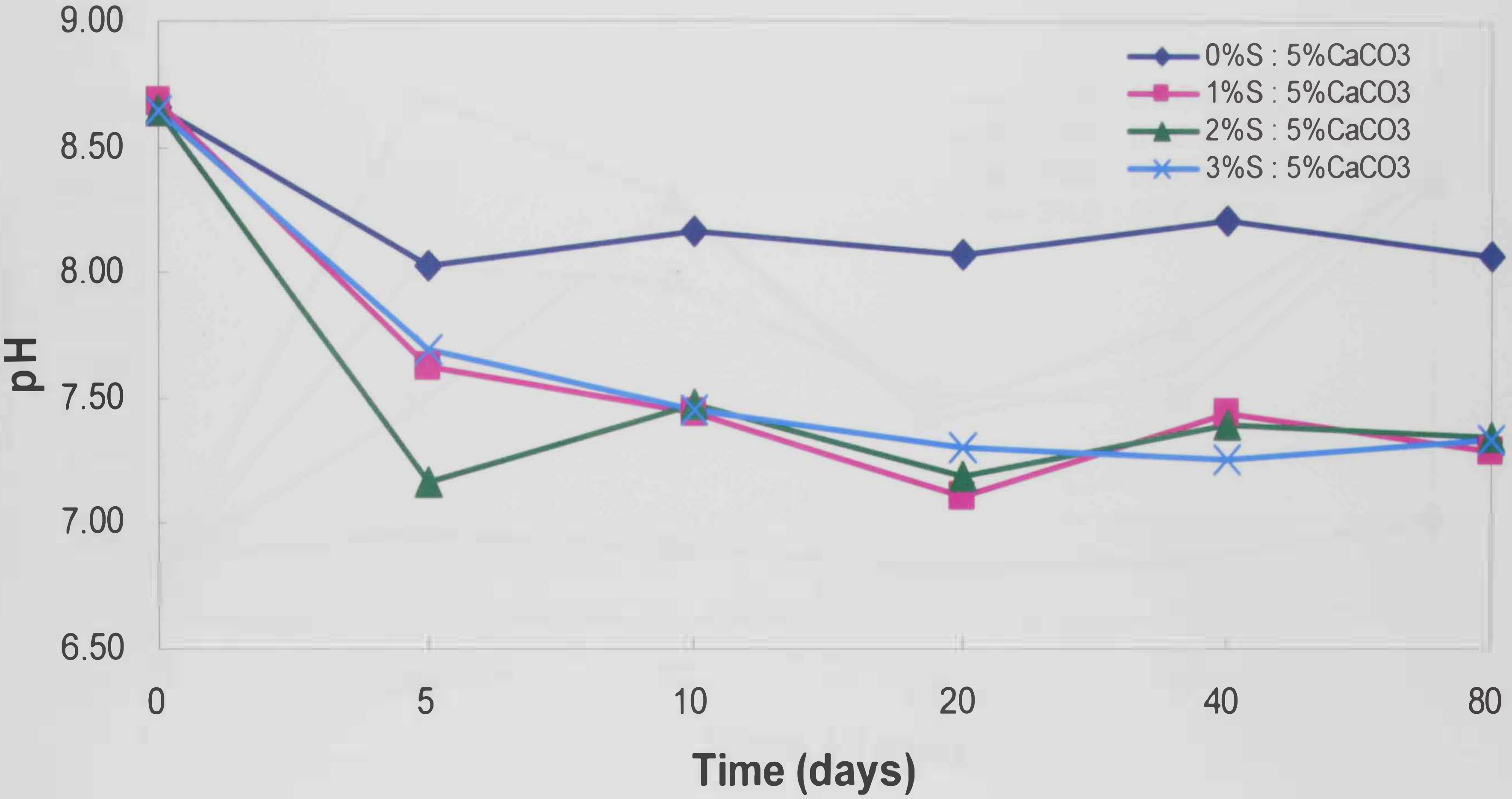


Figure 4.9: Variation of pH with time and amount of added elemental sulfur for mix design type I samples (with addition of 5% $CaCO_3$).

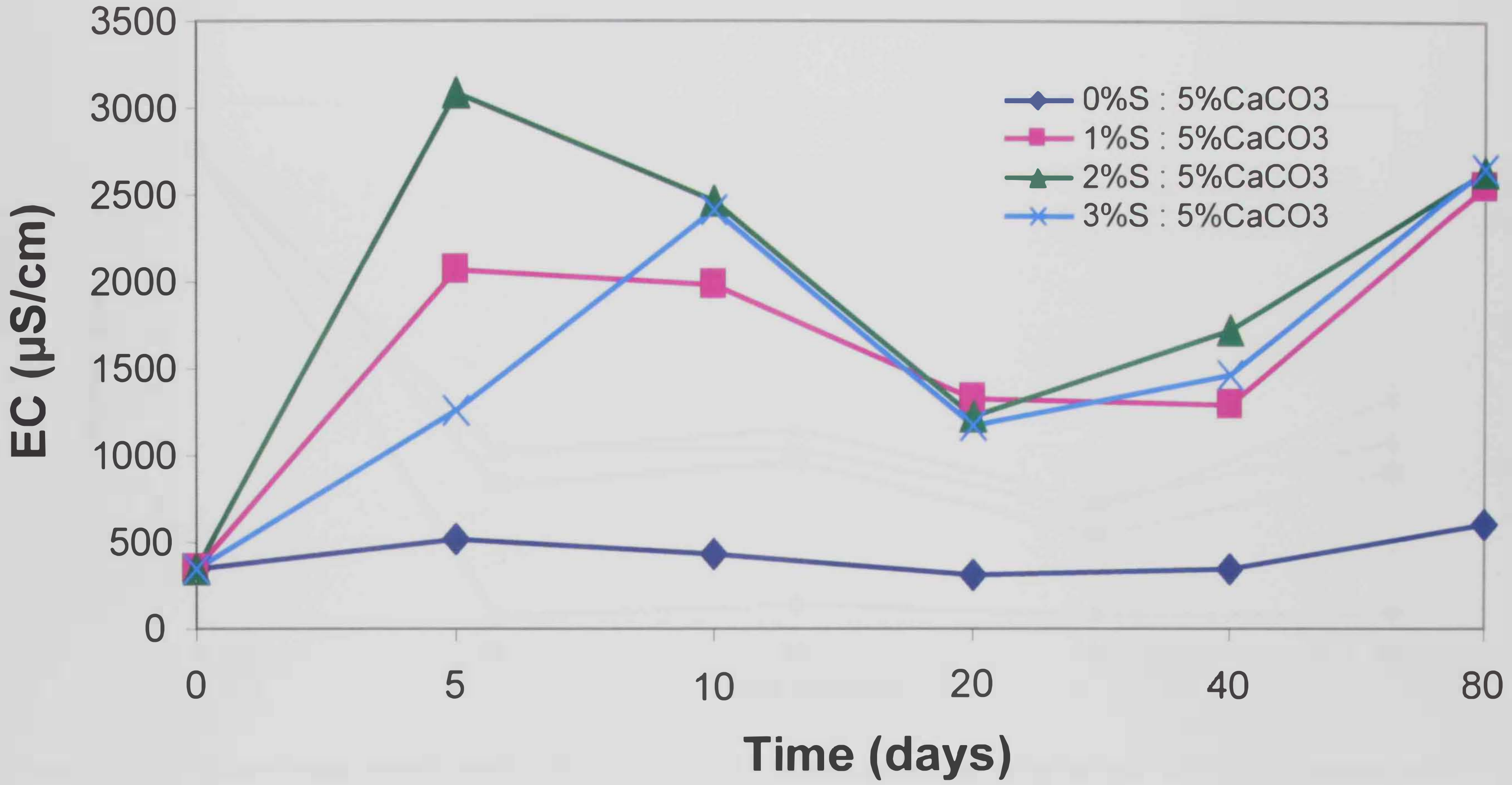


Figure 4.10: Variation of electrical conductivity (EC) with time and amount of added elemental sulfur for mix design type I samples (with addition of 5% $CaCO_3$).

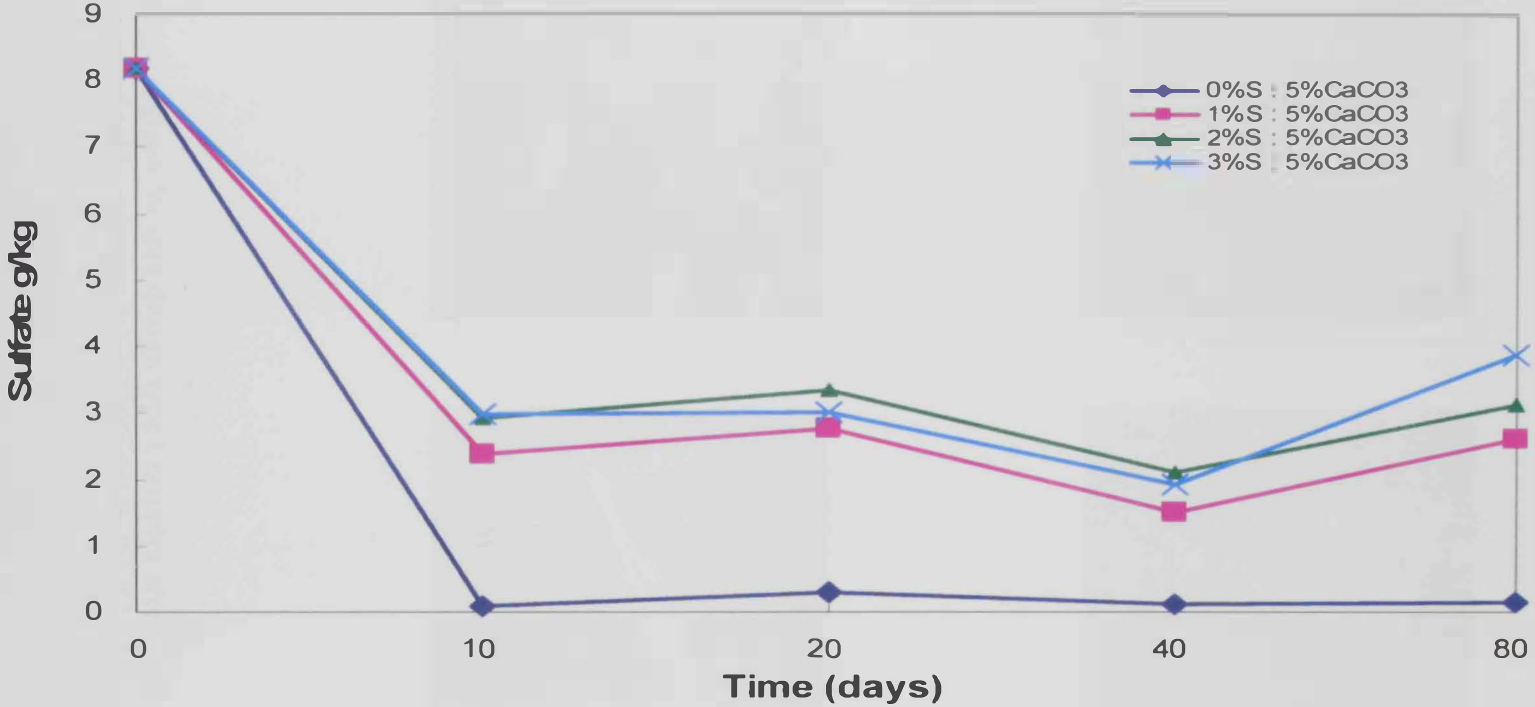
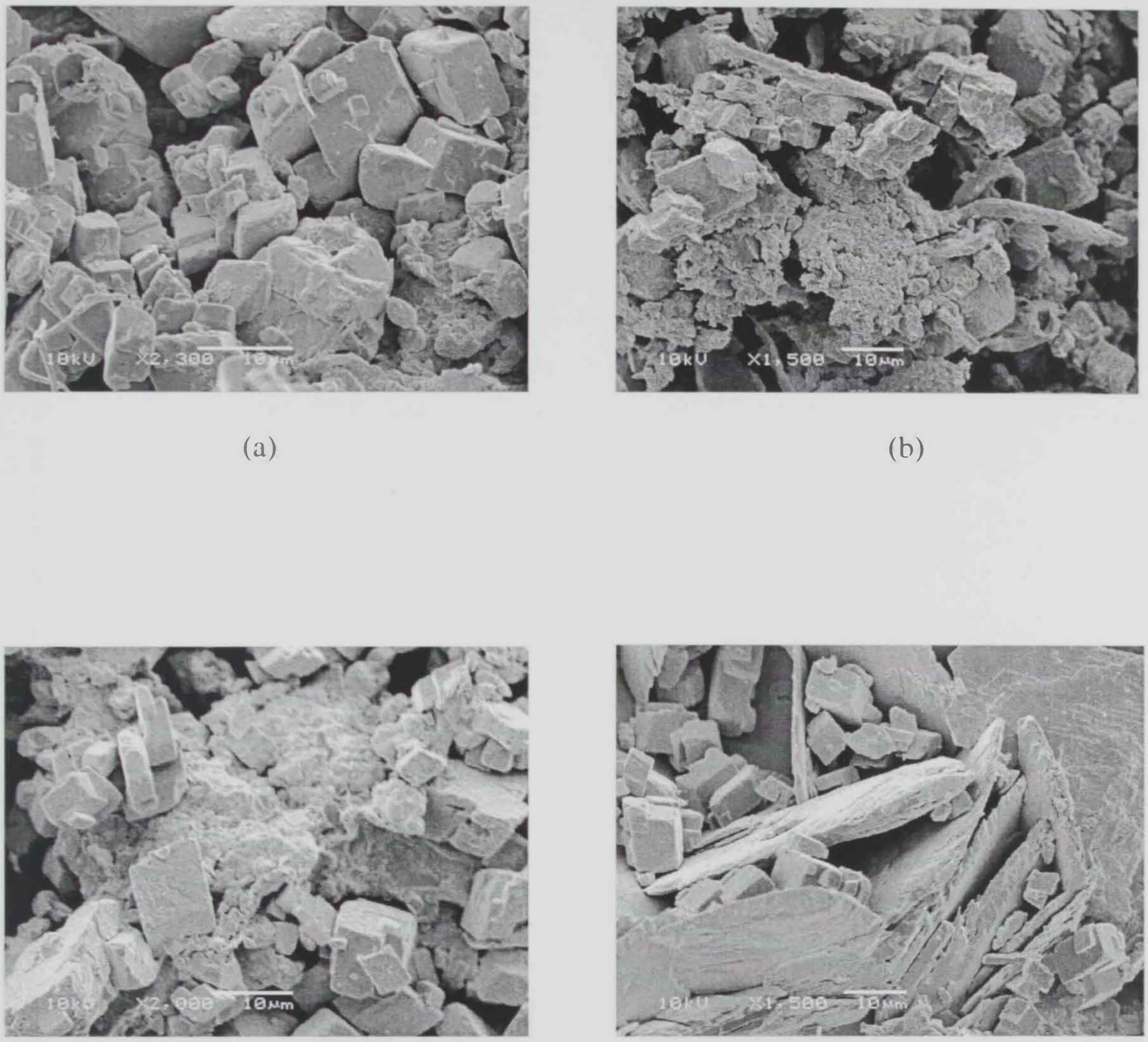


Figure 4.11: Variation of water soluble sulfate with time and amount of added elemental sulfur for mix design type 1 samples (with addition of 5% $CaCO_3$).



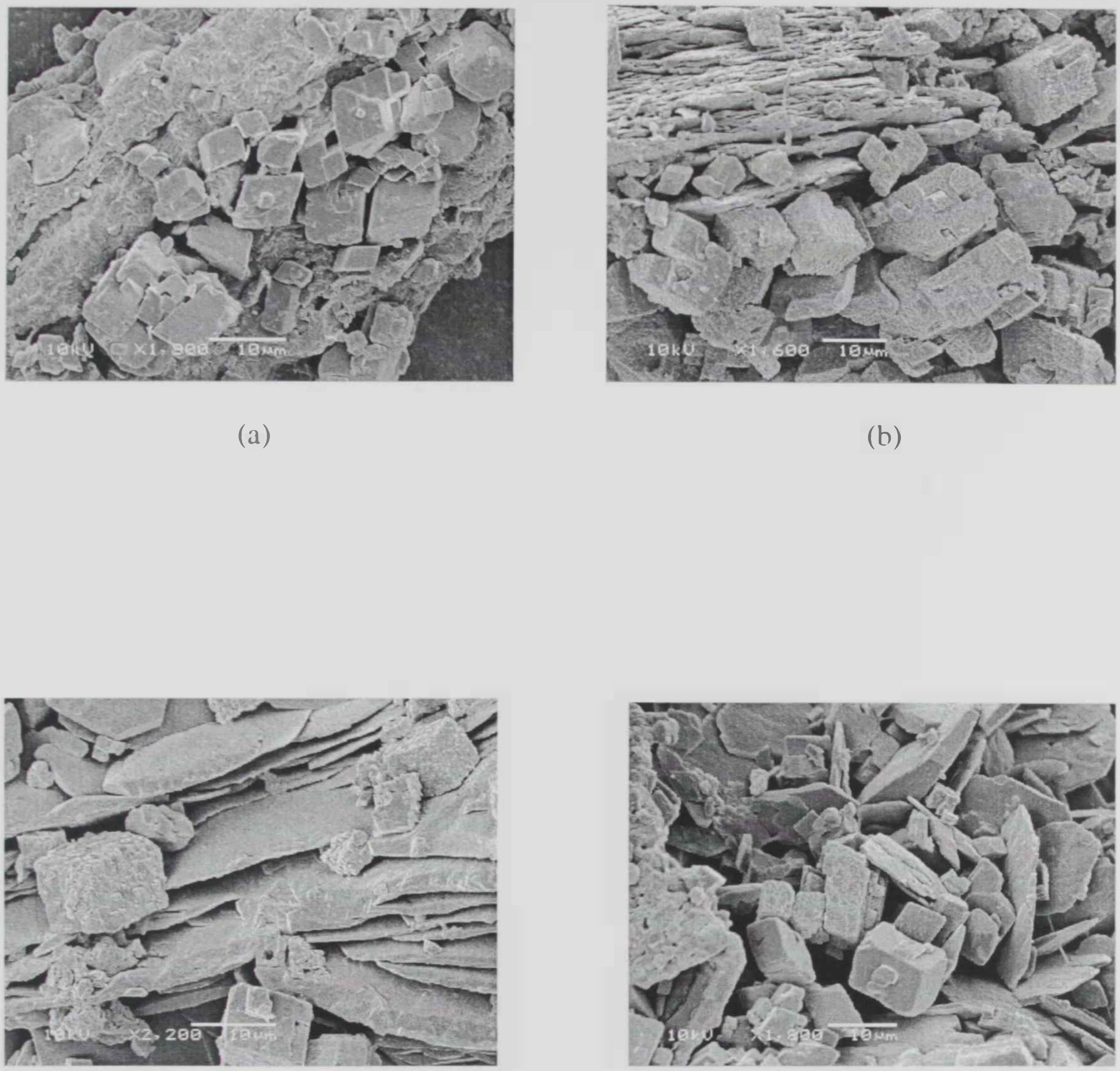
(a)

(b)

(c)

(d)

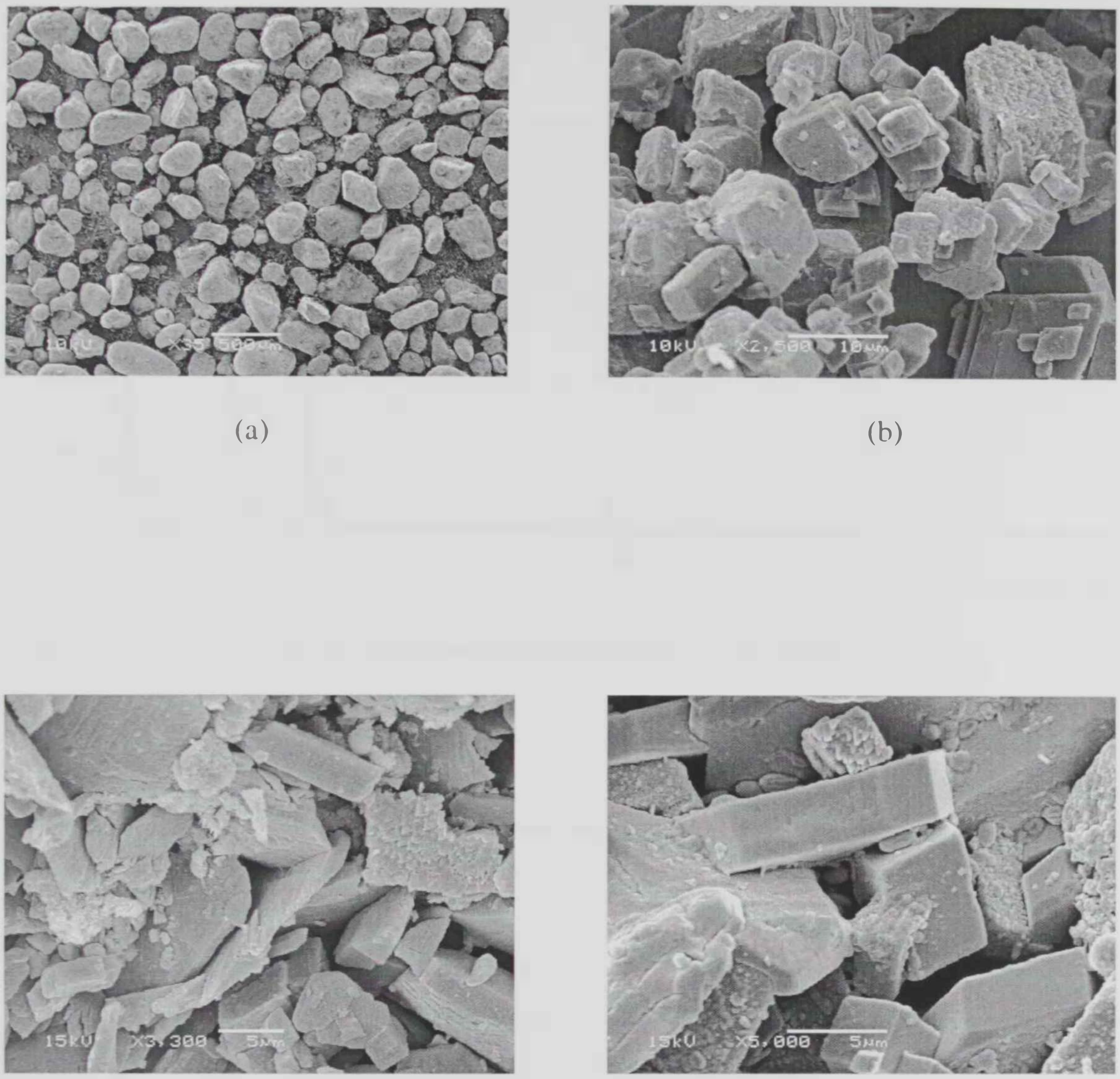
Figure 4.12: SEM micrograph for mix design type I samples after 20 days at different magnification levels and sulfur content: (a) X2300: 0%S; (b) X1500: 1%S; (c) X2000: 2%S; (d) X1500: 3%S.



(a) (b)

(c) (d)

Figure 4.13: SEM micrograph for mix design type I samples after 40 days at different magnification levels and sulfur content: (a) X1900: 0%S; (b) X1600: 1%S; (c) X2200: 2%S; (d) X1300: 3%S.



(a) (b)

(c) (d)

Figure 4.14: SEM micrograph for mix design type I samples after 80 days at different magnification levels and sulfur content: (a) X35: 0%S; (b) X2500: 1%S; (c) X3300: 2%S; (d) X5000: 3%S.

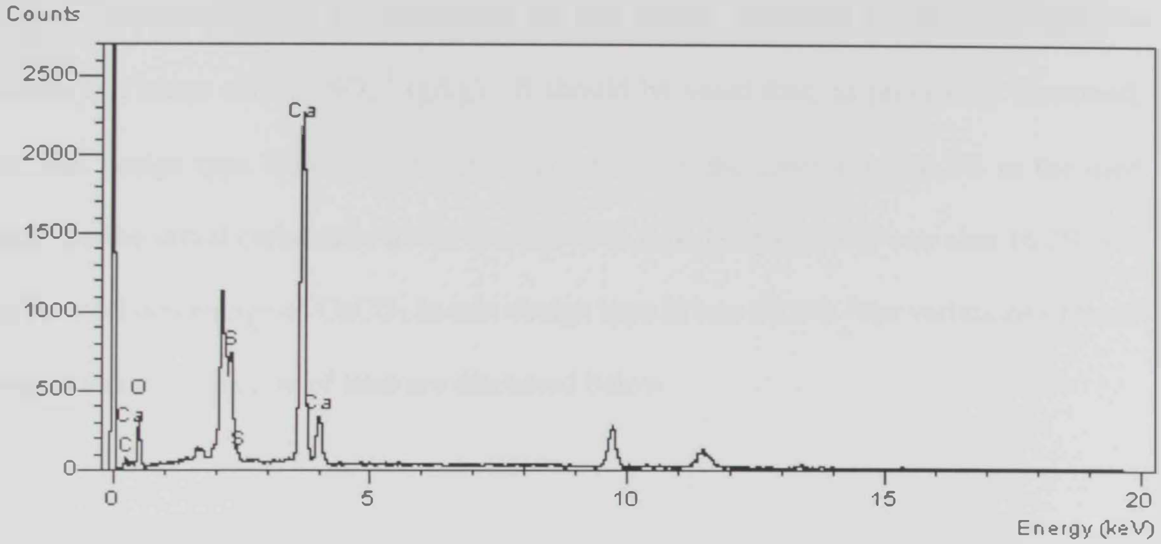


Figure 4.15: EDX graph for mix design type I sample 7 (2%S) after 80 days

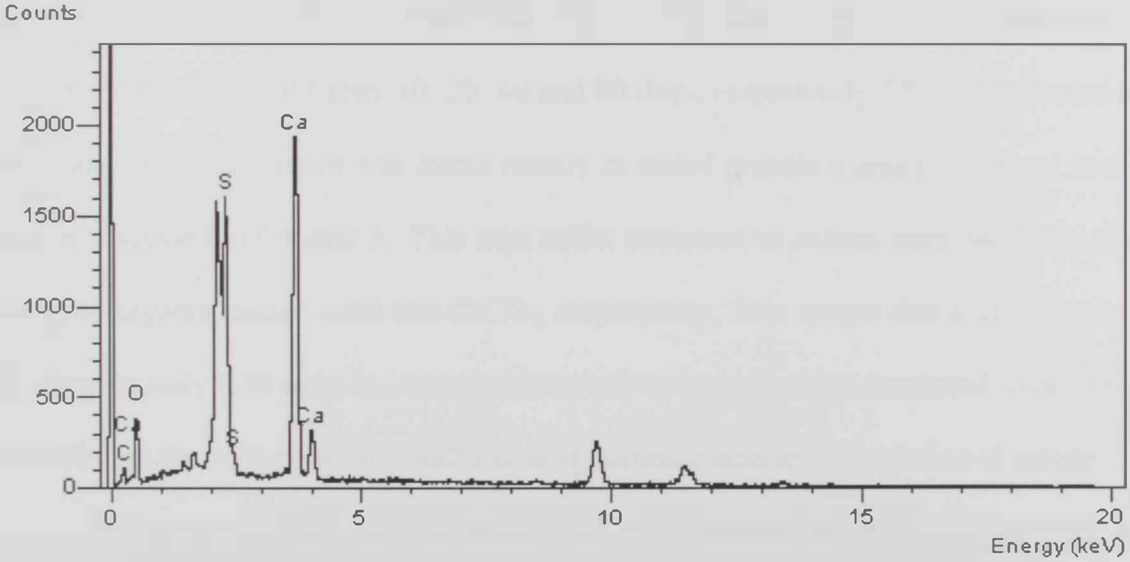


Figure 4.16: EDX graph for mix design type I sample 8 (3%S) after 80 days

4.5 EFFECT OF ELEMENTAL SULFUR APPLICATION ON MIX DESIGN TYPE II:

The effect of added elemental sulfur on mix design type II (with addition of 10% $CaCO_3$) was determined by measuring the pH levels, electrical conductivity (EC) in µS/cm and water soluble SO_4^{-2} (g/kg). It should be noted that, as previously discussed, the mix design type II contained initial carbonates in the amount of 16.2% in the used sand. So the initial carbonates in the sand used in mix design type II was also 16.2% and so the total percentage of $CaCO_3$ in mix design type II was 26.2%. The variations of these parameters as a function of time are discussed below.

4.5.1 pH Variation:

The variation of pH as a function of time and sulfur addition is shown in Figure 4.17. The experimental results of pH variation of the mix design type II samples without addition of elemental sulfur increased from 8.65 to 9.00 after 5 days but then reduced to 8.25, 8.35, 8.16 and 8.07 after 10, 20, 40 and 80 days, respectively. This is attributed to the amount of sulfur which was found mainly in added organic manure (1%) and in the sand as discussed in Chapter 3. This total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic matter, sand and $CaCO_3$, respectively. This means that a pH reduction of approximately 0.59 units has been achieved after 5 days and pH continued to decrease until 80 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite.

The results indicate that the addition of 1% S reduced the pH level from 8.65 to 7.51, 7.43, 7.38, 7.41 and 7.37 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.14 units has been achieved after 5 days and pH continued to decrease until 20 days due to formation sulfuric acid, carbonic acid and dissolution of calcite. The increase of pH after 40 days could be attributed to the formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. After 80 days, pH decreased again due to formation of tricalcium aluminate (C_3A), tricalcium aluminate hydrate (C_3AH_6), tetracalcium aluminate hydrate (C_4AH_{13}) and calcium monosulfoaluminate.

The addition of 2% S reduced the pH level from 8.66 to 7.45, 7.44, 7.47, 7.36 and 7.43 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.21 units has been achieved after 5 days and pH continued to decrease until 40 days.

The addition of 3% S reduced the pH level from 8.67 to 7.55, 7.41, 7.37, 7.26 and 7.40 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.12 units has been achieved after 5 days and pH continued to decrease until 40 days but increased after 80 days.

Based on both the possible chemical reactions discussed previously as well as the experimental results, the pH first reduced because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it increased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it decreased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of pH variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.020 with 3 degrees of freedom, indicating that addition of sulfur has highly significance (P-value < 0.05) on the changes in pH value. Also there was a little difference in the mean as shown in Table 4.8.

Table 4.8: One – way stacked ANOVA analysis for pH results of mix design type II samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	8.4133	7.6250	7.6350	7.6350
StDiv	0.3501	0.5046	0.5035	0.5109

4.5.2 Electrical Conductivity (EC) Variation:

The variation of EC as a function of time and sulfur addition is shown in Figure 4.18. The EC of the mix design type II samples without addition of elemental sulfur increased from 279 to 352 μS /cm after 5 days then decreased to 305 and 280 μS /cm after 10 and 20 days, respectively. Then it increased to 408 and 511 μS /cm after 40 and 80 days, respectively. This can be attributed to: (1) the amount of organic manure that the mix design type II sample contains (1%); (2) the amount of total sulfur measured as sulfate that the organic manure contains 9409 mg/kg, and (3) the amount of total sulfur measured as sulfate of 326, 0.4 mg/kg in sand and $CaCO_3$, respectively. Due to sulfur oxidation, pH decreased and the amount of soluble ions increased leading to an increase of EC.

The results indicate that the addition of 1%S increased EC from 275 to 1910, 2950, 1041, 1650 and 2570 μS /cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 1635 μS /cm has been achieved after 5 days and EC also increased by 2040 μS /cm after 10 days, but decreased after 20 and 40 days, then increased after 80 days.

Also the addition of 2%S increased EC from 276μS to 2860, 2220, 1100, 1670 and 2680 μS /cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 2584 μS /cm has been achieved after 5 days and EC then decreased after 10, 20 and 40 days but increased after 80 days.

The addition of 3% S also increased EC from 278 to 1564, 2980, 1114, 1880 and 2530 μS /cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 1286 and 2702 μS /cm has been achieved after 5 and 10 days, respectively. The EC then decreased after 20 days but increased after 40 and 80 days. The increase in soluble salts as measured by soil EC was due to dissolution of $CaCO_3$ by H_2SO_4 (Cifuentes and Lindeman, 1993).

Based on both the possible chemical reactions discussed previously as well as the experimental results, the EC first increased because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it decreased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it increased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of EC variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.001 with 3 degrees of freedom, indicating that addition of sulfur has highly

significance (P-value < 0.05) on the changes in EC value. Also there was a difference in the mean as shown in Table 4.9.

Table 4.9: One-way stacked ANOVA analysis for EC results of the mix design type II samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	371.2	2024.2	2106.0	2013.6
StDiv	92.2	754.1	726.8	746.6

4.5.3 Oxidation of Elemental Sulfur:

Oxidation of elemental sulfur was evaluated based on the amount of measured water soluble sulfate. Therefore, Figure 4.19 shows the amount of water soluble sulfate as a function of time and amount of elemental sulfur added. Thus, the Figure indicates that the addition of 1% S, 2%S and 3%S kept the amount of water soluble SO_4^{-2} higher than without addition of elemental sulfur.

In addition of 1%S, the amount of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 3.0, 2.5 and 2.4 g/kg after 10, 20 and 40 days, respectively. Then, it increased to 2.8 g/kg after 80 days. Whereas, the amount of water soluble SO_4^{-2} in samples without addition of elemental sulfur decreased from 8.2 g/kg at 0 day to 0.1 g/kg after 10 days and then remained constant at 0.1, 0.1 and 0.1 g/kg after 20, 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 2% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 2.9 and 2.1 after 10 and 20 days, respectively. Then, it increased to 2.2 and 3.1 g/kg after 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 3% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 3.3 and 2.6 g/kg after 10 and 20 days, respectively. Then, it increased to 3.0 and 4.1 g/kg after 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

It can be observed that the high amount of initial water soluble SO_4^{-2} in all samples was due to addition of organic manure (1%) which had 8.17 g/kg water soluble SO_4^{-2} and sand which had 0.03 g/kg water soluble SO_4^{-2}. Also the presence of water soluble SO_4^{-2} was due to sulfur oxidation which was found mainly in the added organic manure (1%) and in the sand. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic manure, sand and $CaCO_3$ respectively. This initial amount was completely reduced after 10 days in samples without addition of elemental sulfur. Also there were variations of water soluble SO_4^{-2} between the time periods for samples treated by elemental sulfur. This could be attributed to: (1) neutralization of calcium carbonate by H_2SO_4 (Cifuentes and Lindeman, 1993) and formation of both gypsum [$CaSO_4.2H_2O$] and carbonic acid [[H_2CO_3]; (2) formation of calcium monosulfoaluminate (Mohamed

and Antia, 1998; Mohamed 2003); and (3) sulfate reduction into hydrogen sulfide (H_2S) (Lecture 23, February 2001, Alken Murray Corp., March 2001, Potash & Phosphate Institute of Canada, March 2001).

The initial available sulfate in the irrigation water was completely consumed by the substrate as indicated from the results of the reference sample (0%S added). However, with the addition of sulfur, the available sulfate increased during the same period (10 days) due to possible formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it continued to increase from 10 to 20 days due to formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate. From 20 to 40 days, it decreased due to formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. From 40 to 80 days, it increased due to generation of sulfuric acid, carbonic acid and dissolution of calcite.

The experimental results of sulfate variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.000 with 3 degrees of freedom, indicating that addition of sulfur has highly significance (P-value < 0.05) on the changes in sulfate value. Also there was a difference in the mean as shown in Table 4.10.

Table 4.10: One-way stacked ANOVA analysis for sulfate results of the mix design type II samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	0.1000	2.6750	2.5500	3.2500
StDiv	0.0000	0.2754	0.4655	0.6351

4.5.4 Mineral Formation:

To identify whether or not gypsum has been formed, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) were utilized. For mix design type II all samples were examined by XRD analysis, after all time periods (5, 10, 20, 40 and 80 days). In all tested samples, the major mineral found was quartz and some calcite. Also the minor formed minerals were examined after 5, 10, 20 and 40 days. In all samples, plagioclase and calcite were found after 5 and 10 days. After 20, 40 and 80 days the minor mineral was plagioclase but gypsum was found samples treated with 3%S after 20 and 80 days as shown in Table 4.2.

The SEM results for mix design type II samples (9 – 12) after 20, 40 and 80 days are shown in Figures 4.20 to 4.22. Figures 4.20 (a) to (d) show the mix design type II images at magnification levels of X1600, X2500, X1900, and X1200 after 20 days. Figures 4.21 (a) to (d) show the mix design type II images at magnification levels of X2500, X1400, X2500, and X1500 after 40 days. Figures 4.22 (a) to (d) show the mix design type II images at magnification levels of X2300, X2000, X2500, and X4000 after 80 days. The major minerals are quartz and calcite and minor mineral is plagioclase. After 20 days, gypsum was formed in sample 12 (3%S) as shown from Figures 4.20 (a) to (d). No gypsum was formed after 40 days as shown from Figures 4.21 (a) to (d). After 80 days, the micrographs shown in Figures 4.22 (a) to (d) indicate the formation of gypsum rods in mix design type II sample 12 (3%S), which is shown in Figures 4.22 (d).

Furthermore, the Energy Dispersive X-ray (EDX) analysis was done for mix design type II samples 12 after 20 and 80 days to support the existence of minerals as shown in Figures 4.23 and 4.24, respectively.

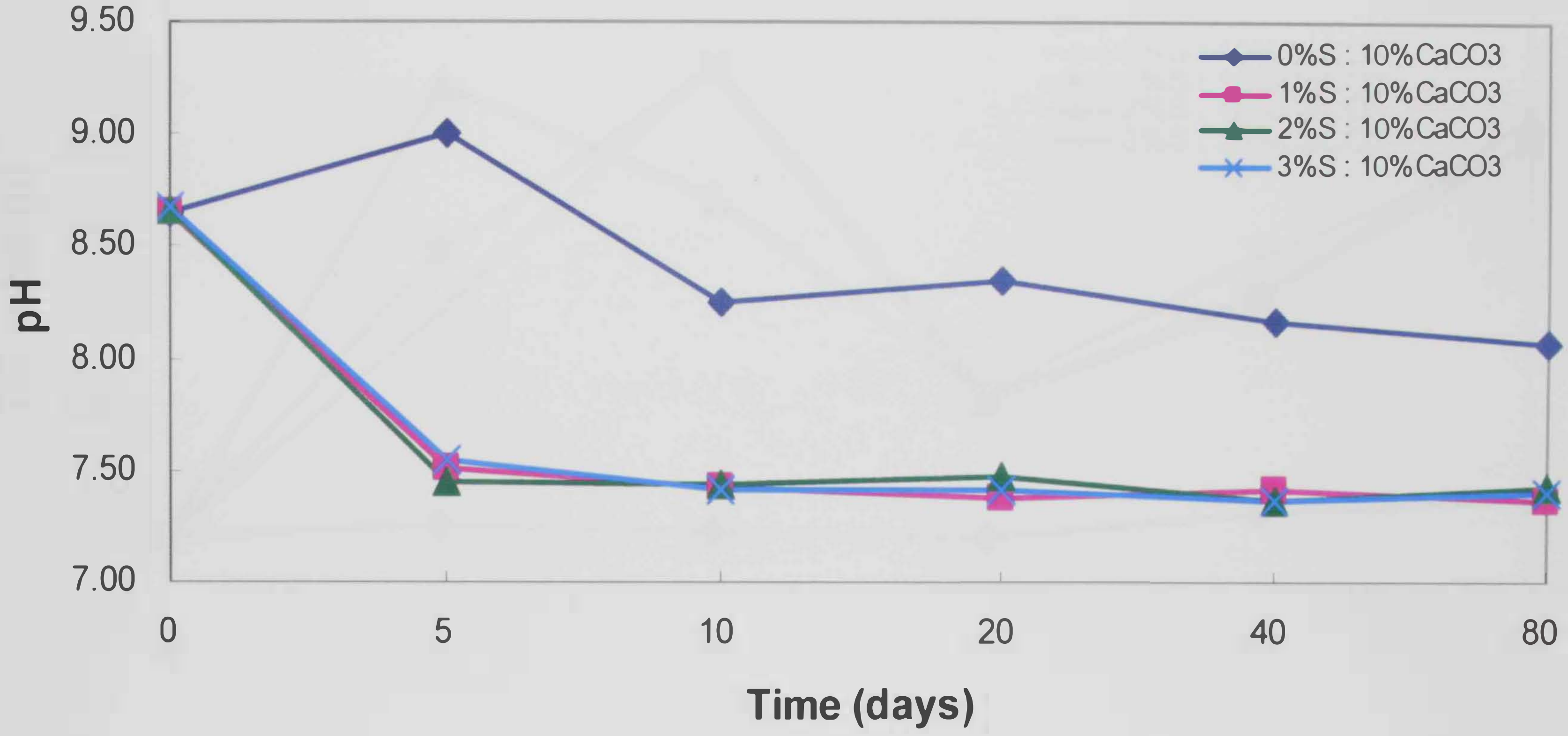


Figure 4.17: Variation of pH with time and amount of added elemental sulfur for mix design type II samples (with addition of 10% $CaCO_3$).

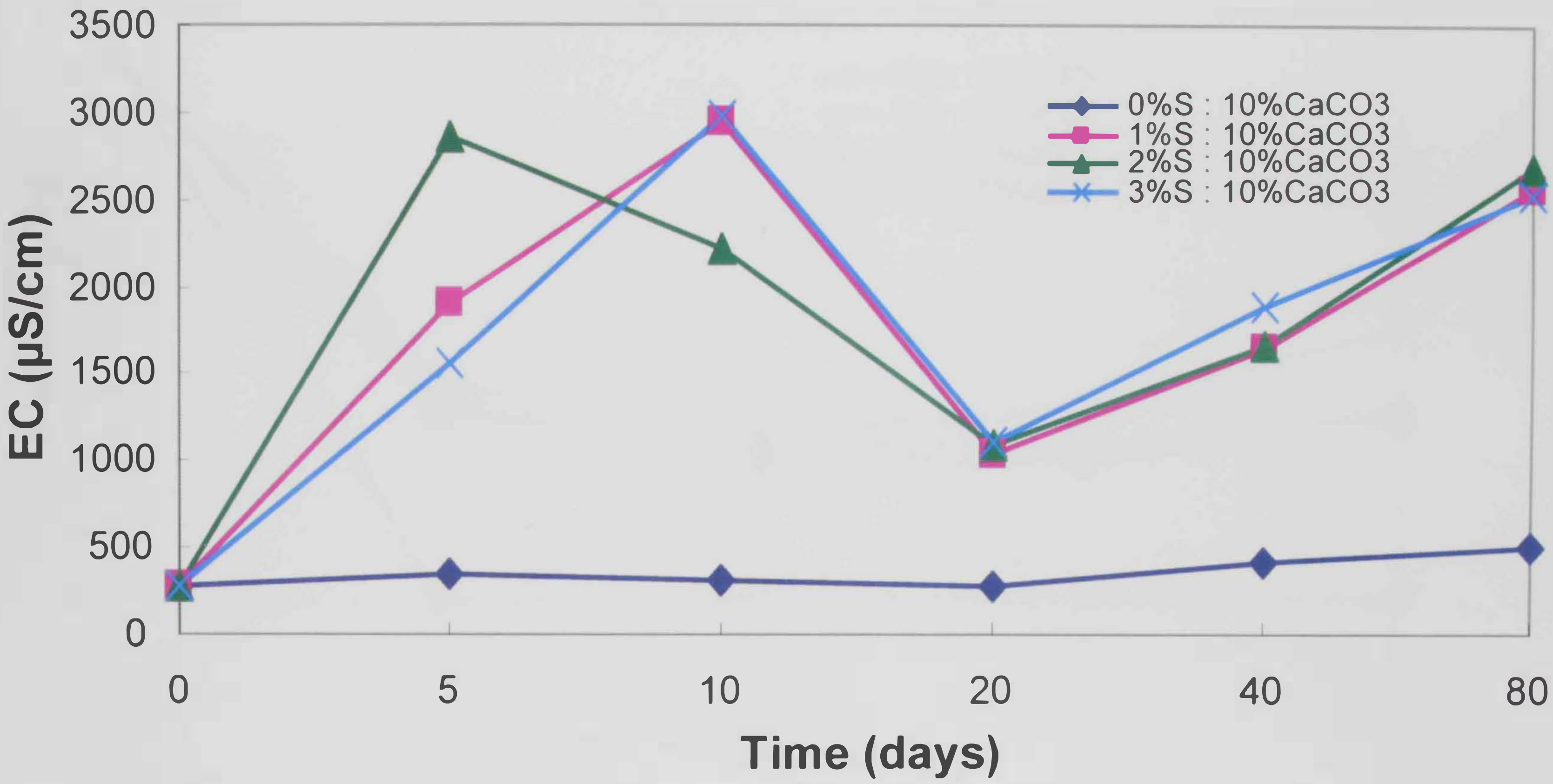


Figure 4.18: Variation of electrical conductivity (EC) with time and amount of added elemental sulfur for mix design type II samples (with addition of 10% $CaCO_3$).

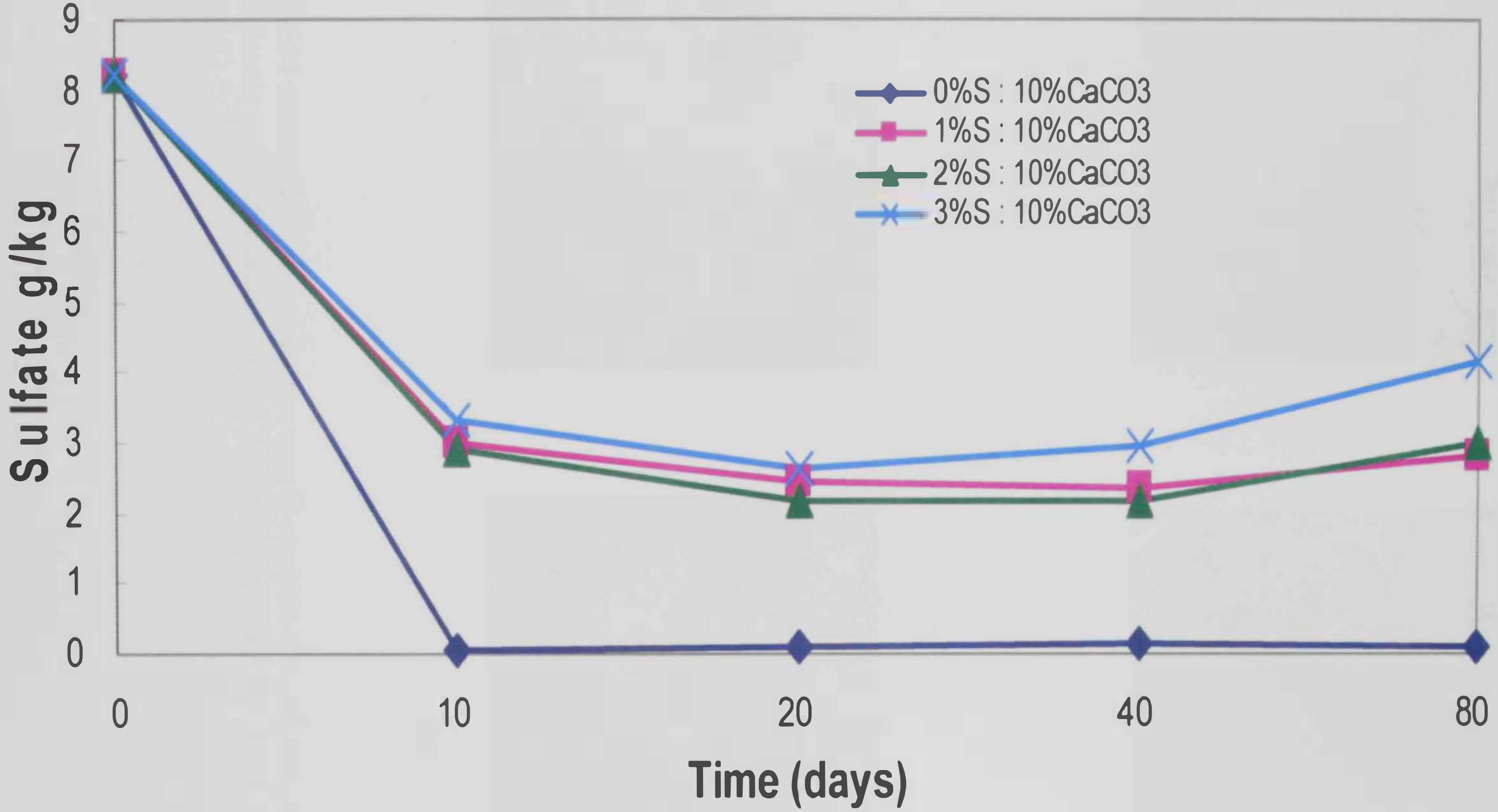
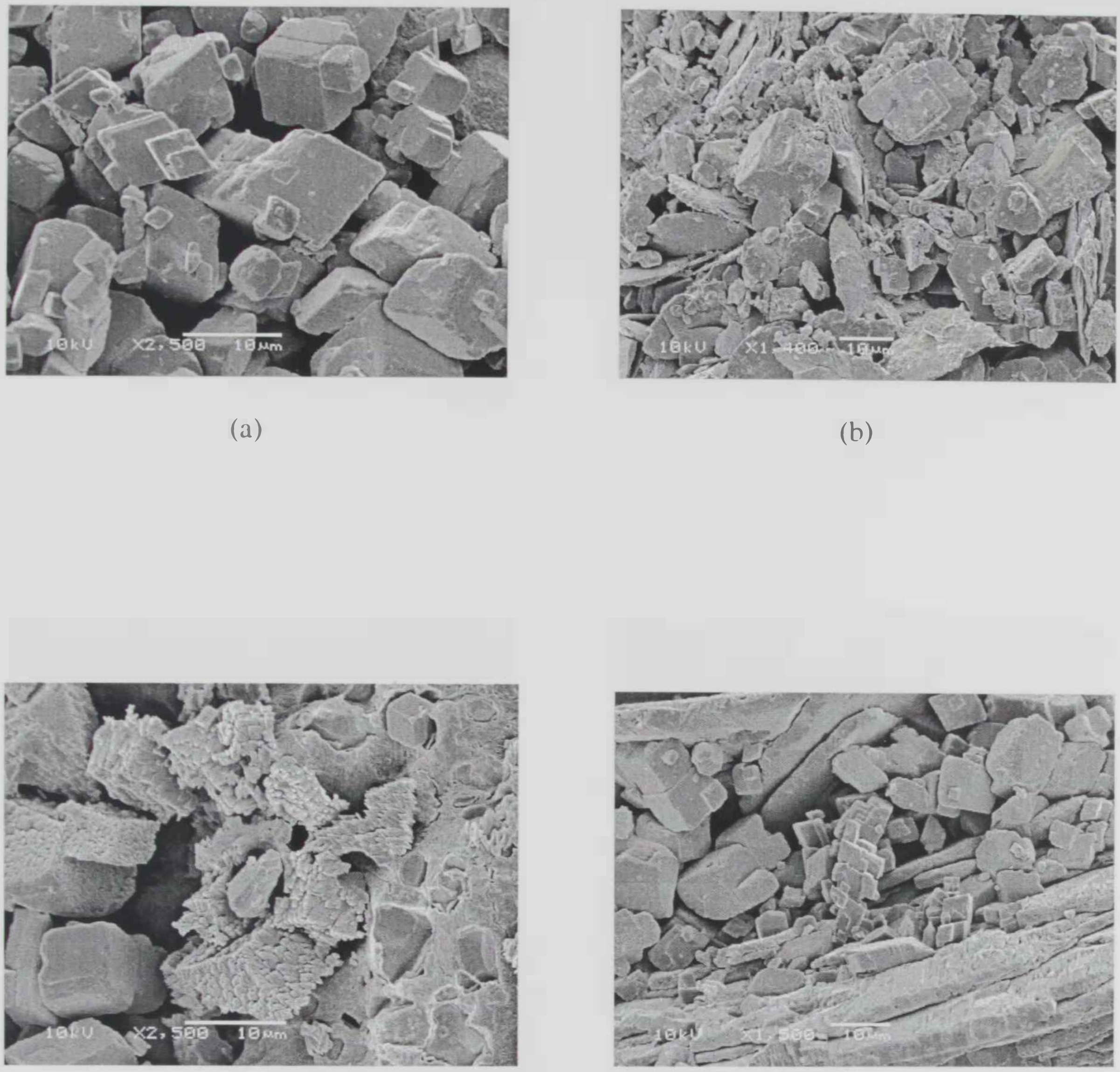


Figure 4.19: Variation of water soluble sulfate with time and amount of added elemental sulfur for mix design type II samples (with addition of 10% $CaCO_3$).

(a) (b)

(c) (d)

Figure 4.20: SEM micrograph for mix design type II samples after 20 days at different magnification levels and sulfur content: (a) X1600: 0%S; (b) X2500: 1%S; (c) X1900: 2%S; (d) X1200: 3%S.



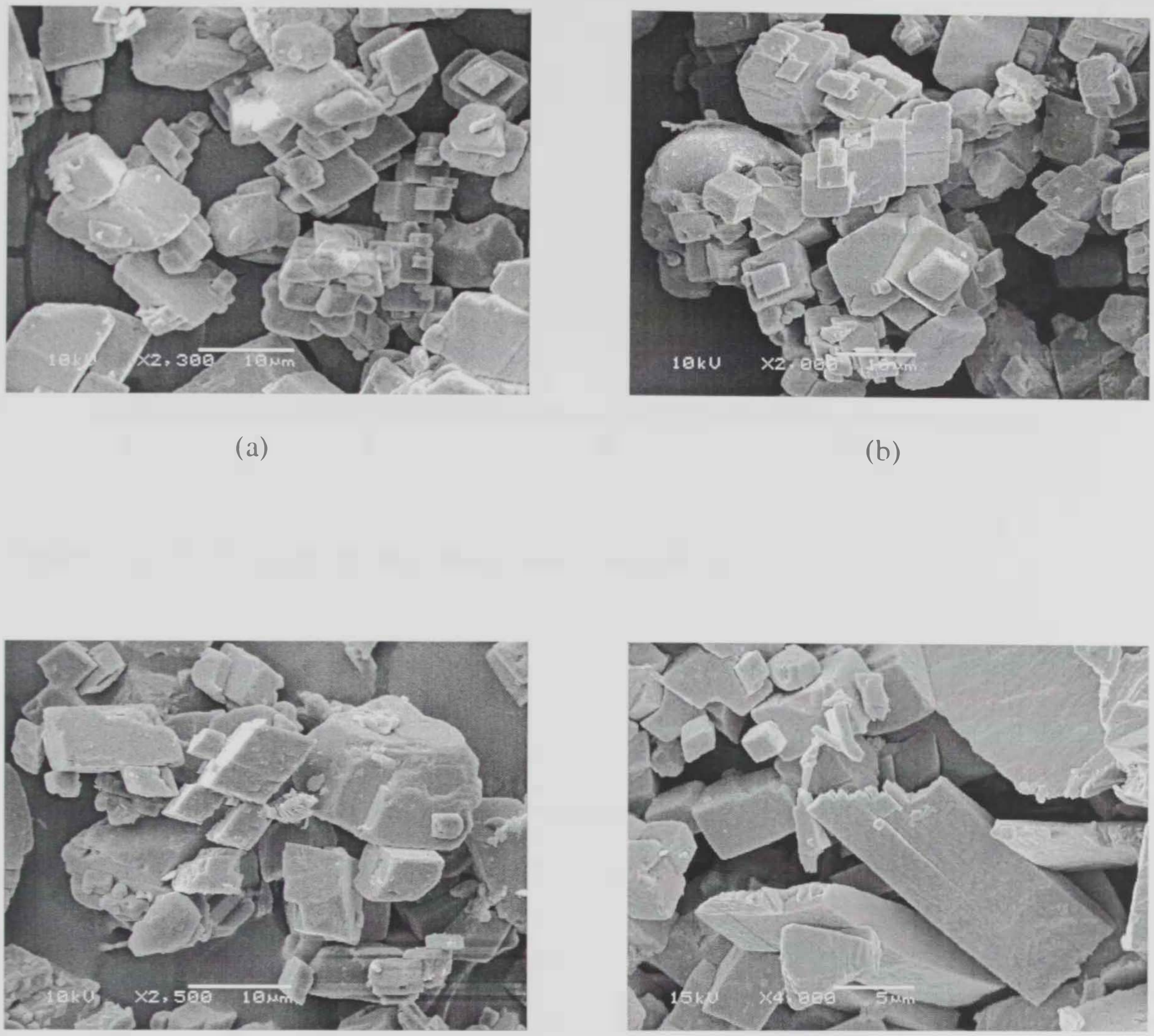
(a)

(b)

(c)

(d)

Figure 4.21: SEM micrograph for mix design type II samples after 40 days at different magnification levels and sulfur content: (a) X2500: 0%S; (b) X1400: 1%S; (c) X2500: 2%S; (d) X1500: 3%S.



(a)

(b)

(c)

(d)

Figure 4.22: SEM micrograph for mix design type II samples after 80 days at different magnification levels and sulfur content: (a) X2300: 0%S; (b) X2000: 1%S; (c) X2500: 2%S; (d) X4000: 3%S.

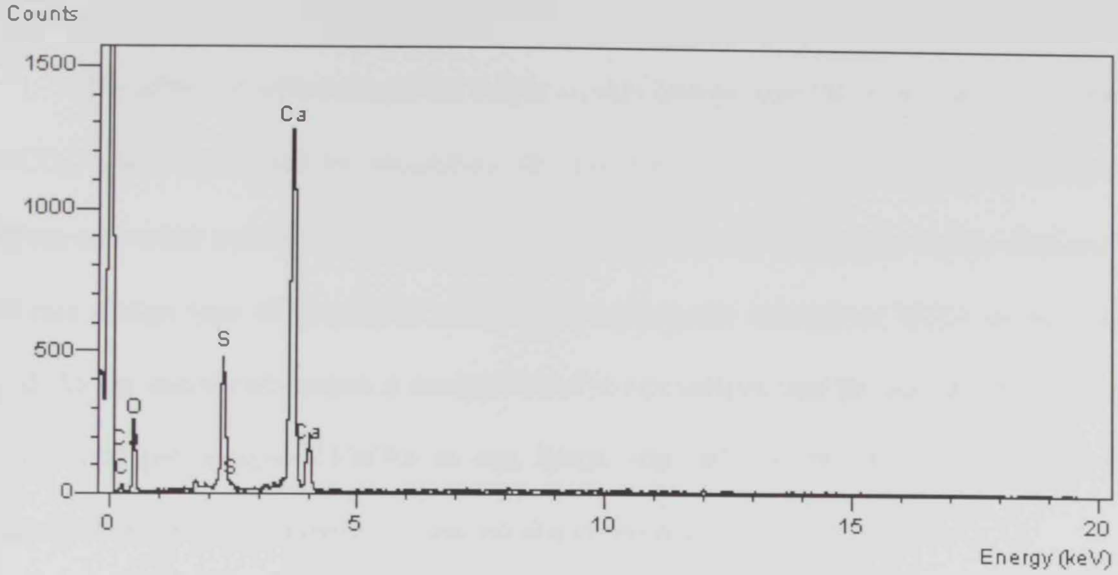


Figure 4.23: EDX graph for mix design type II sample 12 (3%S) after 20 days

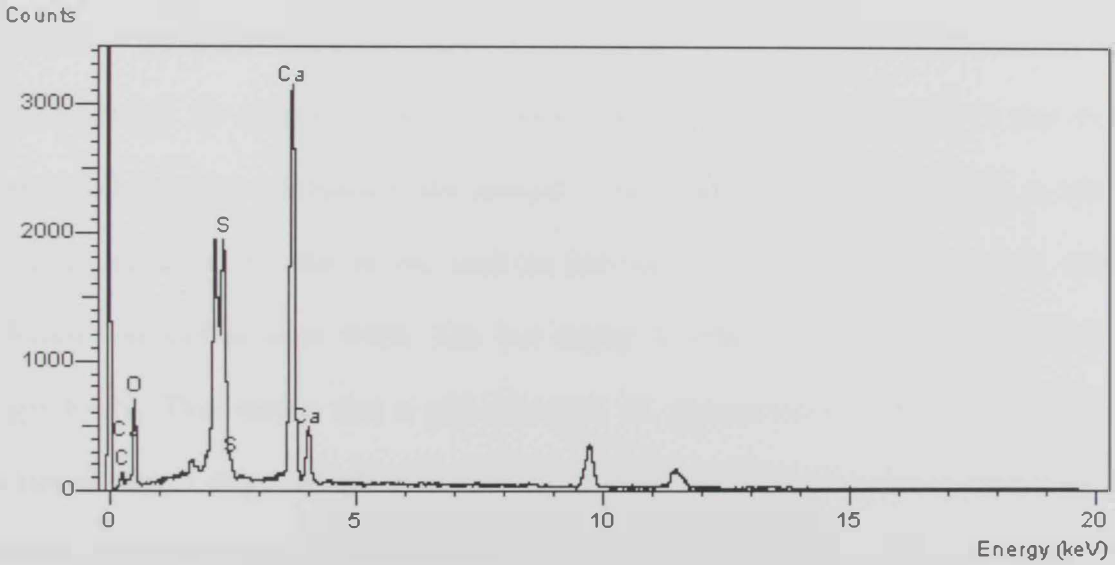


Figure 4.24: EDX graph for mix design type II sample 12 (3%S) after 80 days

4.6 EFFECT OF ELEMENTAL SULFUR APPLICATION ON MIX DESIGN TYPE III:

The effect of added elemental sulfur on mix design type III (with addition of 20% $CaCO_3$) was determined by measuring the pH levels, electrical conductivity (EC) in µS/cm and water soluble SO_4^{-2} (g/kg). It should be noted that, as previously discussed, the mix design type III contained initial carbonates in the amount of 16.2% in the used sand. So the initial carbonates in the sand used in mix design type III was also 16.2% and so the total percentage of $CaCO_3$ in mix design type III was 36.2%. The variations of these parameters as a function of time are discussed below.

4.6.1 pH Variation:

The variation of pH as a function of time and sulfur addition is shown in Figure 4.25. The experimental results of pH variation of the mix design type III samples without addition of elemental sulfur decreased from 8.51 to 7.22, 7.65 after 5 and 10 days but increased after 20 days 8.30 and then decreased after 40 and 80 days 8.15 and 8.00, respectively. This is attributed to the amount of sulfur which was found mainly in added organic manure (1%) and in the sand as discussed in Chapter 3. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic matter, sand and $CaCO_3$, respectively. This means that a pH reduction of approximately 0.59 units has been achieved after 5 days and pH continued to decrease until 80 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite.

The results indicate that the addition of 1% S reduced the pH level from 8.53 to 7.36, 7.49, 7.35, 7.31 and 7.34 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.17 units has been achieved after 5 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite. The increase of pH after 10 and 80 days could be attributed to the formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. After 20 and 40 days, pH decreased due to formation of tricalcium aluminate (C_3A), tricalcium aluminate hydrate (C_3AH_6), tetracalcium aluminate hydrate (C_4AH_{13}) and calcium monosulfoaluminate.

The addition of 2% S reduced the pH level from 8.46 to 7.41, 7.50, 7.37, 7.38 and 7.30 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.05 units has been achieved after 5 days and pH continued to decrease until 80 days. The addition of 3% S reduced the pH level from 8.47 to 8.50, 7.37, 7.43, 7.39 and 7.29 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.10 units has been achieved after 10 days and pH continued to decrease until 80 days.

Based on both the possible chemical reactions discussed previously as well as results, the pH first reduced because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it increased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it decreased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate.

The experimental results of pH variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.455 with 3 degrees of freedom, indicating that addition of sulfur has no

significance (P-value > 0.05) on the changes in pH value. Also there was a little difference in the mean as shown in Table 4.11.

Table 4.11: One – way stacked ANOVA analysis for pH results of mix design type III samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	7.9717	7.5633	7.5700	7.7417
StDiv	0.4688	0.4776	0.4408	0.5777

4.6.2 Electrical Conductivity (EC) Variation:

The variation of EC as a function of time and sulfur addition is shown in Figure 4.26. The EC of the mix design type III samples without addition of elemental sulfur increased from 369 to 1910 μS/cm after 5 days but decreased to 1681, 294 μS/cm after 10 and 20 days, respectively. Then it increased again to 440 and 747μS/cm after 40 and 80 days, respectively. This can be attributed to: (1) the amount of organic manure that the mix design type III sample contains (1%); (2) the amount of total sulfur measured as sulfate that the organic manure contains 9409 mg/kg, and (3) the amount of total sulfur measured as sulfate of 326, 0.4 mg/kg in sand and $CaCO_3$, respectively. Due to sulfur oxidation, pH decreased and the amount of soluble ions increased leading to an increase of EC.

The results indicate that the addition of 1%S increased EC from 367 to 1870, 2480, 1263, 1642 and 2730 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 1073 μS/cm has been achieved after 5 days and EC also increased by 2040 μS/cm after 10 days, but decreased after 20 and then increased after 40 and 80 days.

Also the addition of 2%S increased EC from 365 to 1870, 2480, 1263, 1642 and 2730 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 1505 and 2115μS/cm has been achieved after 5 and 10 days, respectively. Then EC decreased after 20 days but increased after 40 and 80 days.

The addition of 3% S also increased EC from 356μS to 389, 3170, 988, 2050 and 2820 μS/cm after 5, 10, 20, 40 and 80 days, respectively. This means that EC increase of 2816 μS/cm has been achieved after 10 days. The EC then decreased after 20 days but increased after 40 and 80 days. The increase in soluble salts as measured by soil EC was due to dissolution of $CaCO_3$ by H_2SO_4 (Cifuentes and Lindeman, 1993).

Based on both the possible chemical reactions discussed previously as well as the experimental results, the EC first increased because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it decreased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it increased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of EC variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.264 with 3 degrees of freedom, indicating that addition of sulfur has no significance (P-value > 0.05) on the changes in EC value. Also there was a difference in the mean as shown in Table 4.12.

Table 4.12: One-way stacked ANOVA analysis for EC results of the mix design type III samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	1014.4	1668.2	1997.0	1883.4
StDiv	736.0	591.6	602.4	1182.7

4.6.3 Oxidation of Elemental Sulfur:

Oxidation of elemental sulfur was evaluated based on the amount of measured water soluble sulfate. Therefore, Figure 4.27 shows the amount of water soluble sulfate as a function of time and amount of elemental sulfur added. Thus, the Figure indicates that the addition of 1% S, 2%S and 3%S kept the amount of water soluble SO_4^{-2} higher than without addition of elemental sulfur (control).

In addition of 1%S, the amount of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 2.8, 2.4 and 2.2 g/kg after 10, 20 and 40 days, respectively. Then, it increased to 2.5 g/kg 80 days. Whereas, the amount of water soluble SO_4^{-2} in samples without addition of elemental sulfur decreased from 8.2 g/kg at 0 day to 0.1 g/kg after 10 days and remained constant at 0.1 g/kg after 20, 40 and 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 2% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 days to 3.4, 2.6 and 2.2 g/kg after 10, 20 and 40 days, respectively. Then, it increased to 3.3 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 3% S the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 3.0 and 2.1 after 10 and 20 days, respectively. Then, it increased to 3.1 and 3.4 g/kg after 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

It can be observed that the high amount of initial water soluble SO_4^{-2} in all samples was due to addition of organic manure (1%) which had 8.17 g/kg water soluble SO_4^{-2} and sand which had 0.03 g/kg water soluble SO_4^{-2}. Also the presence of water soluble SO_4^{-2} was due to sulfur oxidation which was found mainly in the added organic manure (1%) and in the sand. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic manure, sand and $CaCO_3$ respectively. This initial amount was completely reduced after 10 days in samples without addition of elemental sulfur. Also there were variations of water soluble SO_4^{-2} between the time periods for samples treated by elemental sulfur. This could be attributed to: (1) neutralization of calcium carbonate by H_2SO_4 (Cifuentes and Lindeman, 1993) and formation of both gypsum [$CaSO_4.2H_2O$] and carbonic acid [[H_2CO_3]; (2) formation of calcium monosulfoaluminate (Mohamed and Antia, 1998; Mohamed 2003); and (3) sulfate reduction into hydrogen sulfide (H_2S)

(Lecture 23, February 2001, Alken Murray Corp., March 2001, Potash & Phosphate Institute of Canada, March 2001).

The initial available sulfate in the irrigation water was completely consumed by the substrate as indicated from the results of the reference sample (0%S added). However, with the addition of sulfur, the available sulfate increased during the same period (10 days) due to possible formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it continued to increase from 10 to 20 days due to formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate. From 20 to 40 days, it decreased due to formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. From 40 to 80 days, it increased due to generation of sulfuric acid, carbonic acid and dissolution of calcite.

The experimental results of sulfate variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.000 with 3 degrees of freedom, indicating that addition of sulfur has highly significance (P-value < 0.05) on the changes in sulfate value. Also there was a difference in the mean as shown in Table 4.13.

Table 4.13: One-way stacked ANOVA analysis for sulfate results of the mix design type III samples

	1 (0%S)	**2 (1%S)**	**3 (2%S)**	**4 (3%S)**
Mean	0.1000	2.4750	2.8750	2.9000
StDiv	0.0000	0.2500	0.5737	0.5598

4.6.4 Mineral Formation:

To identify whether or not gypsum has been formed, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) were utilized. For mix design type III all samples were examined by XRD analysis, after all time periods (5, 10, 20, 40 and 80 days). In all tested samples, the major mineral found was quartz and calcite. Also the minor formed minerals were examined after 5, 10, 20 and 40 days. In all samples, plagioclase and calcite were found as shown in Table 4.2

The SEM results for mix design type III samples (13–16) after 20, 40 and 80 days are shown in Figures 4.28 to 4. 30. Figures 4.28 (a) to (d) show the mix design type III images at magnification levels of X750, X1600, X1700, and X1400 after 20 days. Figures4.29 (a) to (d) show the mix design type III images at magnification levels of X1000, X2500, X1000, and X1600 after 40 days. Figures 4.30 (a) to (d) show the mix design type III images at magnification levels of X1500, X1900, X550, and X2200 after 80 days. The major minerals are quartz and calcite and minor mineral is plagioclase. No gypsum was formed after 20, 40 and 80 days in mix design type III samples.

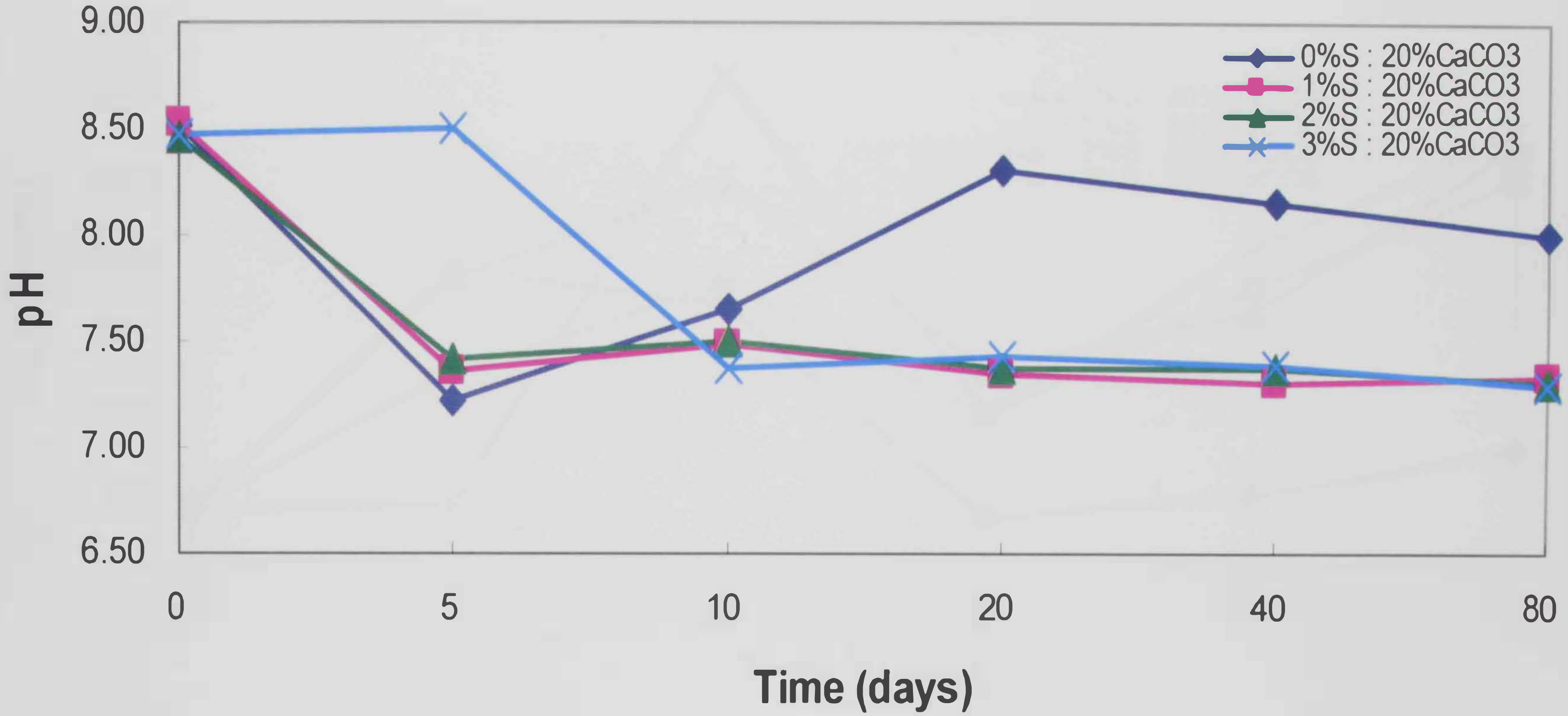


Figure 4.25: Variation of pH with time and amount of added elemental sulfur for mix design type III samples (with addition of 20% $CaCO_3$).

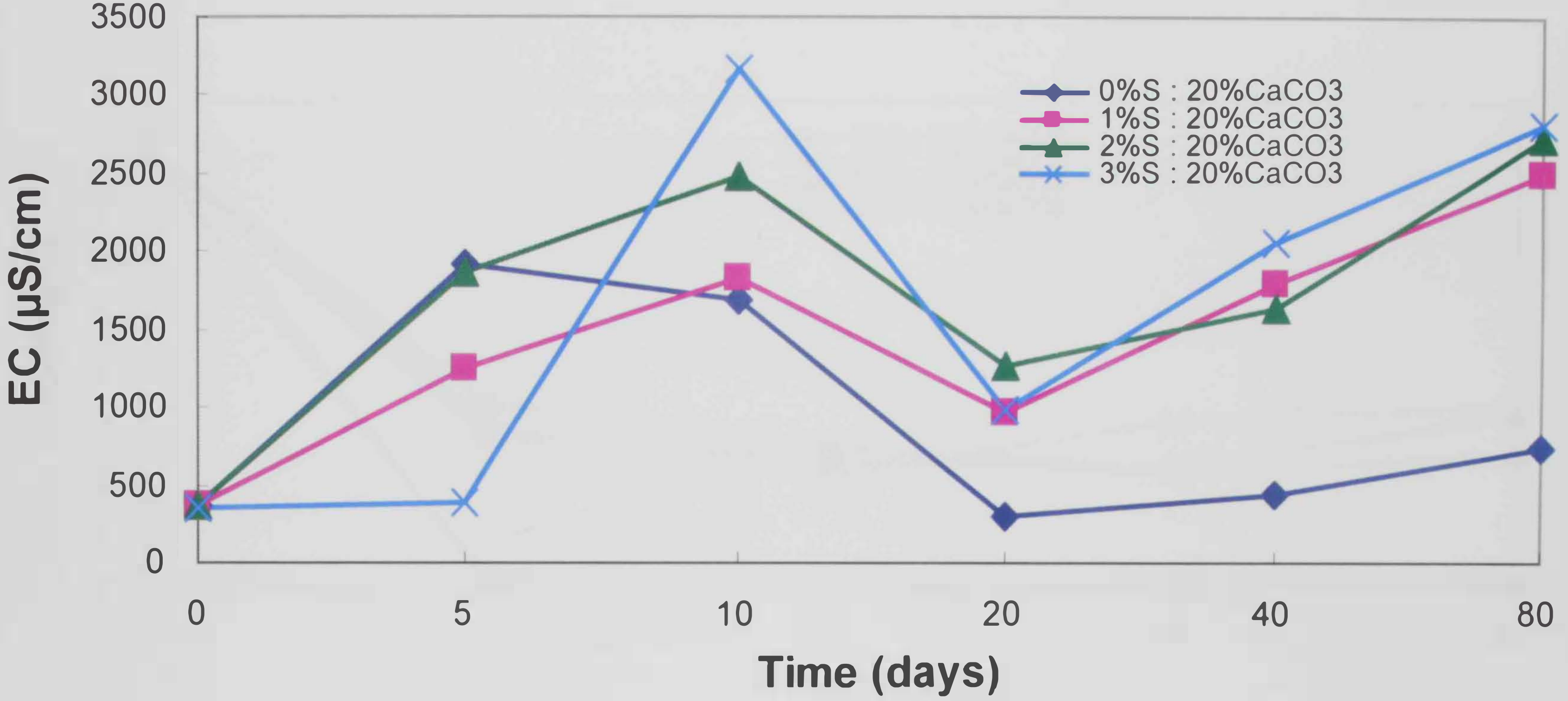


Figure 4.26: Variation of electrical conductivity (EC) with time and amount of added elemental sulfur for mix design type III samples (with addition of 20% $CaCO_3$).

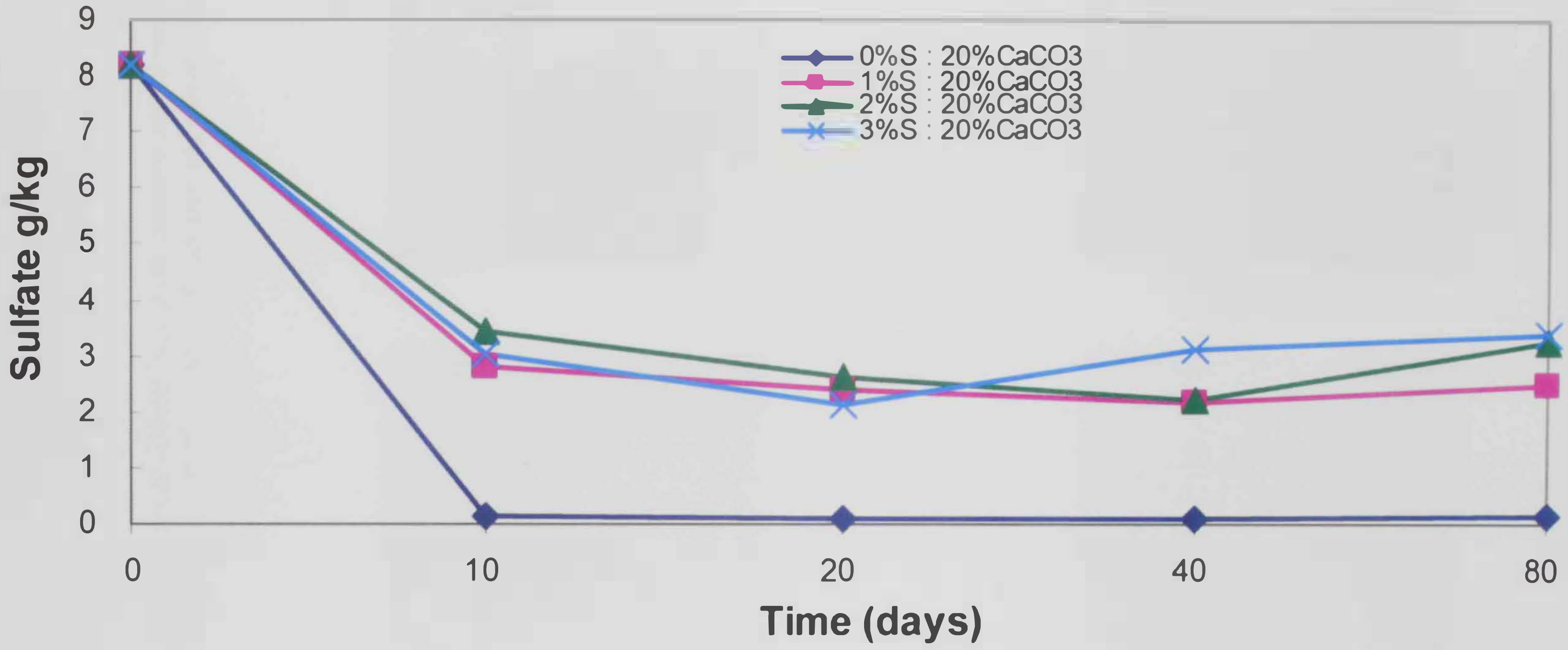
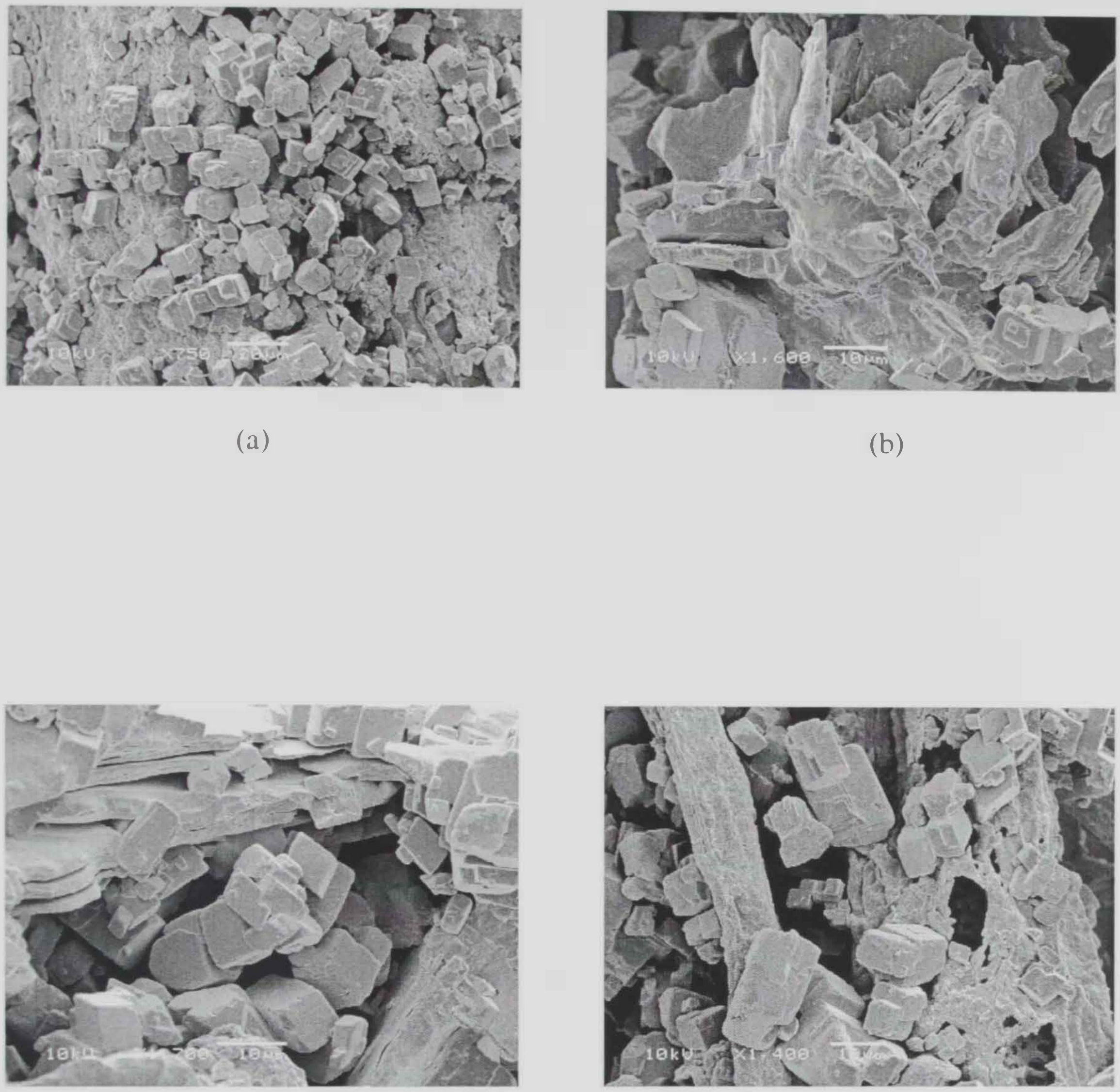


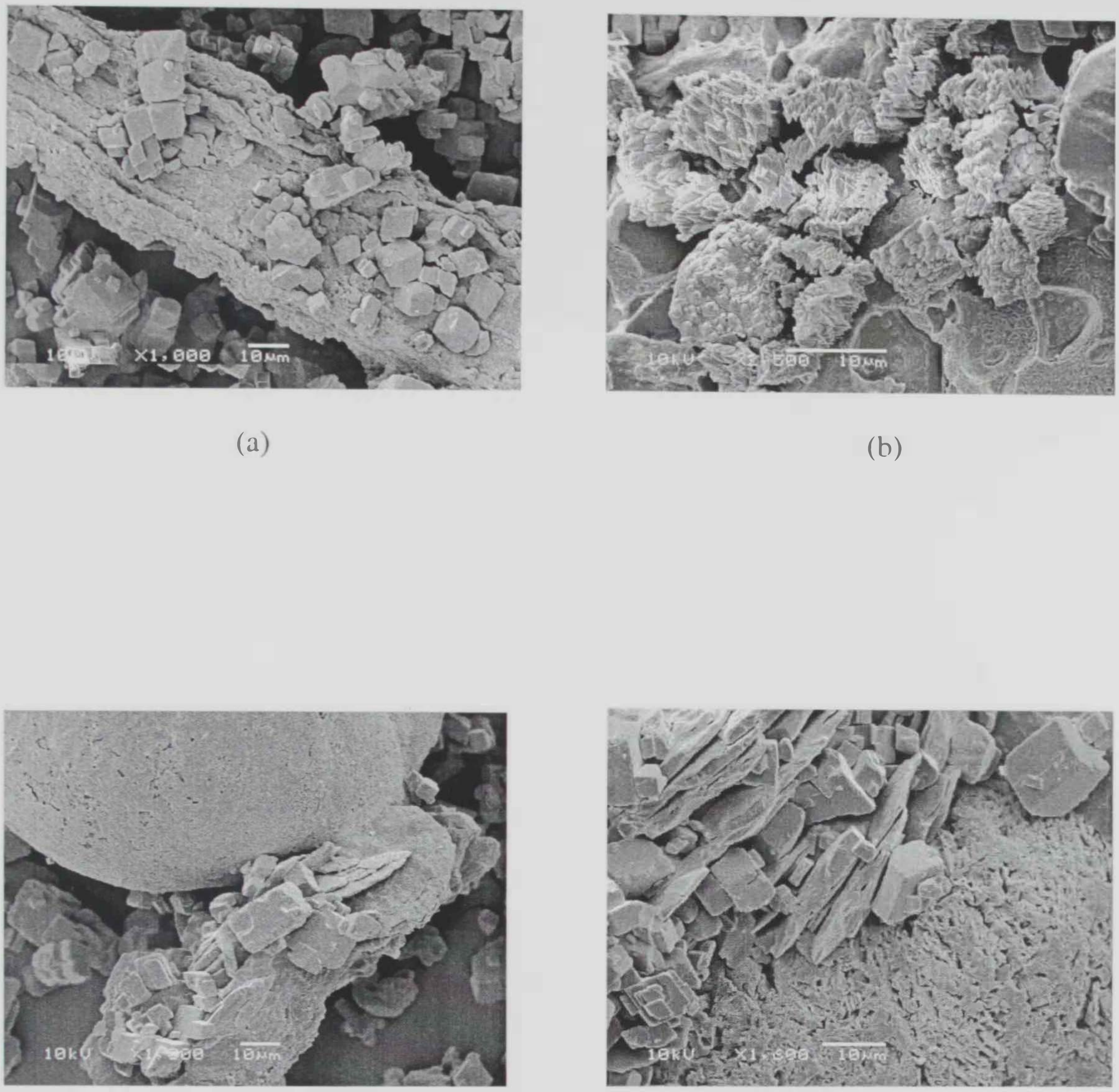
Figure 4.27: Variation of water soluble sulfate with time and amount of added elemental sulfur for mix design type III samples (with addition of 20% $CaCO_3$).



(a) (b)

(c) (d)

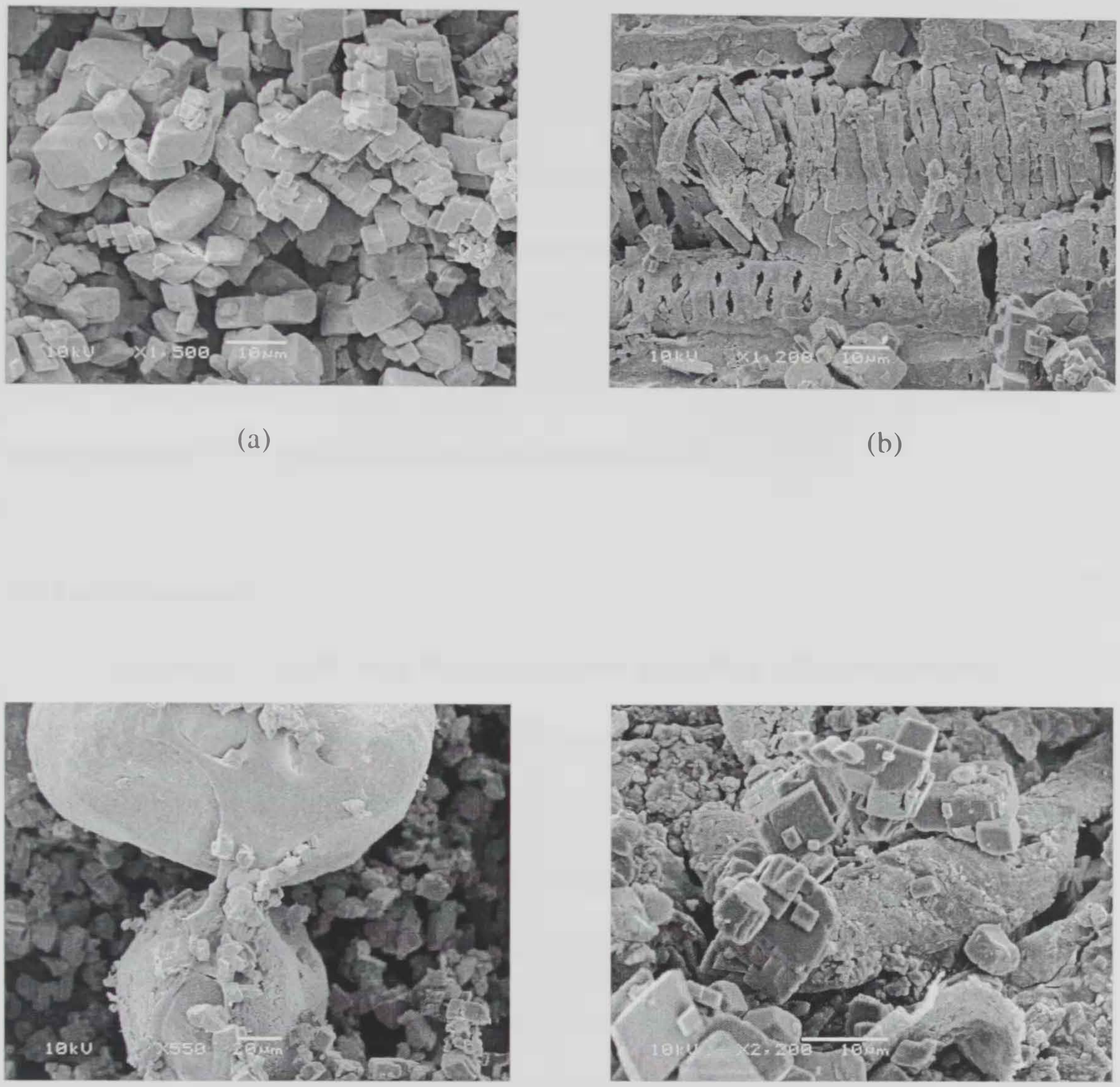
Figure 4.28: SEM micrograph for mix design type III samples after 20 days at different magnification levels and sulfur content: (a) X750: 0%S; (b) X1600: 1%S; (c) X1700: 2%S; (d) X1400: 3%S.



(a) (b)

(c) (d)

Figure 4.29: SEM micrograph for mix design type III samples after 40 days at different magnification levels and sulfur content: (a) X1000: 0%S; (b) X2500: 1%S; (c) X1000: 2%S; (d) X1600: 3%S.



(a) (b)

(c) (d)

Figure 4.30: SEM micrograph for mix design type III samples after 80 days at different magnification levels and sulfur content: (a) X1500: 0%S; (b) X1900: 1%S; (c) X550: 2%S; (d) X2200: 3%S.

4.7 EFFECT OF ELEMENTAL SULFUR APPLICATION ON MIX DESIGN TYPE IV:

The effect of added elemental sulfur on mix design type IV (with addition of 30% $CaCO_3$) was determined by measuring the pH levels, electrical conductivity (EC) in µS/cm and water soluble SO_4^{-2} (g/kg). It should be noted that, as previously discussed, the mix design type IV contained initial carbonates in the amount of 16.2% in the used sand. So the initial carbonates in the sand used in mix design type IV was also 16.2% and so the total percentage of $CaCO_3$ in mix design type IV was 46.2%. The variations of these parameters as a function of time are discussed below.

4.7.1 pH Variation:

The variation of pH as a function of time and sulfur addition is shown in Figure 4.31. The experimental results of pH variation of the mix design type IV samples without addition of elemental sulfur decreased from 8.98 to 8.08 after 5 days but increased to 8.14, 8.18, 8.18 and 8.61 after 10, 20, 40 and 80 days, respectively. This is attributed to the amount of sulfur which was found mainly in added organic manure (1%) and in the sand as discussed in Chapter 3. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic matter, sand and $CaCO_3$, respectively. This means that a pH reduction of approximately 0.59 units has been achieved after 5 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite.

The results indicate that the addition of 1%S reduced the pH level from 8.95 to 7.57, 7.70, 7.46, 7.45 and 7.33 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.38 units has been achieved after 5 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite then increased by 0.13 units after 10 days due to the formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. After 20, 40 and 80 days, pH decreased again due to formation of tricalcium aluminate (C_3A), tricalcium aluminate hydrate (C_3AH_6), tetracalcium aluminate hydrate (C_4AH_{13}) and calcium monosulfoaluminate.

The addition of 2% S reduced the pH level from 8.95 to 7.50, 7.51, 7.60, 7.37 and 7.39 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.25 units has been achieved after 5 days then increased after 10 and 20 days but decreased again after 40 and 80 days.

The addition of 3% S reduced the pH level from 8.89 to 7.51, 7.43, 7.67, 7.34 and 7.39 after 5, 10, 20, 40 and 80 days, respectively. This means that a pH reduction of approximately 1.38 units has been achieved after 5 days then increased after 20 days but decreased again after 40 and 80 days.

Based on both the possible chemical reactions discussed previously as well as results, the pH first reduced because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it increased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it decreased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of pH variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.143 with 3 degrees of freedom, indicating that addition of sulfur has no

significance (P-value > 0.05) on the changes in pH value. Also there was a little difference in the mean as shown in Table 4.14.

Table 4.14: One – way stacked ANOVA analysis for pH results of mix design type IV samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	8.3617	7.7433	7.7200	7.7050
StDiv	0.3573	0.6042	0.6085	0.5919

4.7.2 Electrical Conductivity (EC) Variation:

The variation of EC as a function of time and sulfur addition is shown in Figure 4.32. The EC of the mix design type IV samples without addition of elemental sulfur increased from 353 to 569 μS/cm after 5 days then decreased to 363 and 280 μS/cm after 10 and 20 days, respectively. Then, it increased again to 481 μS/cm after 40 days but decreased again to 457 μS/cm after 80 days. This can be attributed to : (1) the amount of organic manure that the mix design type IV sample contains (1%); (2) the amount of total sulfur measured as sulfate that the organic manure contains 9409 mg/kg, and (3) the amount of total sulfur measured as sulfate of 326, 0.4 mg/kg in sand and $CaCO_3$, respectively. Due to sulfur oxidation, pH decreased and the amount of soluble ions increased leading to an increase of EC.

The results indicate that the addition of the addition of 1%S increased EC from 351 to 1640 μS/cm after 5 days then decreased to 1007 and 955 μS/cm after 10, 20 days but increased again to 1538 and 2450 μS/cm after 40 and 80 days, respectively. This means that EC increase of 1289 μS/cm has been achieved after 5 days and EC also increased by 2099 μS/cm after 80 days.

Also the addition of 2%S increased EC from 349 to 2080, 2210 μS/cm after 5 and 10 days, respectively. Then decreased to 768 μS/cm after 20 days but increased to 1981 and 2510 μS/cm after 40 and 80 days, respectively. This means that EC increase of 1731 μS has been achieved after 5 days.

The addition of 3% S also increased EC from 341 to 1520, 3370 μS/cm after 5 and 10 days, respectively. Then decreased to 667 μS/cm after 20 days but increased again to 1907 and 2740 μS/cm after 40 and 80 days, respectively. This means that EC increase of 1179 and 3029 μS/cm has been achieved after 5 and 10 days, respectively. The increase in soluble salts as measured by soil EC was due to dissolution of $CaCO_3$ by H_2SO_4 (Cifuentes and Lindeman, 1993).

Based on both the possible chemical reactions discussed previously as well as the experimental results, the EC first increased because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it decreased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it increased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of EC variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.008 with 3 degrees of freedom, indicating that addition of sulfur has highly

significance (P-value < 0.05) on the changes in EC value. Also there was a difference in the mean as shown in Table 4.15.

Table 4.15: One-way stacked ANOVA analysis for EC results of the mix design type IV samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	430.0	1518.0	1909.8	2040.8
StDiv	111.4	604.6	668.6	1052.6

4.7.3 Oxidation of Elemental Sulfur:

Oxidation of elemental sulfur was evaluated based on the amount of measured water soluble sulfate. Therefore, Figure 4.33 shows the amount of water soluble sulfate as a function of time and amount of elemental sulfur added. Thus, the Figure indicates that the addition of 1% S, 2%S and 3%S kept the amount of water soluble SO_4^{-2} higher than without addition of elemental sulfur.

In addition of 1%S, the amount of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 2.2 and 1.6 g/kg after 10 and 20 days, respectively. Then, it increased to 1.8 and 2.3 g/kg after 40 and 80 days, respectively. Whereas, the amount of water soluble SO_4^{-2} in samples without addition of elemental sulfur decreased from 8.2 g/kg at 0 day to 0.1 g/kg after 10 days and remained constant at 0.1 g/kg after 20, 40 and 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 2% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 3.0 and 1.5 g/kg after 10 and 20 days, respectively. Then, it increased to 1.7 and 2.4 g/kg after 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 3% S, the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg to 3.2 and 1.4 g/kg after 10 and 20 days, respectively. Then, it increased to 3.0 and 4.2 g/kg after 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

It can be observed that the high amount of initial water soluble SO_4^{-2} in all samples was due to addition of organic manure (1%) which had 8.17 g/kg water soluble SO_4^{-2} and sand which had 0.03 g/kg water soluble SO_4^{-2}. Also the presence of water soluble SO_4^{-2} was due to sulfur oxidation which was found mainly in the added organic manure (1%) and in the sand. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic manure, sand and $CaCO_3$ respectively. This initial amount was completely reduced after 10 days in samples without addition of elemental sulfur. Also there were variations of water soluble SO_4^{-2} between the time periods for samples treated by elemental sulfur. This could be attributed to: (1) neutralization of calcium carbonate by H_2SO_4 (Cifuentes and Lindeman, 1993) and formation of both gypsum [$CaSO_4.2H_2O$] and carbonic acid [[H_2CO_3]; (2) formation of calcium monosulfoaluminate (Mohamed

and Antia, 1998; Mohamed 2003); and (3) sulfate reduction into hydrogen sulfide (H_2S) (Lecture 23, February 2001, Alken Murray Corp., March 2001, Potash & Phosphate Institute of Canada, March 2001).

The initial available sulfate in the irrigation water was completely consumed by the substrate as indicated from the results of the reference sample (0%S added). However, with the addition of sulfur, the available sulfate increased during the same period (10 days) due to possible formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it continued to increase from 10 to 20 days due to formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate. From 20 to 40 days, it decreased due to formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. From 40 to 80 days, it increased due to generation of sulfuric acid, carbonic acid and dissolution of calcite.

The experimental results of sulfate variations were further studied via the use of statistical analysis. The analysis of variance (One-way ANOVA) p- value was found to be 0.001 with 3 degrees of freedom, indicating that addition of sulfur has highly significance ($P\text{-value} < 0.05$) on the changes in sulfate value. Also there was a difference in the mean as shown in Table 4.16.

Table 4.16: One-way stacked ANOVA analysis for sulfate results of the mix design type IV samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	0.1000	1.9750	2.1500	2.9500
StDiv	0.0000	0.3304	0.6856	1.1590

4.7.4 Mineral Formation:

To identify whether or not gypsum has been formed, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) were utilized. For mix design type IV all samples were examined by XRD analysis, after all time periods (5, 10, 20, 40 and 80 days). In all tested samples, the major mineral found was quartz and calcite. Also the minor formed minerals were examined after 5, 10, 20 and 40 days. In all samples, plagioclase and calcite were found but there wasn't any minor mineral in samples treated by 2 and 3%S as shown in Table 4.2.

The SEM results for mix design type IV samples (17 – 20) after 20, 40 and 80 days are shown in Figures 4.34- 4. 36. Figures 4.4 (a) to (d) show the mix design type IV images at magnification levels of X2000, X2000, X1700, and X1900 after 20 days. Figures4.35 (a) to (d) show the mix design type IV images at magnification levels of X1900, X2000, X2700, and X1300 after 40 days. Figures 4.36 (a) to (d) show the mix design type IV images at magnification levels of X2000, X1400, X1000, and X1700 after 80 days. The major minerals are quartz and calcite and minor mineral is plagioclase. No gypsum was formed after 20, 40 and 80 days in mix design type IV samples.

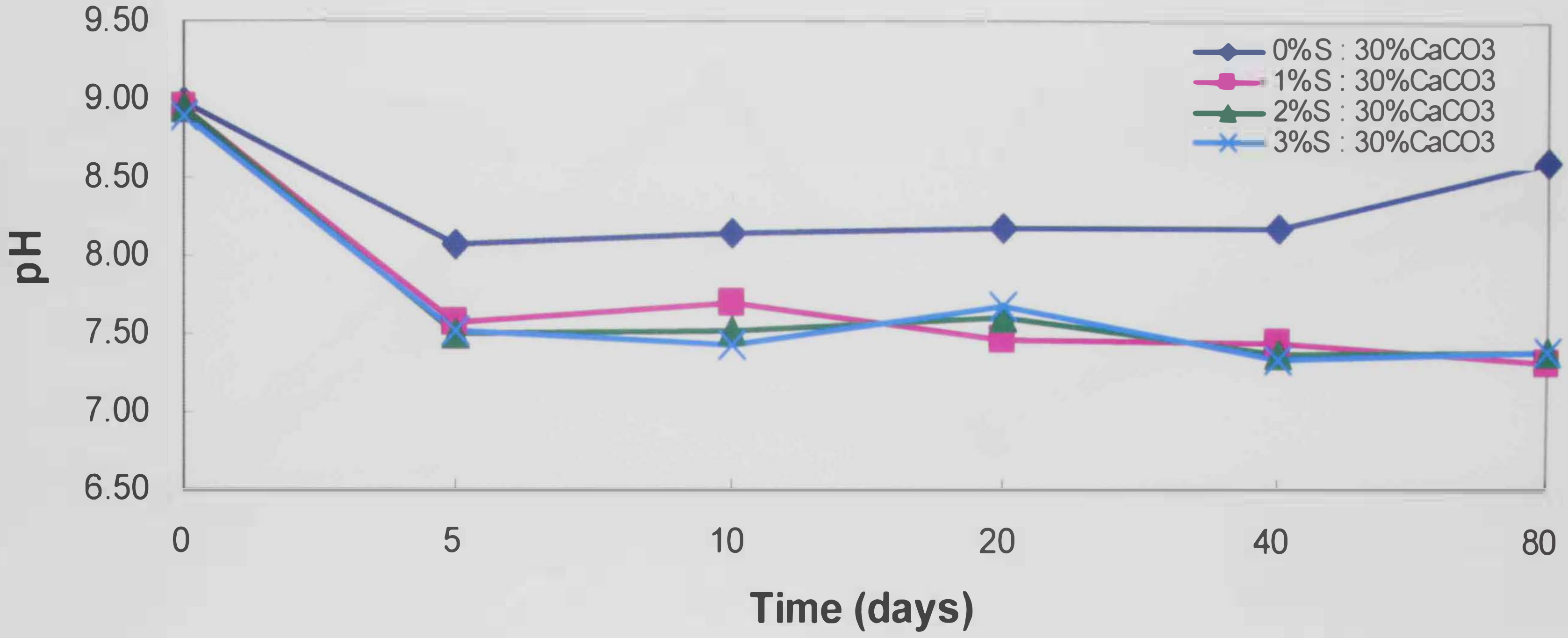


Figure 4.31: Variation of pH with time and amount of added elemental sulfur for mix design type IV samples (with addition of 30% $CaCO_3$).

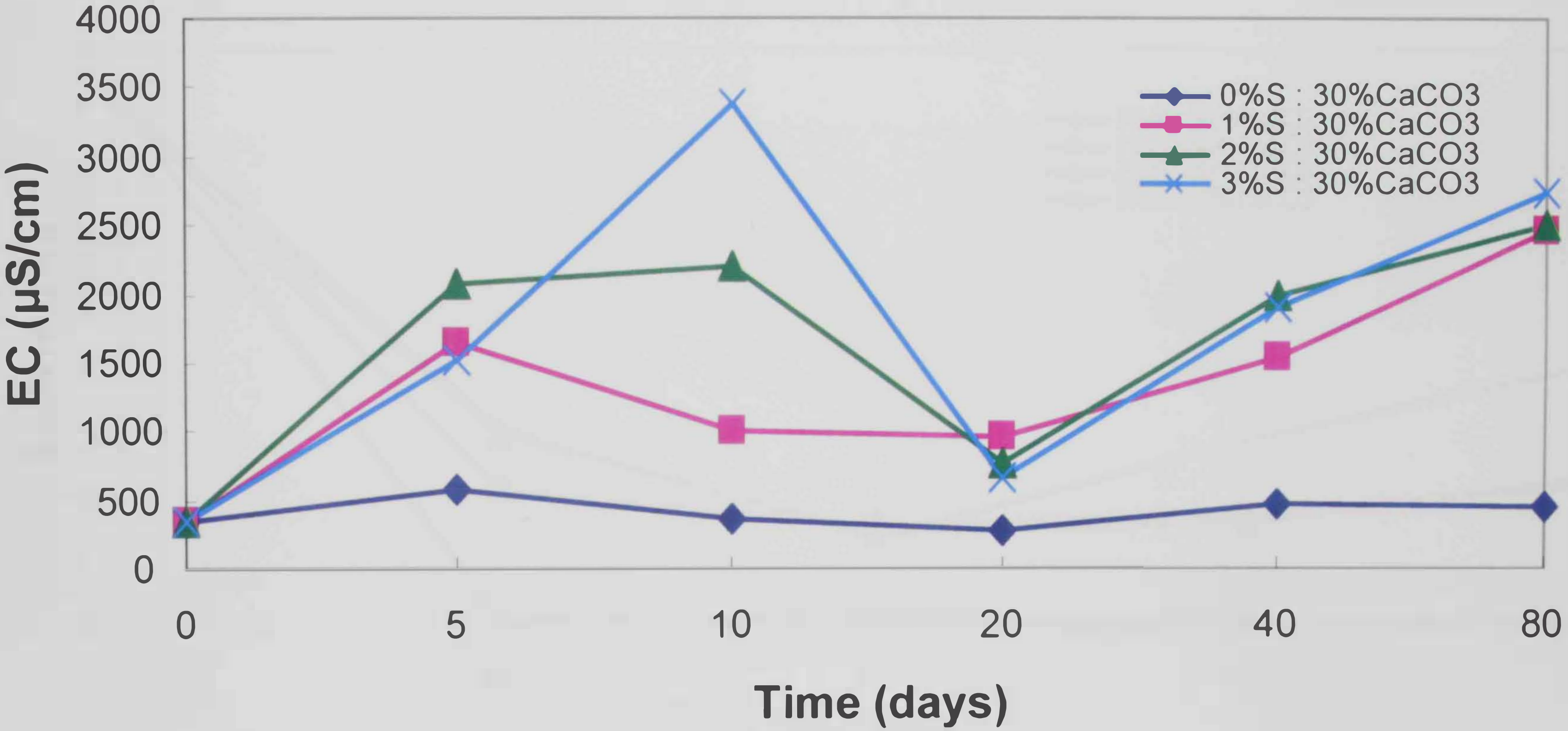


Figure 4.32: Variation of electrical conductivity (EC) with time and amount of added elemental sulfur for mix design type IV samples (with addition of 30% $CaCO_3$).

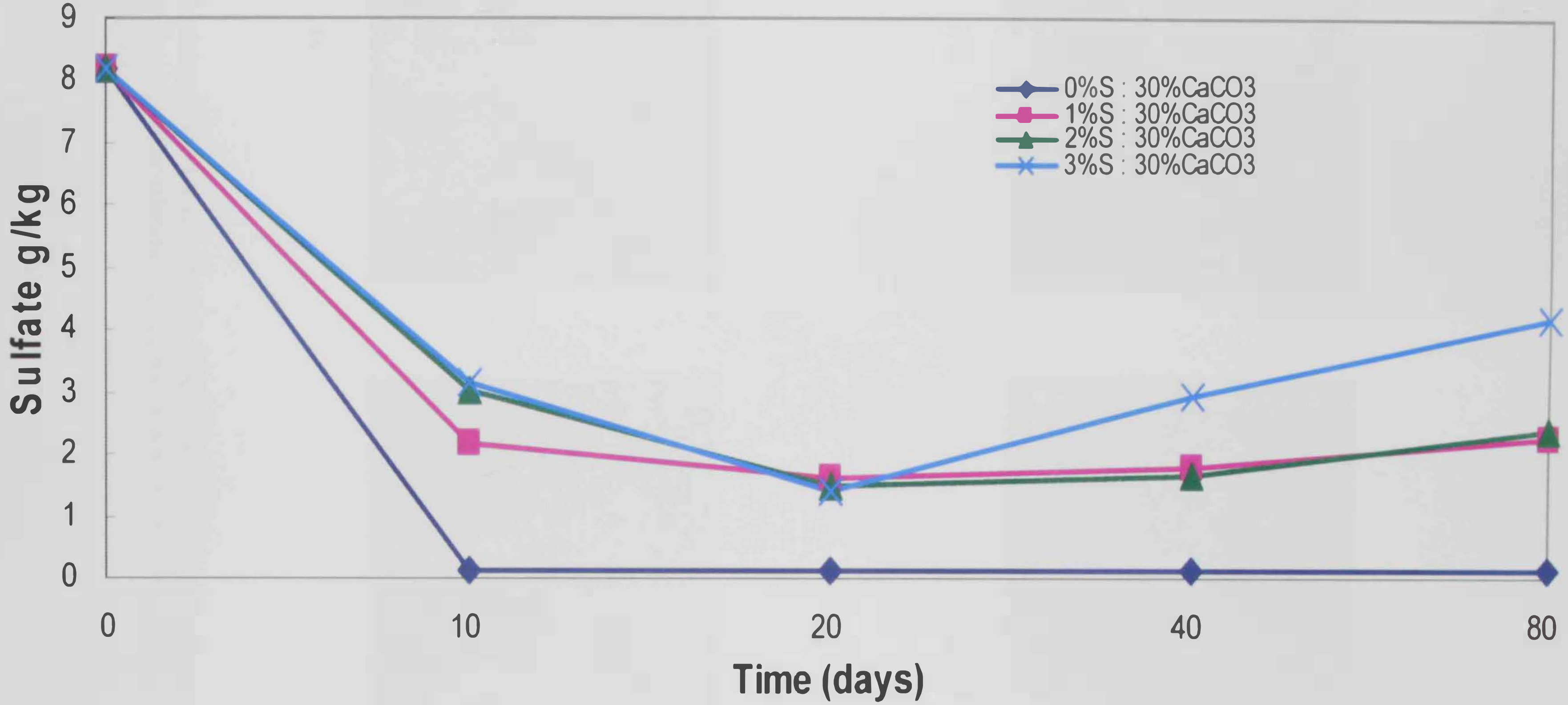
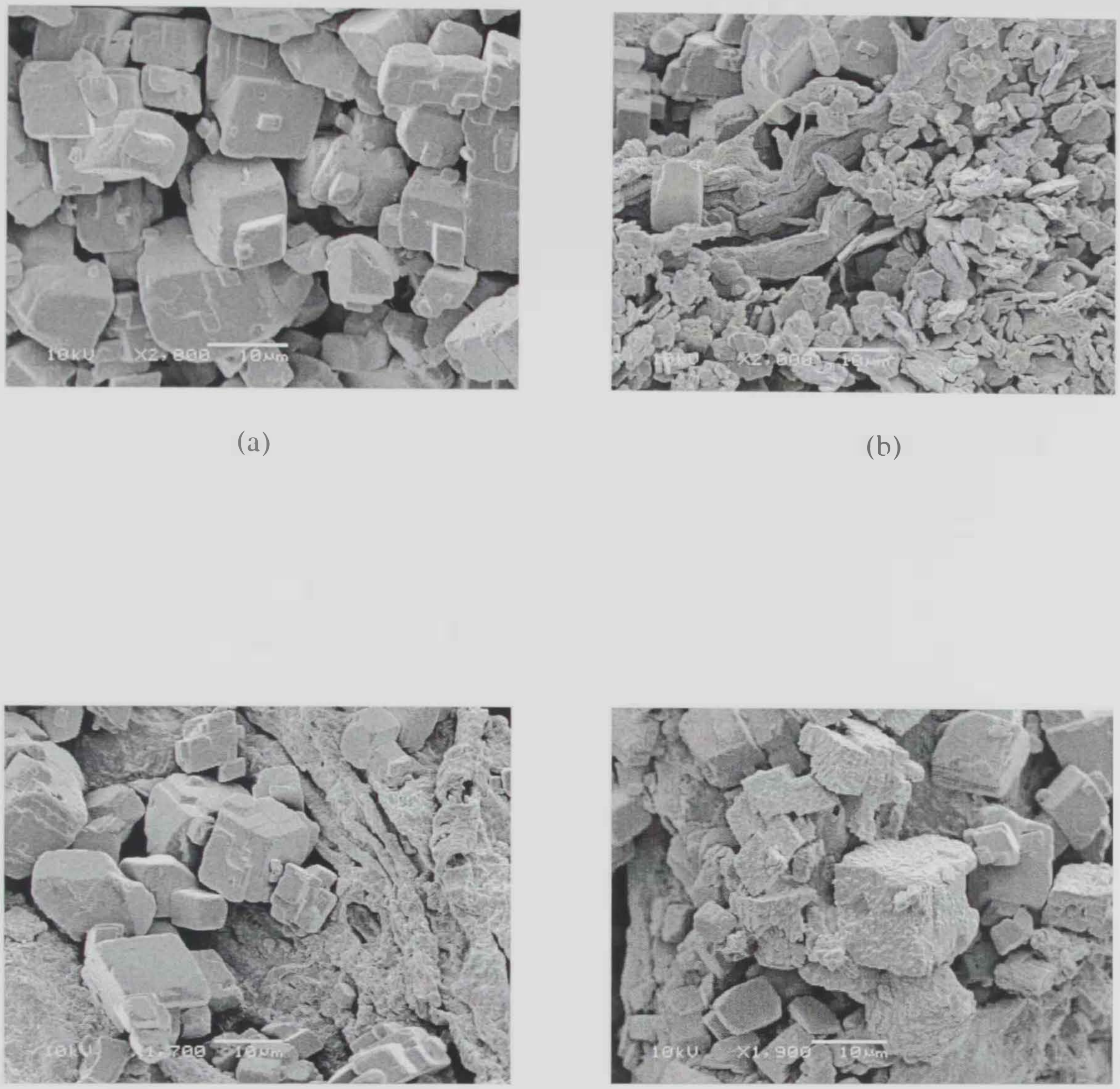


Figure 4.33: Variation of water soluble sulfate with time and amount of added elemental sulfur for mix design type IV samples (with addition of 30% $CaCO_3$).



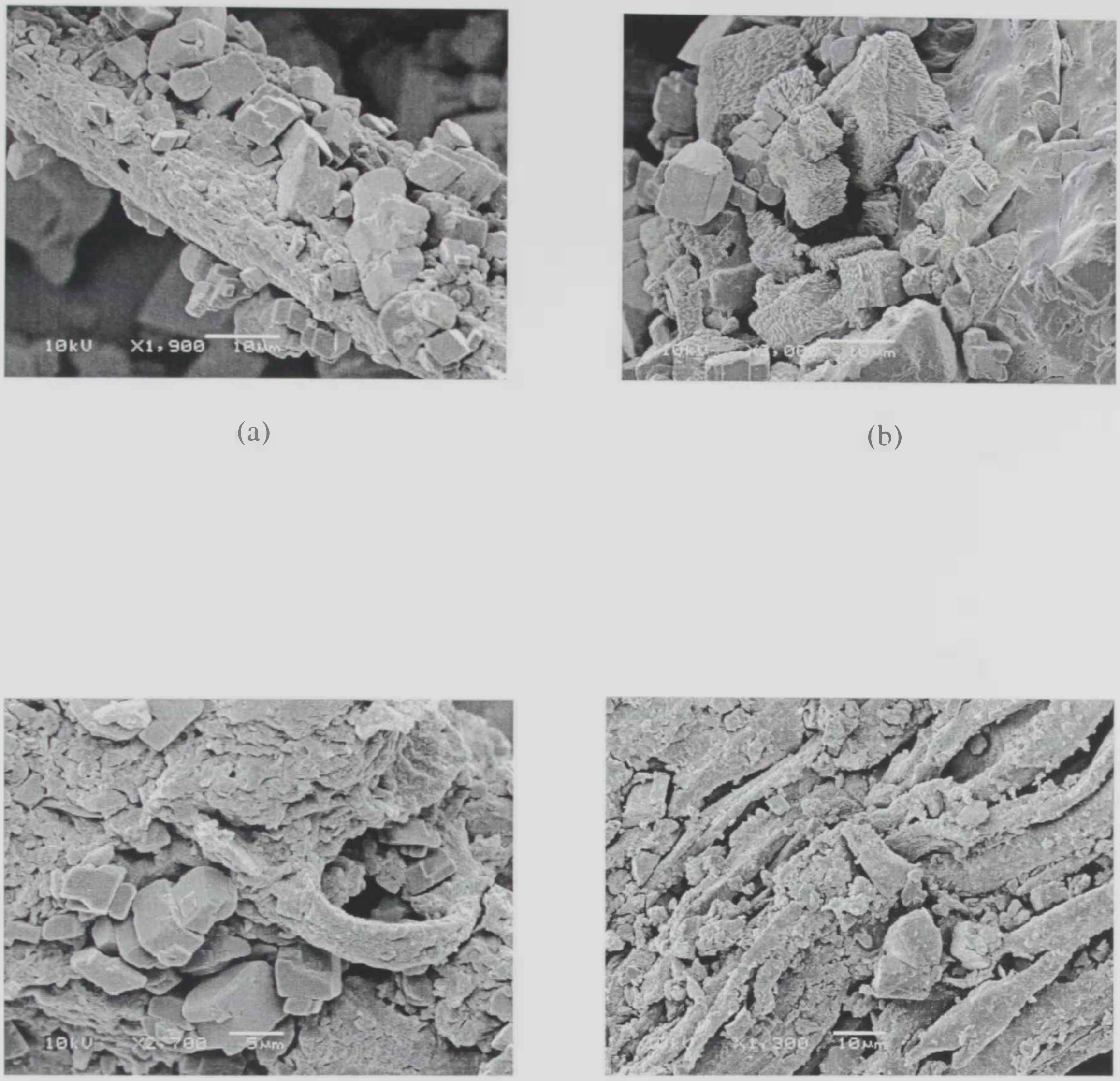
(a)

(b)

(c)

(d)

Figure 4.34: SEM micrograph for mix design type IV samples after 20 days at different magnification levels and sulfur content: (a) X2000: 0%S; (b) X2000: 1%S; (c) X1700: 2%S; (d) X1900: 3%S.



(a) (b)

(c) (d)

Figure 4.35: SEM micrograph for mix design type IV samples after 40 days at different magnification levels and sulfur content: (a) X1900: 0%S; (b) X2000: 1%S; (c) X2700: 2%S; (d) X1300: 3%S.

(a) (b)

(c) (d)

Figure 4.36: SEM micrograph for mix design type IV samples after 80 days at different magnification levels and sulfur content: (a) X2000: 0%S; (b) X1400: 1%S; (c) X1000: 2%S; (d) X1600: 3%S.

4.8 EFFECT OF ELEMENTAL SULFUR APPLICATION ON MIX DESIGN TYPE V:

The effect of added elemental sulfur on mix design type V (with addition of 40% $CaCO_3$) was determined by measuring the pH levels, electrical conductivity (EC) in µS/cm and water soluble SO_4^{-2} (g/kg). It should be noted that, as previously discussed, the mix design type V contained initial carbonates in the amount of 16.2% in the used sand. So the initial carbonates in the sand used in mix design type V was also 16.2% and so the total percentage of $CaCO_3$ in mix design type V was 56.2%. The variations of these parameters as a function of time are discussed below.

4.8.1 pH Variation:

The variation of pH as a function of time and sulfur addition is shown in Figure 4.37. The experimental results of pH variation of the mix design type V samples without addition of elemental sulfur decreased from 8.92 to 7.99 after 5 days but increased to 8.25 after 10 days then decreased again to 8.14, 8.09 and 8.0 after 20, 40 and 80 days, respectively. This is attributed to the amount of sulfur which was found mainly in added organic manure (1%) and in the sand as discussed in Chapter 3. The total sulfur measured as sulfate were 9409, 326, 0.4 mg/kg in organic matter, sand and $CaCO_3$, respectively. This means that a pH reduction of approximately 0.59 units has been achieved after 5 days and pH continued to decrease until 80 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite.

The results indicate that the addition of 1% S reduced the pH level from 8.89 to 7.61 and 7.59 after 5 and 10 days, respectively. Then it increased to 7.78 after 20 days but then decreased to 7.37 and 7.44 after 40 and 80 days, respectively. This means that a pH reduction of approximately 1.28 units has been achieved after 5 days due to formation of sulfuric acid, carbonic acid and dissolution of calcite. Then, increased by 0.19 units after 20 days due to the formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide but decreased again until 80 days due to formation of tricalcium aluminate (C_3A), tricalcium aluminate hydrate (C_3AH_6), tetracalcium aluminate hydrate (C_4AH_{13}) and calcium monosulfoaluminate.. The addition of 2% S reduced the pH level from 8.89 to 7.28 after 5 days then increased to 7.41, 7.89, after 10 and 20 days, respectively. Then, pH decreased again to 7.44 and 7.41 after 40 and 80 days, respectively. This means that a pH reduction of approximately 1.71 units has been achieved after 5 days.

The addition of 3% S reduced the pH level from 8.91 to 7.21 after 5 days then increased to 7.49 and 7.66 after 10 and 20 days, respectively. Then it decreased again to 7.39 and 7.40 after 40 and 80 days, respectively. This means that a pH reduction of approximately 1.70 units has been achieved after 5.

Based on both the possible chemical reactions discussed previously as well as results, the pH first reduced because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it increased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it decreased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of pH variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.296 with 3 degrees of freedom, indicating that addition of sulfur has no significance (P-value > 0.05) on the changes in pH value. Also there was a little difference in the mean as shown in Table 4.17.

Table 4.17: One – way stacked ANOVA analysis for pH results of mix design type V samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	8.2317	7.7800	7.7200	7.6767
StDiv	0.3506	0.5623	0.6102	0.6217

4.8.2 Electrical Conductivity (EC) Variation:

The variation of EC as a function of time and sulfur addition is shown in Figure 4.38. The EC of the mix design type V samples without addition of elemental sulfur increased from 328 to 340 and 522 μS/cm after 5 and 10 days, respectively. Then, decreased to 307 μS/cm after 20 days but increased again to 469 and 610 μS/cm after 40 and 80 days, respectively. This can be attributed to: (1) the amount of organic manure that the mix design type V sample contains (1%); (2) the amount of total sulfur measured as sulfate that the organic manure contains 9409 mg/kg, and (3) the amount of total sulfur measured as sulfate of 326, 0.4 mg/kg in sand and $CaCO_3$, respectively. Due to sulfur oxidation, pH decreased and the amount of soluble ions increased leading to an increase of EC.

The results indicate that the addition of 1%S increased EC from 329 to 609 and 1625 μS/cm after 5 and 10 days then decreased to 1050 μS/cm after 20 days but increased again to 1620 and 2440 μS/cm after 40 and 80 days, respectively. This means that EC increase of 1296 μS/cm has been achieved after 10 days.

Also the addition of 2%S increased EC from 323 to 1681, 3030 μS/cm after 5 and 10 days, respectively. Then, decreased to 883 μS/cm after 20 days but increased to 1350 and 2280 μS/cm after 40 and 80 days, respectively. This means that EC increase of 1352 and 2707 μS/cm has been achieved after 5 and 10 days, respectively.

The addition of 3% S also increased EC from 326 to 1960, 2540 μS/cm after 5 and 10 days, respectively. Then, decreased to 628 μS/cm after 20 days but increased again to 1961 and 2530 μS/cm after 40 and 80 days, respectively. This means that EC increase of 1634 and 2214 μS/cm has been achieved after 5 and 10 days, respectively. The increase in soluble salts as measured by soil EC was due to dissolution of $CaCO_3$ by H_2SO_4 (Cifuentes and Lindeman, 1993).

Based on both the possible chemical reactions discussed previously as well as the experimental results, the EC first increased because of formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it decreased because of formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. Then it increased again because of formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calciummonosulfoaluminate.

The experimental results of EC variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.000 with 3 degrees of freedom, indicating that addition of sulfur has highly

significance (P-value < 0.05) on the changes in EC value. Also there was a difference in the mean as shown in Table 4.18.

Table 4.18: One-way stacked ANOVA analysis for EC results of the mix design type V samples

	1 (0%S)	2 (1%S)	3 (2%S)	4 (3%S)
Mean	449.6	1468.8	1844.8	1923.8
StDiv	126.2	690.1	835.3	779.3

4.8.3 Oxidation of Elemental Sulfur:

Oxidation of elemental sulfur was evaluated based on the amount of measured water soluble sulfate. Therefore, Figure 4.39 shows the amount of water soluble sulfate as a function of time and amount of elemental sulfur added. Thus, the Figure indicates that the addition of 1% S, 2%S and 3%S kept the amount of water soluble SO_4^{-2} higher than without addition of elemental sulfur.

In addition of 1%S, the amount of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 day to 1.8 and 1.2 g/kg after 10 and 20 days, respectively. Then, it increased to 1.8 and 2.1 g/kg after 40 and 80 days, respectively. Whereas, the amount of water soluble SO_4^{-2} in samples without addition of elemental sulfur decreased from 8.2 g/kg at 0 day to 0.1 after 10 days and then remained constant at 0.1 g/kg after 20, 40 and 80 days, respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur. Also in addition of

2% S the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 days to 2.0. 1.6 and 1.6 g/kg after 10. 20 and 40 days. respectively. Then. it increased to 2.3 g/kg after 80 days. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

Also in addition of 3% S. the amounts of water soluble SO_4^{-2} decreased from 8.2 g/kg at 0 days to 2.1 and 1.7 g/kg after 10 and 20 days. respectively. Then. it increased to 2.1 and 2.2 g/kg after 40 and 80 days. respectively. This means that oxidation of elemental sulfur continued to progress with some variations between time periods but resulting in higher amount of available water soluble sulfate than in samples without addition of elemental sulfur.

It can be observed that the high amount of initial water soluble SO_4^{-2} in all samples was due to addition of organic manure (1%) which had 8.17 g/kg water soluble SO_4^{-2} and sand which had 0.03 g/kg water soluble SO_4^{-2}. Also the presence of water soluble SO_4^{-2} was due to sulfur oxidation which was found mainly in the added organic manure (1%) and in the sand. The total sulfur measured as sulfate were 9409. 326. 0.4 mg/kg in organic manure. sand and $CaCO_3$ respectively. This initial amount was completely reduced after 10 days in samples without addition of elemental sulfur. Also there were variations of water soluble SO_4^{-2} between the time periods for samples treated by elemental sulfur. This could be attributed to: (1) neutralization of calcium carbonate by H_2SO_4 (Cifuentes and Lindeman, 1993) and formation of both gypsum [$CaSO_4.2H_2O$] and carbonic acid [[H_2CO_3]; (2) formation of calcium monosulfoaluminate (Mohamed and Antia. 1998; Mohamed 2003); and (3) sulfate reduction into hydrogen sulfide (H_2S)

(Lecture 23, February 2001, Alken Murray Corp., March 2001, Potash & Phosphate Institute of Canada, March 2001).

The initial available sulfate in the irrigation water was completely consumed by the substrate as indicated from the results of the reference sample (0%S added). However, with the addition of sulfur, the available sulfate increased during the same period (10 days) due to possible formation of sulfuric acid, carbonic acid and dissolution of calcite. Then it continued to increase from 10 to 20 days due to formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate and calcium monosulfoaluminate. From 20 to 40 days, it decreased due to formation of secondary gypsum, calcite, calcium hydroxide and ionization of calcium hydroxide. From 40 to 80 days, it increased due to generation of sulfuric acid, carbonic acid and dissolution of calcite.

The experimental results of sulfate variations were further studied via the use of statistical analysis. The analysis of variance (One-way stacked ANOVA) p- value was found to be 0.000 with 3 degrees of freedom, indicating that addition of sulfur has highly significance ($P\text{-value} < 0.05$) on the changes in sulfate value. Also there was a difference in the mean as shown in Table 4.19.

Table 4.19: One-way stacked ANOVA analysis for sulfate results of the mix design type V samples

	1 (0%S)	**2 (1%S)**	**3 (2%S)**	**4 (3%S)**
Mean	0.1000	1.7250	1.8750	2.0250
StDiv	0.0000	0.3775	0.3403	0.2217

4.8.4 Mineral Formation:

To identify whether or not gypsum has been formed, x-ray diffraction analysis (XRD), scanning electron microscope (SEM) and Energy Dispersive X-ray (EDX) were utilized. For mix design type V all samples were examined by XRD analysis, after all time periods (5, 10, 20, 40 and 80 days). In all tested samples, the major mineral found was quartz and calcite. Also the minor formed minerals were examined after 5, 10, 20 and 40 days. In all samples, plagioclase and calcite were found but there wasn't any minor mineral in mix design type V samples treated by 3%S after 80 days as shown in Table 4.1.

The SEM results for mix design type V samples (21-24) after 20, 40 and 80 days are shown in Figures 4.40- 4.42. Figures 4.40 (a) to (d) show the mix design type V images at magnification levels of X4300, X1100, X4000, and X2000 after 20 days. Figures 4.41 (a) to (d) show the mix design type V images at magnification levels of X650, X1500, X1800, and X2500 after 40 days. Figures 4.42 (a) to (d) show the mix design type V images at magnification levels of X1800, X1300, X2500, and X2000 after 80 days. The major minerals are quartz and calcite and minor mineral is plagioclase. No gypsum was formed after 20, 40 and 80 days in mix design type V samples.

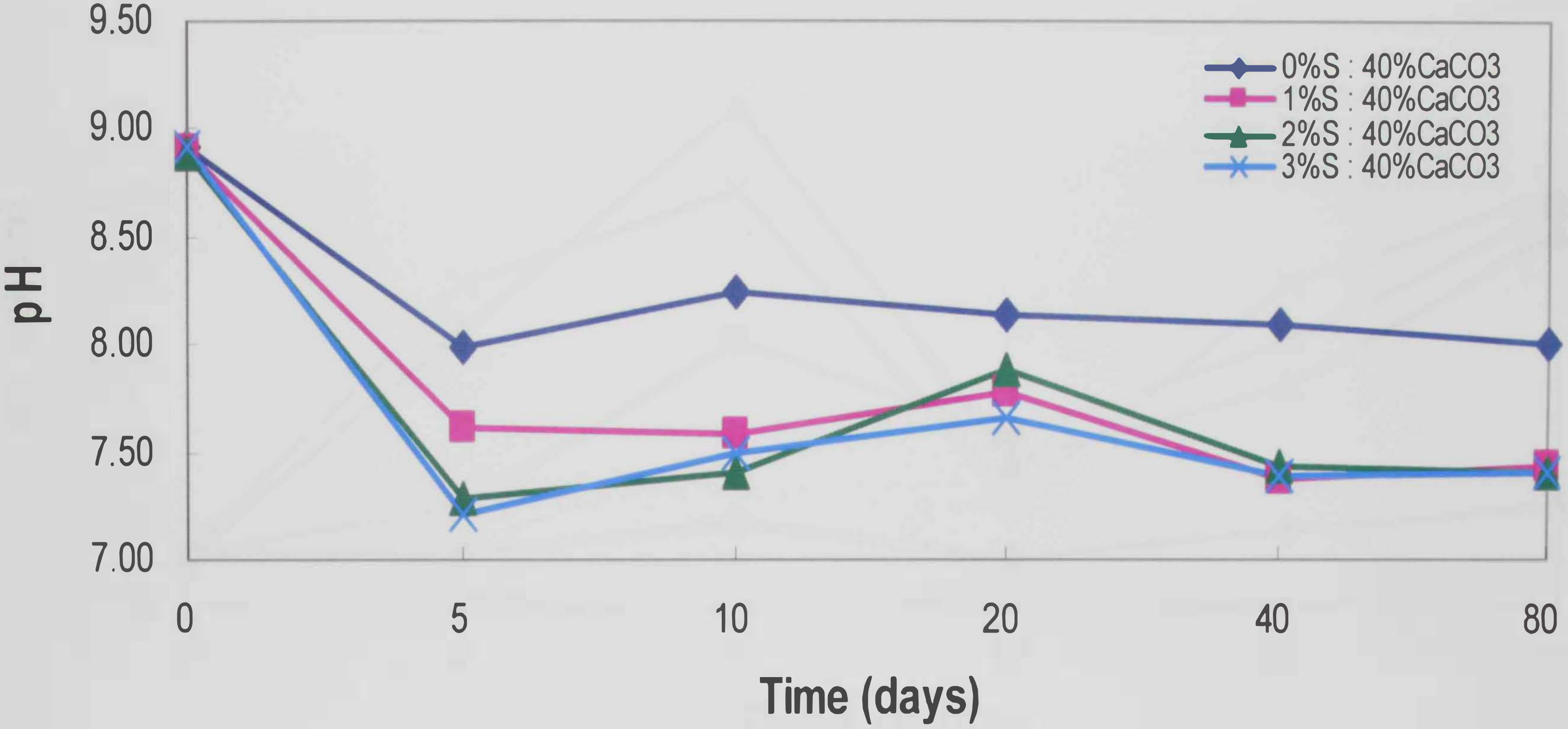


Figure 4.37: Variation of pH with time and amount of added elemental sulfur for mix design type V samples (with addition of 40% $CaCO_3$).

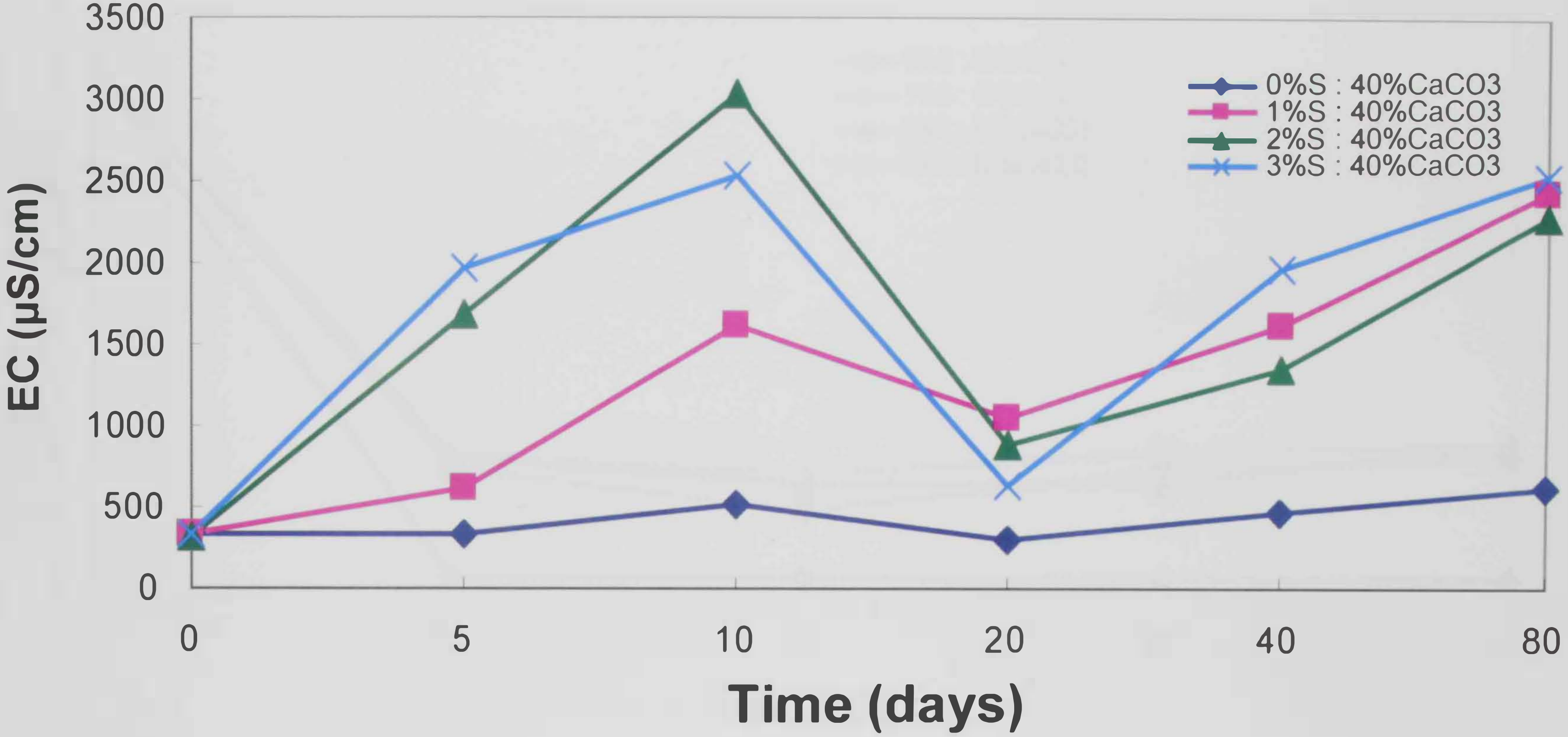


Figure 4.38: Variation of electrical conductivity (EC) with time and amount of added elemental sulfur for mix design type V samples (with addition of 40% $CaCO_3$).

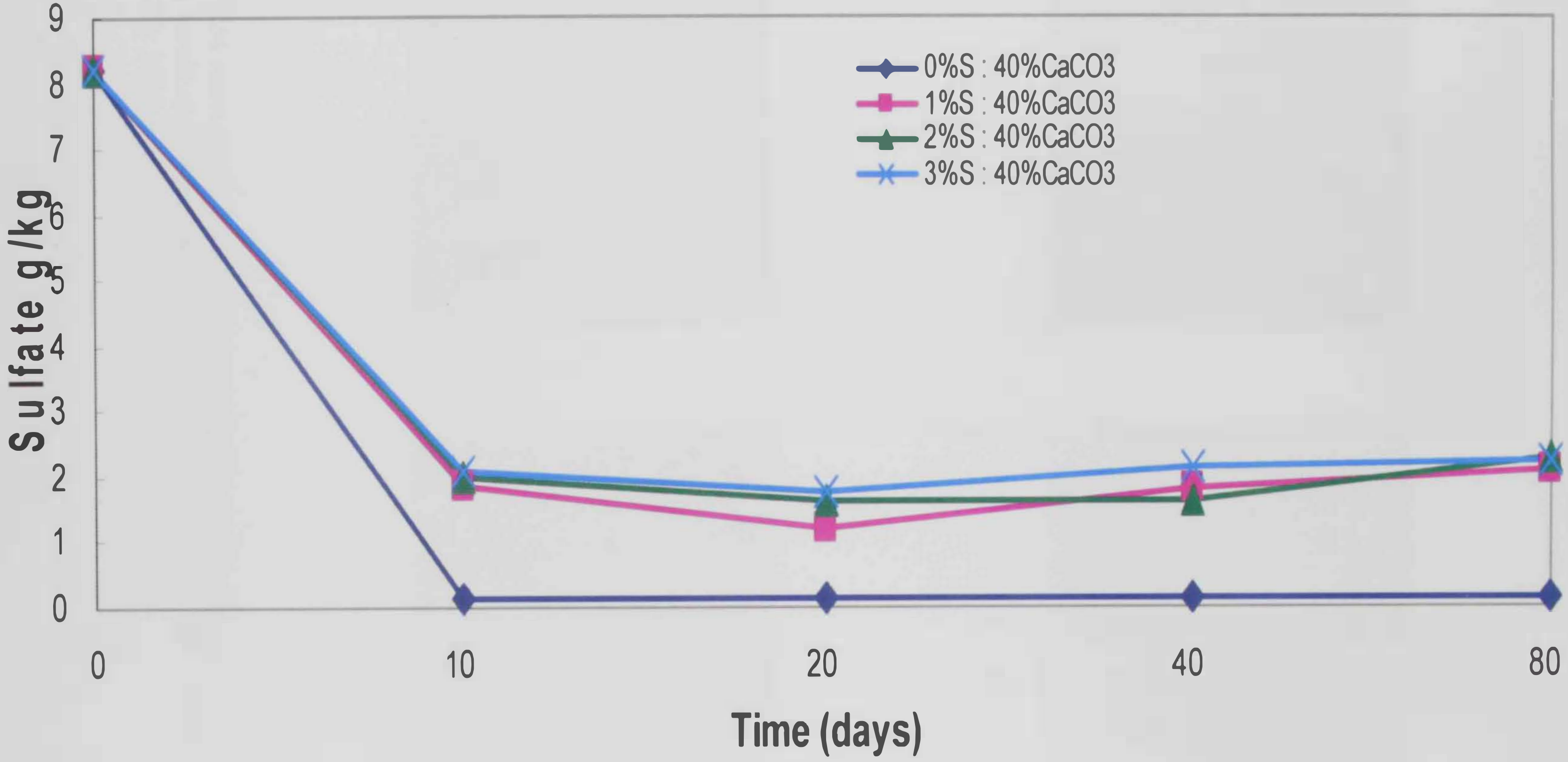
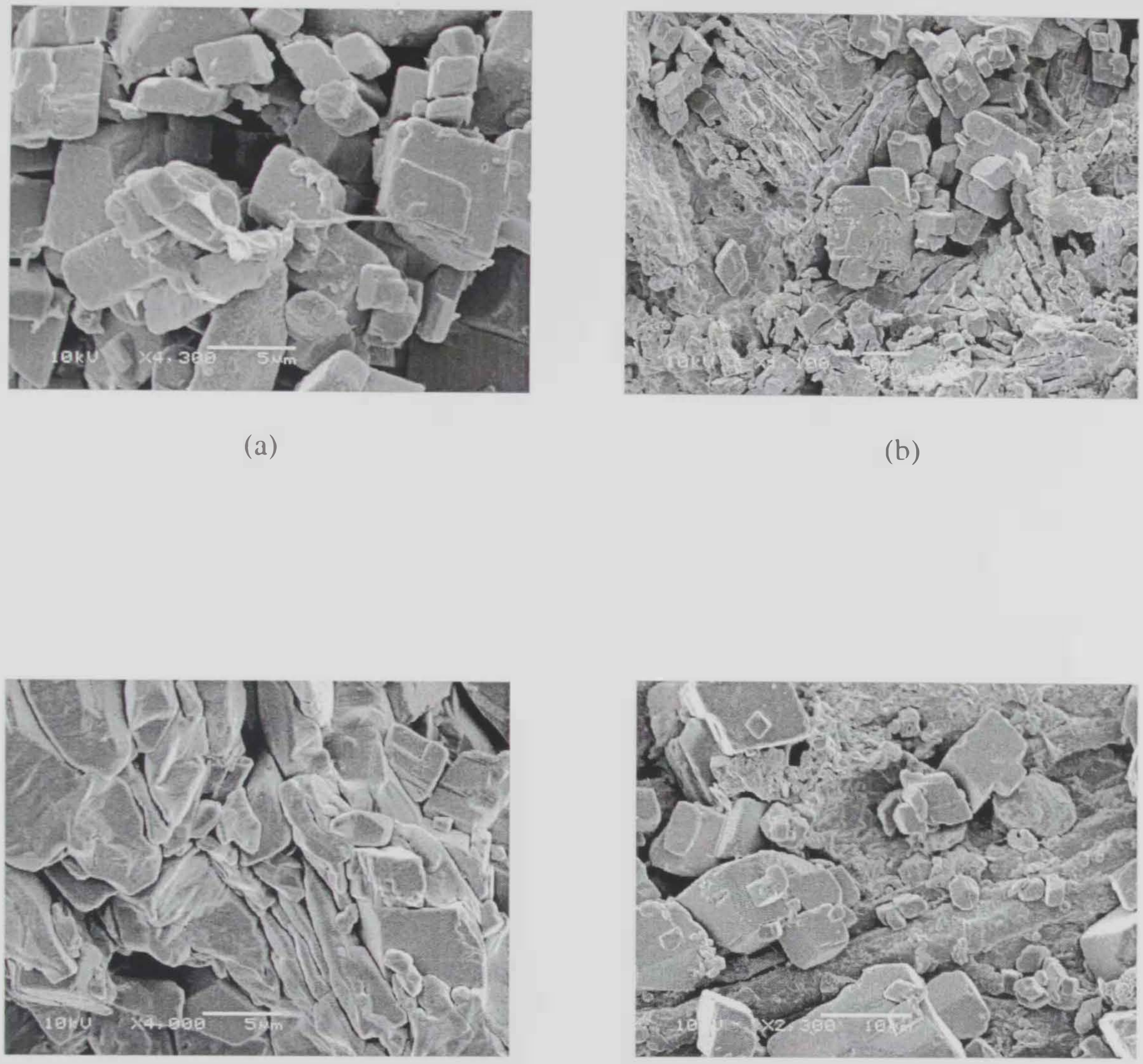


Figure 4.39: Variation of water soluble sulfate with time and amount of added elemental sulfur for mix design type V samples (with addition of 40% $CaCO_3$).



(a)

(b)

(c)

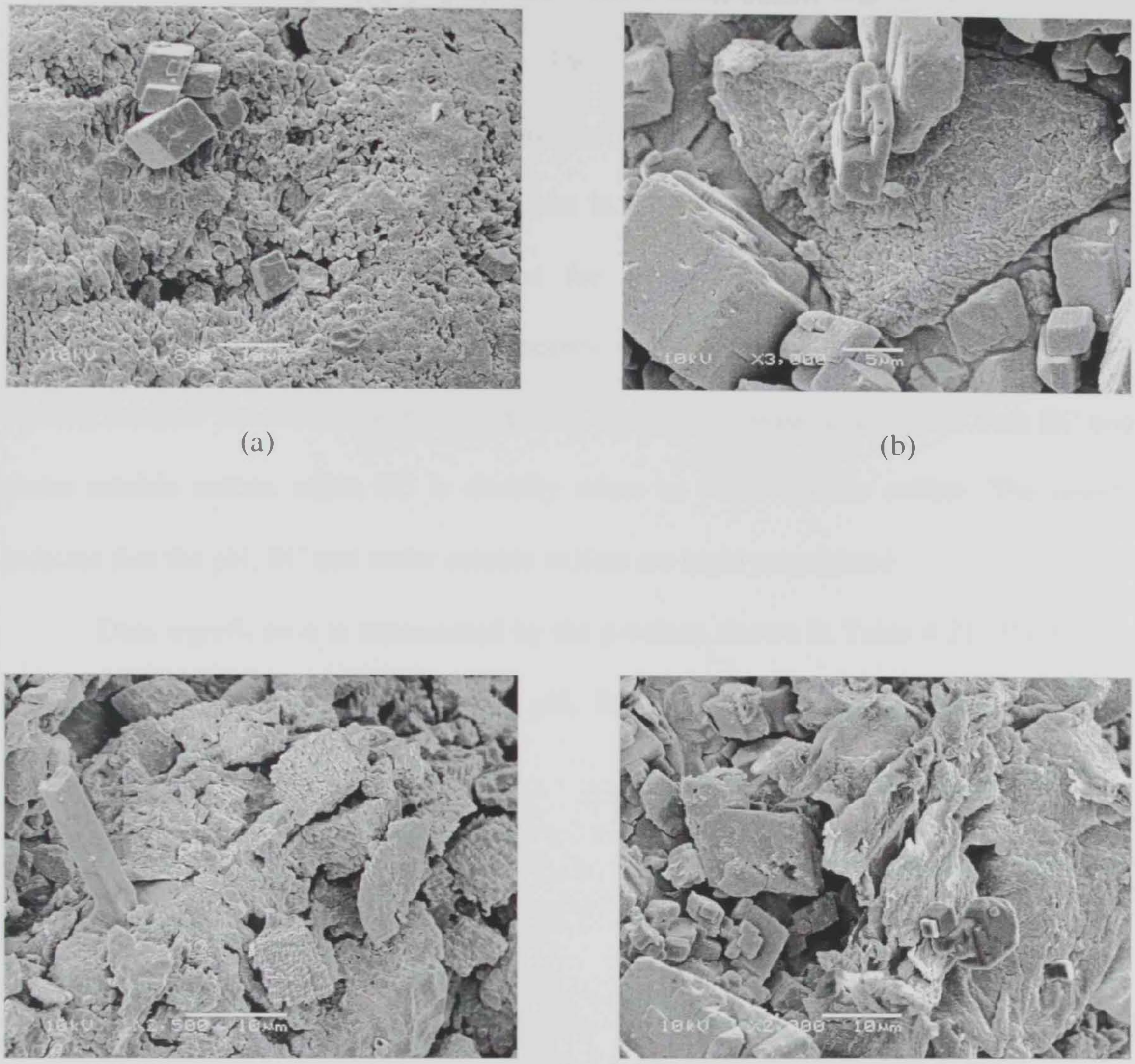
(d)

Figure 4.40: SEM micrograph for mix design type V samples after 20 days at different magnification levels and sulfur content: (a) X4300: 0%S; (b) X1100: 1%S; (c) X4000: 2%S; (d) X2300: 3%S.

(a) (b)

(c) (d)

Figure 4.41: SEM micrograph for mix design type V samples after 40 days at different magnification levels and sulfur content: (a) X650: 0%S; (b) X1500: 1%S; (c) X1800: 2%S; (d) X2500: 3%S.



(a) (b)

(c) (d)

Figure 4.42: SEM micrograph for mix design type V samples after 80 days at different magnification levels and sulfur content: (a) X1600: 0%S; (b) X3000: 1%S; (c) X2500: 2%S; (d) X2300: 3%S.

4.9 CORRELATION ANALYSIS:

Correlation analysis for pH, EC and water soluble sulfate was performed by using MINTAB software (Pearson correlation). The experimental results of pH, EC and water soluble sulfate for all the tested 120 samples shown in Table 4.20 were used in the analysis. From the results which are shown in Table 4.21 for Pearson correlation and significance (p-value). Negative values for Pearson correlation indicate that the parameters are inversely related while positive values indicate that the parameters are directly related. Therefore, the table indicates the pH is inversely related to both EC and water soluble sulfate while EC is directly relate to water soluble sulfate. The results indicate that the pH, EC and water soluble sulfate are highly correlated.

Data significance is represented by the p-values shown in Table 4.21. The results indicate that the relationships between pH, EC and water soluble sulfate are highly significant (p-value < 0.05).

Table 4.20: Results of pH, EC and water soluble sulfate (120 samples) for all time periods

Sample No.	Mix design type	Samples	Time periods (days)	pH	EC	sulfate
1	basic mix Design	0%S : 0%CaCO3	5	8.06	625	*
2		1%S : 0%CaCO3		7.23	2570	*
3		2%S : 0%CaCO3		7.3	1024	*
4		3%S : 0%CaCO3		7.07	2630	*
5	mix Design type I	0%S : 5%CaCO3	5	8.02	522	*
6		1%S : 5%CaCO3		7.62	2070	*
7		2%S : 5%CaCO3		7.16	3090	*
8		3%S : 5%CaCO3		7.69	1261	*
9	mix Design type II	0%S : 10%CaCO3	5	9	352	*
10		1%S : 10%CaCO3		7.51	1910	*
11		2%S : 10%CaCO3		7.45	2860	*
12		3%S : 10%CaCO3		7.55	1564	*
13	mix Design type III	0%S : 20%CaCO3	5	7.22	1910	*
14		1%S : 20%CaCO3		7.36	1240	*
15		2%S : 20%CaCO3		7.41	1870	*
16		3%S : 20%CaCO3		7.5	1690	*
17	mix Design type IV	0%S : 30%CaCO3	5	8.08	569	*
18		1%S : 30%CaCO3		7.57	1640	*
19		2%S : 30%CaCO3		7.5	2080	*
20		3%S : 30%CaCO3		7.51	1520	*
21	mix Design type V	0%S : 40%CaCO3	5	7.99	340	*
22		1%S : 40%CaCO3		7.61	609	*
23		2%S : 40%CaCO3		7.28	1681	*
24		3%S : 40%CaCO3		7.21	1960	*
25	basic mix Design	0%S : 0%CaCO3	10	7.77	537	0.2
26		1%S : 0%CaCO3		7.24	3220	3
27		2%S : 0%CaCO3		7.29	2500	3.4
28		3%S : 0%CaCO3		7.39	2480	3.4
29	mix Design type I	0%S : 5%CaCO3	10	8.16	423	0.1
30		1%S : 5%CaCO3		7.44	1988	2.4
31		2%S : 5%CaCO3		7.47	2470	2.9
32		3%S : 5%CaCO3		7.45	2410	3
33	mix Design type II	0%S : 10%CaCO3	10	8.25	305	0.1
34		1%S : 10%CaCO3		7.43	2950	3
35		2%S : 10%CaCO3		7.44	2220	2.9
36		3%S : 10%CaCO3		7.41	2980	3.3

Table 4.19 continued

37	mix Design type III	0%S : 20%CaCO3	10	7.65	1681	0.1
38		1%S : 20%CaCO3		7.49	1828	2.8
39		2%S : 20%CaCO3		7.5	2480	3.4
40		3%S : 20%CaCO3		7.37	3170	3
41	mix Design type IV	0%S : 30%CaCO3	10	8.14	363	0.1
42		1%S : 30%CaCO3		7.7	1007	2.2
43		2%S : 30%CaCO3		7.51	2210	3
44		3%S : 30%CaCO3		7.43	3370	3.2
45	mix Design type V	0%S : 40%CaCO3	10	8.25	522	0.1
46		1%S : 40%CaCO3		7.59	1625	1.8
47		2%S : 40%CaCO3		7.41	3030	2
48		3%S : 40%CaCO3		7.49	2540	2.1
49	basic mix Design	0%S : 0%CaCO3	20	7.69	1313	0.4
50		1%S : 0%CaCO3		6.88	1457	3.7
51		2%S : 0%CaCO3		7.15	1551	4.5
52		3%S : 0%CaCO3		6.68	1524	5.2
53	mix Design type I	0%S : 5%CaCO3	20	8.07	310	0.3
54		1%S : 5%CaCO3		7.11	1330	2.8
55		2%S : 5%CaCO3		7.19	1226	3.3
56		3%S : 5%CaCO3		7.3	1178	3
57	mix Design type II	0%S : 10%CaCO3	20	8.35	280	0.1
58		1%S : 10%CaCO3		7.38	1041	2.5
59		2%S : 10%CaCO3		7.47	1100	2.1
60		3%S : 10%CaCO3		7.41	1114	2.6
61	mix Design type III	0%S : 20%CaCO3	20	8.3	294	0.1
62		1%S : 20%CaCO3		7.35	974	2.4
63		2%S : 20%CaCO3		7.37	1263	2.6
64		3%S : 20%CaCO3		7.43	988	2.1
65	mix Design type IV	0%S : 30%CaCO3	20	8.18	280	0.1
66		1%S : 30%CaCO3		7.46	955	1.6
67		2%S : 30%CaCO3		7.6	768	1.5
68		3%S : 30%CaCO3		7.67	667	1.4
69	mix Design type V	0%S : 40%CaCO3	20	8.14	307	0.1
70		1%S : 40%CaCO3		7.78	1050	1.2
71		2%S : 40%CaCO3		7.89	883	1.6
72		3%S : 40%CaCO3		7.66	628	1.7
73	basic mix Design	0%S : 0%CaCO3	40	7.96	654	0.2
74		1%S : 0%CaCO3		7.19	1400	2.2
75		2%S : 0%CaCO3		7.13	1600	2.5
76		3%S : 0%CaCO3		7.12	2050	2.8

Table 4.19 continued

77	mix Design type I	0%S : 5%CaCO3	40	8.21	339	0.1
78		1%S : 5%CaCO3		7.44	1300	1.5
79		2%S : 5%CaCO3		7.4	1730	2.1
80		3%S : 5%CaCO3		7.26	1460	1.9
81	mix Design type II	0%S : 10%CaCO3	40	8.17	408	0.1
82		1%S : 10%CaCO3		7.41	1650	2.4
83		2%S : 10%CaCO3		7.36	1670	2.2
84		3%S : 10%CaCO3		7.37	1880	3
85	mix Design type III	0%S : 20%CaCO3	40	8.15	440	0.1
86		1%S : 20%CaCO3		7.31	1799	2.2
87		2%S : 20%CaCO3		7.38	1642	2.2
88		3%S : 20%CaCO3		7.39	2050	3.1
89	mix Design type IV	0%S : 30%CaCO3	40	8.18	481	0.1
90		1%S : 30%CaCO3		7.45	1538	1.8
91		2%S : 30%CaCO3		7.37	1981	1.7
92		3%S : 30%CaCO3		7.34	1907	3
93	mix Design type V	0%S : 40%CaCO3	40	8.09	469	0.1
94		1%S : 40%CaCO3		7.37	1620	1.8
95		2%S : 40%CaCO3		7.44	1305	1.6
96		3%S : 40%CaCO3		7.39	1961	2.1
97	basic mix Design	0%S : 0%CaCO3	80	7.87	733	0.2
98		1%S : 0%CaCO3		7.26	3290	3.9
99		2%S : 0%CaCO3		7.28	2700	3.3
100		3%S : 0%CaCO3		7.27	2630	3.2
101	mix Design type I	0%S : 5%CaCO3	80	8.07	600	0.1
102		1%S : 5%CaCO3		7.29	2550	2.6
103		2%S : 5%CaCO3		7.35	2630	3.1
104		3%S : 5%CaCO3		7.34	2650	3.9
105	mix Design type II	0%S : 10%CaCO3	80	8.07	511	0.1
106		1%S : 10%CaCO3		7.37	2570	2.8
107		2%S : 10%CaCO3		7.43	2680	3
108		3%S : 10%CaCO3		7.4	2530	4.1
109	mix Design type III	0%S : 20%CaCO3	80	8	747	0.1
110		1%S : 20%CaCO3		7.34	2500	2.5
111		2%S : 20%CaCO3		7.3	2730	3.3
112		3%S : 20%CaCO3		7.29	2820	3.4
113	mix Design type IV	0%S : 30%CaCO3	80	7.51	457	0.1
114		1%S : 30%CaCO3		7.33	2450	2.3
115		2%S : 30%CaCO3		7.39	2510	2.4
116		3%S : 30%CaCO3		7.39	2740	4.2

Table 4.19 continued

117	mix Design type V	0%S : 40%CaCO3	80	8	610	0.1
118		1%S : 40%CaCO3		7.44	2440	2.1
119		2%S : 40%CaCO3		7.41	2280	2.3
120		3%S : 40%CaCO3		7.4	2530	2.2

* Results are not available

Table 4.21: Pearson correlation and significance.

		pH	**EC**
EC	Pearson correlations	- 0.689	
	P- value	0.000	
SULFATE	Pearson correlations	- 0.869	0.773
	P- value	0.000	0.000

CHAPTER 5

SUMMARY, CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH

5.1 SUMMARY:

In this study soil samples obtained from AlAin area, in United Arab Emirates were characterized for its physical, chemical and mineralogical analysis. Granular sulfur samples obtained from Al Ruwais Refinery were collected and analyzed for its physical and chemical analysis. Water samples identified as irrigation water were collected from Al Ruwais area and analyzed for its chemical constituents. Organic matter identified as organic manure, which is used for agriculture purposes, was obtained and characterized for its chemical constituents. Commercial calcium carbonate samples were obtained and analysis for its chemical composition.

Different designs mixes were prepared based on its content of sulfur and calcium carbonate. Different application rates of elemental sulfur (0, 1, 2, and 3%S) were added to soils having different amounts of calcium carbonates (i.e., 16.2, 21.2, 26.2, 36.2, 46.2, and 56.2% of $CaCO_3$ for basic mix design, and mix designs types I, II, III, IV, and V, respectively). Experiments were conducted for these mixes. Testing temperature was set at 39°C and periods of time of 5, 10, 20, 40, and 80 days. Water was added as required until saturation level was achieved. After each time period, pH, EC and sulfate were examined for each sample. Also, each sample was examined for minerals formation by x-ray diffraction analysis, scanning electron microscope (SEM), and energy dispersive x-ray analysis (EDX).

Data was analyzed statistically by using MINITAB software; one- way stacked ANOVA was used to calculate the significance between sulfur application rates for each mix design. Also, data were analyzed to calculate the correlation between pH, EC, and sulfate by using Pearson correlation.

5.2 CONCLUSION:

The results of this investigation could be concluded as discussed below:

5.2.1 pH Variations:

a) For samples containing 16.2% $CaCO_3$ and 1%S, pH decreased by about 0.7 unit after 20 days of treatment.

b) For samples containing 16.2% $CaCO_3$ and 2%S, pH decreased by about 1 unit after 20 days of treatment. pH remains more or less constant after this time.

c) Samples containing 16.2% $CaCO_3$ and 3%S, pH decreased by about 1.8 units after 20 days of treatment. pH remains more or less constant after this time.

Statistical analysis indicates that sulfur addition for all treatments of basic mix design, mix design type I, mix design type III, mix design type IV, and mix design type V has no influence on pH changes but has high significance on pH changes for mix design type II. However, there was no difference between the sulfur application rates.

5.2.2 Electrical Conductivity (EC) Variations:

a) For samples containing 16.2% $CaCO_3$ and 1%S, EC increases slightly as time increased.

b) For samples containing 16.2% $CaCO_3$ and 2%S, EC increased up to 10 days, decreased during time period from 10-20 days, and then increased again.

c) Samples containing 16.2% $CaCO_3$ and 3%S, EC increased up to 5 days, decreased during time period from 10-20 days, and then increased again.

Statistical analysis indicates that sulfur addition for all treatments of basic mix design, mix design type I, mix design type II, mix design type IV, and mix design type V has highly influence on EC changes but has no significance on EC changes for mix design type III.

5.2.3 Oxidation of Elemental Sulfur:

a) For samples containing 16.2% $CaCO_3$ and 1%S, the available water-soluble sulfate was consumed after 10 days.

b) For samples containing 16.2% $CaCO_3$ and 2%S, about 3 g/kg water soluble sulfate was available after 10 days and decreased to about 2 g/kg after 40 days of treatment.

c) Samples containing 16.2% $CaCO_3$ and 3%S, about 3.4 g/kg water soluble sulfate was available after 10 days and decreased to about 2.8 g/kg after 40 days of treatment and then increased to 3.2 g/kg after 80 days.

Statistical analysis indicates that sulfur addition for all treatments of all mixes has high influence on sulfur oxidation but has no significance on for mix design type III. Available water-soluble sulfate was highly correlated with EC. As sulfate increases, EC increases and vice versa.

5.2.4 Mineral Formation:

a) The recorded changes in both pH and EC were divided into three zones where different chemical reactions took place. Formation of sulfuric acid, carbonic acid and dissolution of calcite were identified as the contributing mechanisms in zone I. In zone II, the contributing mechanisms were formation of secondary gypsum, calcite, calcium hydroxide, and ionization of calcium hydroxide. For zone III, the formation of tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate, and monosulfoaluminate were identified as the contributing mechanisms.

b) In each zone, there was a strong correlation between pH and EC. As sulfate increases, EC increases and vice versa.

c) The recorded changes in water-soluble sulfate could be attributed to:

(1) Formation of sulfuric acid, carbonic acid and dissolution of calcite, for the case of an increase of the available water soluble sulfate.

(2) The formation of secondary gypsum, calcite, calcium hydroxide, ionization of calcium hydroxide, tricalcium aluminate, tricalcium aluminate hydrate, tetracalcium aluminate hydrate, and monosulfoaluminate.

d) Gypsum formation was clearly identified via x-ray diffraction analysis (XRD), scanning electron microscope (SEM), and energy dispersive x-ray analysis (EDX) for sample containing 16.2% $CaCO_3$ and 3%S.

5.2.5 Effect of Calcium Carbonate Addition:

a) As the amount of calcium carbonate increases to 21.2%, gypsum was clearly identified by XRD, SEM, and EDX for samples containing 2 and 3%S.

b) Any additional increase in $CaCO_3$ results in similar behavior to that repeated for samples containing 16.2%.

c) Statistical analysis of the experimental results reveals that changes in pH and EC due to sulfur application were highly significant indicating that samples containing 26.2% $CaCO_3$ and 25S would perform very well. Therefore, we conclude that for field application, these percentages should be adopted to obtain the desired reduction in pH and increase in EC and available water-soluble sulfate.

5.2.6 Potential Use of Elemental Sulfur for Soil Treatment:

It can be concluded that elemental sulfur is an effective amendment technique for the United Arab Emirates alkaline soils. The experimental results have indicated that 1% of elemental sulfur would be enough to reduce soil pH to a level that allows soil to be utilized for agriculture purpose.

5.3 RECOMMENDATIONS FOR FUTURE RESEARCH:

Our recommends for future research are:

1) The time period to be longer than 80 days. It may be 6 months or 1 year;

2) The calcium carbonate should be increased to 70 – 80% in the soil;

3) The temperature should be higher than 39°C by 6 degrees or more; and

4) Microbiological analysis should be performed as a function of time to identify the oxidizing/ reducing bacteria.

CHAPTER 6

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APPENDEX A

```
-----   10-Jun-03 11:47:08 AM   --------------------

Welcome to Minitab, press F1 for help.


Retrieving worksheet from file: C:\MTBWIN\DATA\0%.MTW
# Worksheet was saved on Sun Jun 08 2003

Results for: 0%.MTW

One-way ANOVA: C6 versus C7 (for pH of basic mix design)

Analysis of Variance for C6
Source     DF        SS        MS        F         P
C7          3     1.604     0.535     2.20    0.120
Error      20     4.867     0.243
Total      23     6.471
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  --------+---------+---------+-------
-
1           6    7.9700    0.2725                    (---------*--------
--)
2           6    7.3717    0.5375    (---------*----------)
3           6    7.4267    0.4874     (----------*---------)
4           6    7.3350    0.6105   (---------*----------)
                                   --------+---------+---------+-------
-
Pooled StDev =   0.4933                  7.20      7.60      8.00

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0111

Critical value = 3.96

Intervals for (column level mean) - (row level mean)

                 1           2           3

       2   -0.1992
            1.3959

       3   -0.2542     -0.8525
            1.3409      0.7425

       4   -0.1625     -0.7609     -0.7059
            1.4325      0.8342      0.8892


Retrieving worksheet from file: C:\MTBWIN\DATA\5%.MTW
# Worksheet was saved on Sun Jun 08 2003

Results for: 5%.MTW

One-way ANOVA: C6 versus C7 (for pH of mix design type I)
```

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3     1.729     0.576     2.41    0.097
Error      20     4.776     0.239
Total      23     6.505
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  --------+---------+---------+-------
-
1           6    8.1983    0.2364               (-------*-------)
2           6    7.5967    0.5575    (-------*-------)
3           6    7.5350    0.5545  (--------*-------)
4           6    7.6150    0.5301    (-------*--------)
                                   --------+---------+---------+-------
-
Pooled StDev =   0.4887                      7.50      8.00      8.50

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0111

Critical value = 3.96

Intervals for (column level mean) - (row level mean)

                  1          2          3

       2    -0.1883
             1.3917

       3    -0.1267    -0.7283
             1.4533     0.8517

       4    -0.2067    -0.8083    -0.8700
             1.3733     0.7717     0.7100


Retrieving worksheet from file: C:\MTBWIN\DATA\10%.MTW
# Worksheet was saved on Mon Jun 09 2003

Results for: 10%.MTW
```

One-way ANOVA: C6 versus C7 **(for pH of mix design type II)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3     2.750     0.917     4.11    0.020
Error      20     4.459     0.223
Total      23     7.209
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ------+---------+---------+---------
+
1           6    8.4133    0.3501                 (-------*-------)
2           6    7.6250    0.5046  (--------*-------)
```

```
3            6    7.6350    0.5035    (-------*-------)
4            6    7.6350    0.5109    (-------*-------)
                                     ------+---------+---------+---------
+
Pooled StDev =    0.4722                  7.50      8.00      8.50
9.00

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0111

Critical value = 3.96

Intervals for (column level mean) - (row level mean)

                1           2           3

       2     0.0250
             1.5517

       3     0.0150     -0.7733
             1.5417      0.7533

       4     0.0150     -0.7733     -0.7633
             1.5417      0.7533      0.7633


Retrieving worksheet from file: C:\MTBWIN\DATA\20%.MTW
# Worksheet was saved on Mon Jun 09 2003

Results for: 20%.MTW
```

One-way ANOVA: C6 versus C7 **(for pH of mix design type III)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3     0.663     0.221     0.91    0.455
Error      20     4.880     0.244
Total      23     5.543
                                     Individual 95% CIs For Mean
                                     Based on Pooled StDev
Level       N      Mean     StDev    ------+---------+---------+---------
+
1           6    7.9717    0.4688                  (-----------*-----------
)
2           6    7.5633    0.4776    (-----------*-----------)
3           6    7.5700    0.4408    (-----------*-----------)
4           6    7.7417    0.5777         (-----------*-----------)
                                     ------+---------+---------+---------
+
Pooled StDev =    0.4939                  7.35      7.70      8.05
8.40

Tukey's pairwise comparisons

    Family error rate = 0.0500
```

```
Individual error rate = 0.0111

Critical value = 3.96

Intervals for (column level mean) - (row level mean)

                 1            2            3

       2    -0.3902
             1.2069

       3    -0.3969      -0.8052
             1.2002       0.7919

       4    -0.5685      -0.9769      -0.9702
             1.0285       0.6202       0.6269


Retrieving worksheet from file: C:\MTBWIN\DATA\30%.MTW
# Worksheet was saved on Mon Jun 09 2003

Results for: 30%.MTW
```

One-way ANOVA: C6 versus C7 **(for pH of mix design type IV)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3     1.841     0.614     2.02    0.143
Error      20     6.066     0.303
Total      23     7.908
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ------+---------+---------+---------
+
1           6    8.3617    0.3573                 (--------*---------)
2           6    7.7433    0.6042   (---------*--------)
3           6    7.7200    0.6085   (--------*---------)
4           6    7.7050    0.5919   (--------*--------)
                                   ------+---------+---------+---------
+
Pooled StDev =   0.5507                7.50      8.00      8.50
9.00

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0111

Critical value = 3.96

Intervals for (column level mean) - (row level mean)

                 1            2            3

       2    -0.2720
             1.5087
```

```
        3     -0.2487     -0.8670
               1.5320      0.9137

        4     -0.2337     -0.8520     -0.8754
               1.5470      0.9287      0.9054


Retrieving worksheet from file: C:\MTBWIN\DATA\40%.MTW
# Worksheet was saved on Mon Jun 09 2003

Results for: 40%.MTW
```

One-way ANOVA: C6 versus C7 **(for pH of mix design type V)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3     1.185     0.395     1.32    0.296
Error      20     5.990     0.300
Total      23     7.175
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ------+---------+---------+---------
+
1           6    8.2317    0.3506            (---------*--------)
2           6    7.7800    0.5623   (---------*--------)
3           6    7.7200    0.6102  (--------*---------)
4           6    7.6767    0.6217 (---------*--------)
                                   ------+---------+---------+---------
+
Pooled StDev =   0.5473                 7.50      8.00      8.50
9.00

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0111

Critical value = 3.96

Intervals for (column level mean) - (row level mean)

                   1           2           3

        2     -0.4331
               1.3364

        3     -0.3731     -0.8248
               1.3964      0.9448

        4     -0.3298     -0.7814     -0.8414
               1.4398      0.9881      0.9281
```

APPENDEX B

```
MINIITAB project
——————    23-Jun-03 11:28:44 AM    ————————————————————————


One-way ANOVA: C6 versus C7 (for EC of basic mix design type)


Analysis of Variance for C6
Source      DF        SS        MS        F        P
C7           3   8005960   2668653     6.48    0.004
Error       16   6585383    411586
Total       19  14591343
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level        N      Mean     StDev --------+---------+---------+-------
-
1            5     772.4     310.2 (-------*------)
2            5    2387.4     919.5                    (-------*------)
3            5    1875.0     702.9              (------*-------)
4            5    2242.8     458.9                  (-------*-------)

                                   --------+---------+---------+-------
-
Pooled StDev =    641.6                  800      1600      2400

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0113

Critical value = 4.05

Intervals for (column level mean) - (row level mean)

                1           2           3

       2    -2777
             -453

       3    -2265        -650
               59        1674

       4    -2632       -1017       -1530
             -308        1307         794


Kruskal-Wallis Test: C6 versus C7

Kruskal-Wallis Test on C6

C7          N    Median    Ave Rank        Z
1           5     654.0         3.2    -3.19
2           5    2570.0        14.0     1.53
3           5    1600.0        11.6     0.48
4           5    2480.0        13.2     1.18
Overall    20                  10.5
```

```
H = 10.58  DF = 3  P = 0.014
```

One-way ANOVA: C6 versus C7 **(for EC of mix design type I)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3   8712938   2904313     6.42    0.005
Error      16   7240456    452529
Total      19  15953394
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  --+---------+---------+---------+---
-
1           5     438.8     122.2  (-----*------)
2           5    1475.0     877.2           (------*-----)
3           5    2229.2     744.2                   (-----*------)
4           5    1791.8     686.9               (-----*-----)
                                   --+---------+---------+---------+---
-
Pooled StDev =    672.7              0      1000      2000      3000

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0113

Critical value = 4.05

Intervals for (column level mean) - (row level mean)

                 1           2           3

       2     -2255
               182

       3     -3009       -1973
              -572         464

       4     -2571       -1535        -781
              -135         902        1656


Saving file as: C:\Program Files\MTBWIN\Data\EC1%S.MTW
```

One-way ANOVA: C6 versus C7 **(for EC of mix design type II)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3  10568449   3522816     8.47    0.001
Error      16   6651707    415732
Total      19  17220156
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ----+---------+---------+---------+-
-
1           5     371.2      92.2   (-------*------)
```

```
2           5    2024.2     754.1                          (------*------
-)
3           5    2106.0     726.8                            (------*-----
--)
4           5    2013.6     746.6                          (------*------
-)
                                           ----+---------+---------+---------+-
-
Pooled StDev =    644.8                        0       800      1600      2400

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0113

Critical value = 4.05

Intervals for (column level mean) - (row level mean)

                 1           2           3

        2     -2821
               -485

        3     -2903       -1250
               -567        1086

        4     -2810       -1157       -1075
               -475        1178        1260

Saving file as: C:\Program Files\MTBWIN\Data\EC10%.MTW
```

One-way ANOVA: C6 versus C7 **(for EC of mix design type III)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3   2894305    964768     1.45    0.264
Error      16  10613449    663341
Total      19  13507754
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  -------+---------+---------+--------
-
1           5    1014.4     736.0  (----------*-----------)
2           5    1668.2     591.6            (----------*----------)
3           5    1997.0     602.4                (-----------*---------
-)
4           5    1883.4    1182.7               (----------*----------)
                                   -------+---------+---------+--------
-
Pooled StDev =    814.5                 700      1400      2100

Tukey's pairwise comparisons
```

```
    Family error rate = 0.0500
Individual error rate = 0.0113

Critical value = 4.05

Intervals for (column level mean) - (row level mean)

                  1            2            3

         2    -2129
                821

         3    -2458        -1804
                493         1146

         4    -2344        -1690        -1362
                606         1260         1589


Saving file as: C:\Program Files\MTBWIN\Data\EC20%.MTW
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(for EC of mix design type IV)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3   8015271   2671757     5.53    0.008
Error      16   7731858    483241
Total      19  15747129
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ---+---------+---------+---------+--
-
1           5     430.0     111.4  (-------*--------)
2           5    1518.0     604.6               (-------*-------)
3           5    1909.8     668.6                    (-------*-------)
4           5    2040.8    1052.6                     (--------*------
-)
                                   ---+---------+---------+---------+--
-
Pooled StDev =    695.2              0       800      1600      2400

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0113

Critical value = 4.05

Intervals for (column level mean) - (row level mean)

                  1            2            3

         2    -2347
                171
```

```
        3       -2739       -1651
                 -221         867

        4       -2870       -1782       -1390
                 -352         736        1128


Saving file as: C:\Program Files\MTBWIN\Data\EC ANOVA.MPJ
Saving file as: C:\Program Files\MTBWIN\Data\EC30%.MTW
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(for EC of mix design type V)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3   6891574   2297191     5.11    0.011
Error      16   7188620    449289
Total      19  14080194
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ---+---------+---------+---------+--
-
1           5     449.6     126.2   (-------*-------)
2           5    1468.8     690.1             (-------*-------)
3           5    1844.8     835.3                 (-------*-------)
4           5    1923.8     779.3                  (-------*-------)
                                   ---+---------+---------+---------+--
-
Pooled StDev =    670.3               0       800      1600      2400

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0113

Critical value = 4.05

Intervals for (column level mean) - (row level mean)

                    1           2           3

        2       -2233
                  195

        3       -2609       -1590
                 -181         838

        4       -2688       -1669       -1293
                 -260         759        1135


Saving file as: C:\Program Files\MTBWIN\Data\EC ANOV.MPJ
Saving file as: C:\Program Files\MTBWIN\Data\EC40%.MTW
```

APPENDEX C

```
MINIITAB project
-----    23-Jun-03 11:28:44 AM    --------------------
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(Sulfate of basic mix design)**

```
Analysis of Variance for C6
Source     DF        SS        MS       F        P
C7          3    30.647    10.216    16.96   0.000
Error      12     7.228     0.602
Total      15    37.874
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ----+---------+---------+---------+-
-
1           4    0.2500    0.1000  (-----*----)
2           4    3.2000    0.7703                      (----*-----)
3           4    3.4250    0.8221                       (-----*----)
4           4    3.6500    1.0630                         (----*-----)
                                   ----+---------+---------+---------+-
-
Pooled StDev =   0.7761              0.0       1.5       3.0       4.5

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0117

Critical value = 4.20

Intervals for (column level mean) - (row level mean)

                 1           2           3

       2   -4.5798
           -1.3202

       3   -4.8048     -1.8548
           -1.5452      1.4048

       4   -5.0298     -2.0798     -1.8548
           -1.7702      1.1798      1.4048



Kruskal-Wallis Test: C6 versus C7

Kruskal-Wallis Test on C6

C7          N    Median    Ave Rank         Z
1           4    0.2000         2.5     -2.91
2           4    3.3500        10.0      0.73
3           4    3.3500        10.6      1.03
4           4    3.3000        10.9      1.15
Overall    16                   8.5
```

```
H = 8.54  DF = 3  P = 0.036
H = 8.61  DF = 3  P = 0.035 (adjusted for ties)

* NOTE * One or more small samples
Saving file as: C:\Program Files\MTBWIN\Data\SO4 0%.MTW
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(Sulfate of mix design type I)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3    20.537     6.846    21.30    0.000
Error      12     3.857     0.321
Total      15    24.394
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ----+---------+---------+---------+-
-
1           4    0.1500    0.1000  (----*----)
2           4    2.3250    0.5737                   (----*-----)
3           4    2.8500    0.5260                        (----*----)
4           4    2.9500    0.8185                        (-----*----)
                                   ----+---------+---------+---------+-
-
Pooled StDev =   0.5670              0.0       1.2       2.4       3.6

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0117

Critical value = 4.20

Intervals for (column level mean) - (row level mean)

                 1           2           3

       2   -3.3656
           -0.9844

       3   -3.8906     -1.7156
           -1.5094      0.6656

       4   -3.9906     -1.8156     -1.2906
           -1.6094      0.5656      1.0906


Saving file as: C:\Program Files\MTBWIN\Data\SO4 5%.MTW
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(Sulfate of mix design type II)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
```

```
C7           3    23.392     7.797    44.82    0.000
Error       12     2.087     0.174
Total       15    25.479
                                    Individual 95% CIs For Mean
                                    Based on Pooled StDev
Level       N      Mean     StDev   ---+---------+---------+---------+--
-
1           4    0.1000    0.0000   (---*---)
2           4    2.6750    0.2754                        (--*---)
3           4    2.5500    0.4655                      (---*---)
4           4    3.2500    0.6351                            (---*---)
                                    ---+---------+---------+---------+--
-
Pooled StDev =   0.4171              0.0       1.2       2.4       3.6

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0117

Critical value = 4.20

Intervals for (column level mean) - (row level mean)

                  1           2           3

       2    -3.4509
            -1.6991

       3    -3.3259     -0.7509
            -1.5741      1.0009

       4    -4.0259     -1.4509     -1.5759
            -2.2741      0.3009      0.1759


Kruskal-Wallis Test: C6 versus C7

Kruskal-Wallis Test on C6

C7          N    Median    Ave Rank         Z
1           4    0.1000         2.5     -2.91
2           4    2.6500         9.5      0.49
3           4    2.5500         8.8      0.12
4           4    3.1500        13.3      2.30
Overall    16                   8.5

H = 10.52  DF = 3  P = 0.015
H = 10.74  DF = 3  P = 0.013 (adjusted for ties)

* NOTE * One or more small samples
Saving file as: C:\Program Files\MTBWIN\Data\SO4 10%.MTW
Macro is running ... please wait
```

```
One-way ANOVA: C6 versus C7 (Sulfate of mix design type III)

Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3    21.522     7.174    40.70    0.000
Error      12     2.115     0.176
Total      15    23.637
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ---+---------+---------+---------+--
-
1           4    0.1000    0.0000  (---*---)
2           4    2.4750    0.2500                   (---*--)
3           4    2.8750    0.5737                      (---*---)
4           4    2.9000    0.5598                      (---*---)
                                   ---+---------+---------+---------+--
-
Pooled StDev =   0.4198               0.0       1.2       2.4       3.6

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0117

Critical value = 4.20

Intervals for (column level mean) - (row level mean)

                  1          2          3

      2     -3.2566
            -1.4934

      3     -3.6566    -1.2816
            -1.8934     0.4816

      4     -3.6816    -1.3066    -0.9066
            -1.9184     0.4566     0.8566


Kruskal-Wallis Test: C6 versus C7

Kruskal-Wallis Test on C6

C7           N    Median    Ave Rank         Z
1            4    0.1000         2.5     -2.91
2            4    2.4500         8.6      0.06
3            4    2.9500        11.5      1.46
4            4    3.0500        11.4      1.39
Overall     16                   8.5

H = 9.40  DF = 3  P = 0.024
H = 9.57  DF = 3  P = 0.023 (adjusted for ties)

* NOTE * One or more small samples
Saving file as: C:\Program Files\MTBWIN\Data\SO4 20%.MTW
```

```
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(Sulfate of mix design type IV)**

```
Analysis of Variance for C6
Source      DF        SS        MS        F        P
C7           3    17.462     5.821    12.11    0.001
Error       12     5.767     0.481
Total       15    23.229
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level        N      Mean     StDev ------+---------+---------+---------
+
1            4    0.1000    0.0000  (-----*-----)
2            4    1.9750    0.3304                (-----*------)
3            4    2.1500    0.6856                  (-----*-----)
4            4    2.9500    1.1590                       (------*----
-)
                                   ------+---------+---------+---------
+
Pooled StDev =    0.6933                0.0       1.2       2.4
3.6

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0117

Critical value = 4.20

Intervals for (column level mean) - (row level mean)

                  1           2           3

       2    -3.3309
            -0.4191

       3    -3.5059     -1.6309
            -0.5941      1.2809

       4    -4.3059     -2.4309     -2.2559
            -1.3941      0.4809      0.6559


Kruskal-Wallis Test: C6 versus C7

Kruskal-Wallis Test on C6

C7           N   Median   Ave Rank        Z
1            4   0.1000        2.5    -2.91
2            4   2.0000        9.3     0.36
3            4   2.0500        9.9     0.67
4            4   3.1000       12.4     1.88
Overall     16                 8.5
```

```
H = 9.44  DF = 3  P = 0.024
H = 9.59  DF = 3  P = 0.022 (adjusted for ties)

* NOTE * One or more small samples
Saving file as: C:\Program Files\MTBWIN\Data\SO4 30%.MTW
Macro is running ... please wait
```

One-way ANOVA: C6 versus C7 **(Sulfate of mix design type V)**

```
Analysis of Variance for C6
Source     DF        SS        MS        F        P
C7          3    9.6319    3.2106    41.76    0.000
Error      12    0.9225    0.0769
Total      15   10.5544
                                   Individual 95% CIs For Mean
                                   Based on Pooled StDev
Level       N      Mean     StDev  ---+---------+---------+---------+--
-
1           4    0.1000    0.0000  (---*----)
2           4    1.7250    0.3775                       (----*---)
3           4    1.8750    0.3403                         (----*---)
4           4    2.0250    0.2217                            (---*---
)
                                   ---+---------+---------+---------+--
-
Pooled StDev =   0.2773             0.00      0.70      1.40      2.10

Tukey's pairwise comparisons

    Family error rate = 0.0500
Individual error rate = 0.0117

Critical value = 4.20

Intervals for (column level mean) - (row level mean)

                1           2           3

      2     -2.2073
            -1.0427

      3     -2.3573     -0.7323
            -1.1927      0.4323

      4     -2.5073     -0.8823     -0.7323
            -1.3427      0.2823      0.4323


Kruskal-Wallis Test: C6 versus C7

Kruskal-Wallis Test on C6

C7          N    Median    Ave Rank        Z
1           4    0.1000         2.5    -2.91
2           4    1.8000         9.3     0.36
```

```
3           4    1.8000        10.0       0.73
4           4    2.1000        12.3       1.82
Overall    16                   8.5

H = 9.33  DF = 3  P = 0.025
H = 9.56  DF = 3  P = 0.023 (adjusted for ties)

* NOTE * One or more small samples
Saving file as: C:\Program Files\MTBWIN\Data\SO4 40%.MTW
Saving file as: C:\Program Files\MTBWIN\Data\SULFATE ANOVA.MPJ
```

APPENDEX D

```
—————   10-Jun-03 11:47:08 AM   ————————————————————

Welcome to Minitab, press F1 for help.

Results for: Worksheet 4


Correlations: pH, EC, SULFATE


             pH       EC
EC       -0.689
          0.000

SULFATE  -0.864    0.772
          0.000    0.000

Cell Contents: Pearson correlation
               P-Value

Saving file as: C:\Program Files\MTBWIN\Data\MINITAB PH -EC
SULFATE.MPJ
* NOTE  * Existing file replaced.
```

الهيدروجيني ولكن لها تأثيرمعنوي عالي علىتغيرات الرقم الهيدروجيني بالنسبة للنموذج الثاني وذلك عن طريق التحليل الاحصاني. في هذا النموذج الثاني هبط الرقم الهيدروجيني الى ١,١٤ ، ١,٢٢ ، ١,٢٧ ، ١,٢٤ ، ١,٢٨ وحدة بعد ٥ ، ١٠ ، ٢٠ ، ٤٠ ، ٨٠ يوما على التوالي. في جميع عينات الدراسة وجد ان اضافات الكبريت العنصري لها تأثير معنوي عالي على خاصية التوصيل الكهرباني وتركيزات السلفات الذائبة في الماء في جميع عينات النماذج ما عدا عينات النموذج الثالث. وعلاوة على ذلك وجد ان تركيزات السلفات الذائبة في الماء مرتبطة بالتغييرات في خاصية التوصيل الكهرباني بحيث اذا زاد تركيز السلفات الذائبة في الماء زادت نسبة التوصيل الكهرباني والعكس صحيح.

بســم الله الرحــمن الرحــيم

ملخص الرسالة

استخدام الكبريت العنصري الناتج من صناعة النفط والغاز في معالجة التربة

تنتج دولة الامارات العربية المتحدة كميات كبيرة من الكبريت العنصري من صناعة النفط والغاز. يستخدم الكبريت العنصري بشكل واسع كتقنية لخفض الرقم الهيدروجيني للتربة القلوية بدلا عن التقنيات الأخرى وذلك لرخص ثمنه ولكونه آمن عند الاستخدام.

في هذه الدراسة تم تحضير نماذج مختلفة تعتمد على مكوناتها من الكبريت العنصري وكربونات الكالسيوم. تم اضافة نسب مختلفة من الكبريت العنصري (٠، ١، ٢، ٣%) ونسب مختلفة من كربونات الكالسيوم الى تربة الكثبان الرملية اضافة الى نسبة كربونات الكالسيوم الطبيعية (١٦,٢ %) لتشكل في النهاية النسب التالية (١٦,٢ ، ٢١,٢ ، ٢٦,٢ ، ٣٦,٢ ، ٤٦,٢ ، ٥٦,٢ %) وهذه النسب تشكل النموذج الاساسي، النموذج الاول, النموذج الثاني، النموذج الثالث، النموذج الرابع، والنموذج الخامس على التوالي. تم كذلك اخذ قياس التغيرات في الرقم الهيدروجيني للتربة وخاصية التوصيل الكهربائي وتركيزات السلفات الذائبة في الماء على فترات من الزمن مختلفة (٠ ، ٥ ، ١٠ ، ٢٠ ، ٤٠ ، ٨٠ يوما) وتم تحليلها احصائيا. وعلاوة على ذلك تم تحديد التحولات المعدنية في التربة باستخدام تقنيات الميكروسكوب الماسح الالكتروني وجهاز حيود الاشعة السينية وجهاز تحليل العناصر عن طريق تشتت الطاقة. وتم ايضا تفسير التحولات المعدنية بواسطة التفاعلات الكيميائية المحتملة ونماذج الديناميكا الحراري.

استنتج من الدراسة ان اضافات الكبريت العنصري لعينات النموذج الاساسي، النموذج الاول، النموذج الثالث، النموذج الرابع، والنموذج الخامس لا يوجد لها تأثيرمعنوي على تغيرات الرقم

جامعة الامارات العربية المتحدة
عمادة الدراسات العليا – برنامج ماجستير علوم بيئة

استخدام الكبريت العنصري الناتج من صناعة النفط والغاز في معالجة التربة

رسالة مقدمة من الطالب
سلطان سيف راشد الشامسي
بكالوريوس علوم زراعية
جامعة السلطان قابوس- عمان (١٩٩٣)

استكمالا لمتطلبات الحصول على درجة الماجستير في علوم البيئة

(يونيو ٢٠٠٣)