USE OF WASTE PYRITE FROM MINERAL PROCESSING PLANTS IN SOIL REMEDIATION

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ABSTRACT

USE OF WASTE PYRITE FROM MINERAL PROCESSING PLANTS IN SOIL REMEDIATION

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Pyrite (FeS_2) is commonly present in complex sulphide ores in significant amounts. After the enrichment of such ores by flotation, pyrite is either produced as a separate concentrate and sold to acid manufactures or removed and disposed off as tailing. Due to lack of demand from manufacturers, most of pyrites is usually disposed off as tailing. Therefore, pyrite is usually a waste from complex sulphide ores. Yet, it may be a remediation additive for calcareous soils and calcareous- alkali soils deficient in Fe and other micronutrients such as Cu, Zn and Mn. Waste pyrite may be also an alternative amendment to gypsum because of the production of sulphuric acid which is effectively used in the reclamation of calcareous alkali soils.

The effectiveness of adding waste pyrite and sulphuric acid produced from waste pyrite to calcareous-alkali soil (Sarayköy-Ankara) and calcareous soil (Gaziantep) was studied under laboratory conditions. Pure gypsum was also used as an amendment for the comparison of the effectiveness of waste pyrite in the reclamation of alkali soils. Gypsum, powder waste pyrite and sulphuric acid were applied to the soil with reference to the gypsum requirement (GR) of the soils. Greenhouse pot tests were carried out with wheat as test plant to determine the effect of waste pyrite treatment on the plant yield (wheat) and on the amount of micronutrient (Fe, Cu, Zn, Mn) essential for plant growth. Hazard potential of pyritic tailings in terms of heavy metal contamination was also taken into account.

The results showed that the soil pH and exchangeable sodium percentage (ESP), indicators of alkalization, decreased upon pyrite addition to calcareous- alkali soils of Sarayköy-Ankara. It was also found that pyritic tailings were effective in the increasing level of essential micronutrients (Fe, Cu, Zn and Mn) for plant growth in both soils. This was ascertained by the dry matter yield of the plants in the green house pot tests. Heavy metal toxicity caused by pyrite which is a rightful concern remained well below the legal limits in the soils. Thus, it was concluded that the application of pyritic tailings promoted rapid amelioration of calcareous-alkali soil (Sarayköy-Ankara) and calcareous soil (Gaziantep) with no deleterious heavy metal contamination.

Keywords: Waste pyrite, pyrite oxidation, column leaching test, greenhouse pot test, calcareous soil, alkali soil.

ÖZ

CEVHER ZENGİNLEŞTİRME TESİSİ ATIK PİRİTLERİNİN TOPRAK ISLAHINDA KULLANILMASI

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Pirit (FeS_2) kompleks sülfürlü cevherlerde önemli miktarlarda bulunmaktadır. Bu cevherler flotasyonla zenginleştirildikten sonra pirit ayrı bir konsantre olarak üretilip asit fabrikalarına satılmakta veya atık olarak bertaraf edilmektedir. Asit fabrikalarından talep azlığı nedeniyle piritin azımsanmayacak bir bölümü atık muamelesi görmektedir. Bu sebeple pirit genel olarak kompleks sülfürlü minerallerin atığı olarak adlandırılmaktadır. Ancak pirit, kireçli topraklar ve kireçli-alkali topraklarda eksikliği görülebilen Fe ve Cu, Zn, Mn gibi mikro besin elementleri ihtiyacını karşılamak için toprak düzenleyici olarak görev alabilir. Pirit ayrıca kireçli-alkali toprakların ıslahında iyileştirici olarak kullanılan sülfürik asit ürettiği için jipse alternatif bir toprak düzenleyici olarak da kullanılabilir.

Bu çalışmada, atık piritin ve atık piritten üretilmiş sülfürik asitin kireçli-alkali topraklar (Sarayköy-Ankara) ve kireçli topraklar (Gaziantep) üzerinde etkisi laboratuvar koşulları altında araştırılmıştır. Alkali toprakların ıslahında piritik atıkların etkinlik derecesini araştırmak için ayrıca saf jips kullanılmıştır. Jips, toz halindeki atık pirit ve atık piritten üretilmiş sülfürik asit, toprakların ıslahı için gerekli olan jips gereksinimleri göz önünde bulundurularak topraklara uygulanmıştır. Piritik atıklarla iyileştirilen topraklar üzerinde, bitki verimini ve bitki gelişimi için gerekli olan mikro besin elementlerinin (Fe, Cu, Zn ve Mn) miktarını incelemek için, test bitkisi olarak buğday kullanılarak serada saksı denemeleri yapılmıştır. Bu araştırmalar yapılırken atık piritin sebep olabileceği ağır metal kirliği de göz önünde bulundurulmuştur.

Test sonuçları, piritin toprağa ilavesiyle, Sarayköy-Ankara kireçli-alkali toprağın pH'sının ve alkaliliğin göstergesi olan değişebilir sodyum oranının azaldığını göstermiştir. Piritik atıklar her iki toprak grubunda da bitki büyümesi için gerekli olan mikro besin elementlerinin (Fe, Cu, Zn ve Mn) artmasında da etkili olmuştur. Bu durum serada yapılan saksı denemelerinde bitkinin kuru ağırlık verimiyle kanıtlanmıştır. Piritin toprağa ilavesiyle toprakların toksiklik seviyesi, yönetmeliklerde belirtilen yasal limitlerin çok altında kalmıştır. Böylece, kireçli (Sarayköy-Ankara) ve kireçli-alkali topraklara (Gaziantep) piritik atıkların uygulanması herhangi bir toprak kirliliğine yol açmadan topraklar üzerinde hızlı bir iyileşme sağlamıştır.

Anahtar Kelimeler: Atık pirit, pirit oksidasyonu, kolon-liç testi, sera-saksı testi, kireçli toprak, alkali toprak.

To My Husband and My Parents

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CHAPTER 1

INTRODUCTION

Mine tailings containing sulfides of copper, iron, manganese and zinc accumulate in large quantities causing a potential pollution hazard and deteriorate the value of the natural environment. Moreover, they provide no economic return to the owner of mine industry but present a costly disposal problem. If disposal could be associated with a benefit to plant growth, a dual advantage would be realized (Divya, 2007).

Tailings from sulfide mines usually contain large amount of pyrite (FeS_2) which is the main source of acid rock drainage and pollute the environment. Pyrite waste must be disposed off under strictly controlled conditions. Yet it has a great potential for restroring the productivity of calcareous and alkali (sodic) lands; and improving the fertility of the soil. The oxidation of pyrite leads to the production of sulphuric acid which reacts with native $CaCO_3$ to produce soluble calcium to replace adsorbed sodium from the exchange complex of alkali soil and brings down to pH and exchangeable sodıum percentage (ESP) and permeability of soil is improved. Pyrite can be also used as a source of micronutrients needed for growth of plant, particularly Fe, Cu, Zn and Mn (Barrau and Berg, 1977). Therefore it can be used as a fertilizer in calcareous soils and calcareous-alkali soils where these elements are deficient.

The problem of soil sodicity (alkalisation) is extensively spread in many countries of the world (Kovda, 1965). This is all the more vital for developing countries where sodicity hinders agricultural production or even make it impossible. Soil alkalisation frequently lead to the deterioration and complete abandonment of agriculture and hence to great economic damage (Somani, 1994). Alkali soil rehabilitation is needed for sustaining food and fuel production for an ever increasing human population and for preserving the environment. According to the United States Salinity Laboratory (Richards, 1954) these soils have exchangeable sodium percentage (ESP) more than 15, pH of saturated soils' paste (pHs) more than 8.5 and electrical conductivity of saturation extracts (ECe) less than 4 dS/m. Alkali soil accumulates salts on its surface and it is difficult for plants to grow on this soil due to the low hydraulic conductivity and the low permeability (Sumner, 1993; Suarez et al., 1984). The addition of divalent cations to soil solution can reduce clay dispersion and cause flocculation of soil particles and increase the hydraulic conductivity of the soil. This replacement finally results in improved soil permeability (Keren and Miyamoto, 1990). Reclamation can be achieved by leaching after chemical amendments are added to the soil (Keren and Miyamoto, 1990).Gypsum ($CaSO_4.2H_2O$) has been used as a soil amendment for reclamation of alkali soils throughout the world (Oster 1982). The reclamation of alkali soil involves the replacement of exchangeable Na^+ with Ca^{2+} (Oster and Frenkel, 1980).

More than 30% of the land surface of the earth was covered by calcareous soil and this type of soil is qualified as pH between 7.5 and 8.5 depending on the amount of calcium carbonate present (Chen and Barak, 1982; Marschner, 1995). In areas with calcareous soils plant growth is usually retarded and/or plant quality is adversely affected as a result of high pH and unavailability of essential micronutrients (Fe, Cu, Zn and Mn). Use of some kinds of materials to improve soil quality is a necessity if such land is to be used for agricultural purposes. When the concentration of an essential micronutrient for plant growth is low, young leaves will be adversely affected leading to stunted growth and loss of yield. This occurrence is rather common especially when the soil is deficient in iron (Jacobs, 2008). Iron deficiencies associated with high pH and calcareous conditions in soils are common and expensive to correct. Only in case of high-return cash crops, it is economically feasible to alleviate this problem. An effective way to correct Fe deficiencies on calcareous soils is the application of Fe chelates, but the cost is high. Iron chelates are effective for periods of only 1-2 years before the chelates are decomposed by microorganisms in the soils. Foliar applications of ferrous and ferric sulfate have also been used as a Fe source on certain plants (Barrau and Berg, 1977).

Pyrite, waste or not, may be an alternative source of iron and acid for the amendment of calcareous soil as iron ions as well as H^+ released upon the oxidation of Pyrite (1. 1):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (1.\ 1)$$

Iron ions produced in this reaction have a double role in the remediation of calcareous soil. On one hand, ferrous ions supplement the soil for plant growth; on the other hand, oxidation of ferrous iron to ferric iron contributes to acid production (1. 2):

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \qquad (1.\ 2)$$

The overall reaction of pyrite oxidation (1. 3):

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-} \qquad (1.\ 3)$$

Sulphuric acid so produced is commonly named as acid rock drainage and lowers the pH of calcareous soil via the following reaction (1. 4) (Ritsema et al. 1993, Mace et al. 1999):

$$H_2SO_4 + CaCO_3 \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \qquad (1.\ 4)$$

In addition to production of acid and iron, pyrite may also contain other useful micronutrients such as Cu, Zn and Mn (Castelo Branco et al. 1999).

The objective of this study is to quantify the efficiency of pyritic tailings as amendments in reclaiming calcareous and alkali soils in comparison to gypsum which is most commonly used for the same end. For this purpose, Na and sodium adsorption ratio (SAR) of the leachates, pH, exchangeable sodium percentage (ESP) and the heavy metal content of soils as well as the plant growth on the same soils were investigated.

CHAPTER 2

LITERATURE SURVEY

2.1 PYRITE

Pyrite (FeS_2) is one of the sulphide mineral and contains several micronutrients as impurities. It is composed of a ferrous (Fe^{2+}) cation and an S_2^{2-} anion with an ideal Fe:S ratio of 1:2. It is the most abundant sulfide mineral in the earth's crust (Barrie et al., 2009). Pure pyrite contains 46.67 percent iron and 53.33 percent sulfur and its crystal display isometric symmetry. It is widely distributed and forms under extremely varied conditions. Pyrite normally occurs in igneous and metamorphic rocks, but in few locations, it is found as a sedimentary deposit (Somani, 1994). Undesirable association of pyrites with minerals having economic value (galena, chalcopyrite, sphalerite, precious metals) needed separation processes such as leaching and flotation. Main reason of acid rock drainage is pyrite oxidation. Therefore, pyrite oxidation is very important environmentally and economically. (Chandra and Gerson, 2010).

2.2 ACID ROCK DRAINAGE

Mine wastes typically contain a high proportion of sulfide minerals. These minerals are formed at high temperatures and pressure within the earth and become unstable when exposed at the earth's surface (Stumm and Morgan, 1981).

Sulphuric acid decrease the water pH and increase the metal extraction from coexisting minerals. Therefore pyrite oxidation causes acidic waters including various metal ions and brings about serious environmental problems. This phenomenon is called as Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD) (Nagasawa et al., 2004). This problem related to active and abandoned mines were generated by poor waste management (Feasby and Jones, 1994)

Acid mine drainage is one of the most significant environmental issues facing the mining industry. It may impact on the immediate and wider environment (Grout and. Levings, 2001). Materials are crashed, having bigger surface area and thus sulphide minerals are exposed to weathering process during mining operations. Sulphide minerals oxidize with water and oxygen at different rates under these conditions. Rate of sulphide oxidation determines whether there is a significant potential for acid rock drainage.

Under the normal soils and water pH (pH 5-7), metals released by weathering of minerals generally precipitate and are relatively immobile. However, under lower pH conditions, these can stay in solution and be transported off site where they may have a deleterious effect on aquatic ecosystems and other downstream water users.

Basic AMD Chemistry

Four chemical reactions commonly accepted represent the chemistry of pyrite oxidation to form acid mine drainage and are given below.

An overall summary reaction is as follows:

$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 \downarrow + 8H_2SO_4$ (2. 1)

The first reaction pf pyrite weathering is pyrite oxidation by oxygen. Sulfur is oxidized to sulfate and ferrous iron is released. This reaction produces two moles of acidity for each mole of pyrite oxidized.

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$ (2. 2)

The second reaction includes the conversion of ferrous iron to ferric iron. One mole of acidty was consumed with the conversion of ferrous iron to ferric iron. The oxidation rate of ferrous to ferric ion was increased by certain bacteria. This reaction is pH dependent. Under acidic conditions (pH 2-3) without bacteria, the reaction proceeds slowly but at pH values around 5 the reaction proceeds faster. This reaction is refered to as the “rate determining step” in the overall acid-generating sequence.

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ (2. 3)

Hydrolysis of iron is the third reaction. Hydrolysis process splits the water molecule. Three moles of acidity are generated as a byproduct. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate (solid) is pH dependent. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate.

$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3\downarrow + 12H^+$ (2. 4)

The fourth reaction is the oxidation of additional pyrite by ferric iron. The ferric iron is generated in reaction steps 1 and 2. This is the cyclic and self propagating part of the overall reaction and takes place very rapidly and continues until either ferric iron or pyrite is depleted. It should be noted that in this reaction iron is the oxidizing agent, not oxygen (Governor, 1999).

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2.\ 5)$$

Removal of air and/or water from the system would stop pyrite oxidation. When pyrite is present under the water table where oxidizing conditions are limited, almost complete absence of oxygen occurs in nature. Pyrite stays unreacted under these conditions. Small amount of pyrite are oxidized with weathering process when pyrite is enclosed in massive rocks. Therefore, only small amount of acid is generated and surrounding alkaline rocks neutralize or dilute this acid. However big amount of pyrite are exposed to oxidizing conditions occurring in mining or other operations, pyrite reacts, dissolves and moves the reaction products (metals, sulphate and acid) through the surface and ground water sources (Skousen and Ziemkiewicz, 1996).

2.2.1 Factors Influencing Acid Mine Drainage

The acid generation potential of mine and release of contaminants is site specific and dependent on a lot of factors. These factors are classified as primary, secondary and tertiary factors. Primary factors include acid production with oxidation. Secondary factors control the oxidation products such as reactions with other minerals consuming acid. Secondary factors react with other minerals or neutralize acid. Tertiary factors are considered in terms of the physical aspects of the waste management unit such as tailing impoundments, waste rock piles, pit walls. Tertiary factors influence the reaction of oxidation, acid migration and consumption (EPA, 1994).

2.2.1.1 Primary Factors

Factors that affect the sulphide oxidation are given below:

- sulphide minerals
- water
- oxygen
- Fe^{3+}
- bacteria
- pH

Both water and oxygen are necessary for acid generation. Water acts as as medium and reactant for oxidation process. Water also transports the product of the oxidation process. To derive the recations, atmospheric oxygen is needed. Oyygen is very important for the bacterial oxidation when the pH value is under 3.5. Sulphide oxidation is limited when the oxygen concentration in the pore spaces of mining waste unit lower than 1 or 2 % (EPA, 1994).

Where oxidation takes place with no bacterial catalysts it is called as abiotic and where the reaction is catalyzed with bacteria it is called as biotic. Different pH values are suitable for different bacteria. The rate of pyrite oxidation is increased by iron oxidizing bacteria such as Thiobacillus ferrooxidans and sulphur oxidizing bacteria such as Thiobacillus thiooxidans.At pH values between 2.4 and 3.6, maximum pyrite oxidation takes place, above this level decrease rapidly (EA, 1997).

The reaction media pH may also affect the equilibrium of ferrous and ferric iron. At low pH ferric iron acts as a powerful oxidizing agent which may attack other sulphide minerals, increasing the sulphide oxidation rate and generation of oxidation products.

At pH values greater than 3.5 ferric iron will precipitate as ferric hydroxide $Fe(OH)_3$ (EA, 1997).

2.2.1.2 Secondary Factors

An important factor affecting the acid generation is the presence of other minerals which neutralize the acidity. Carbonates are the only alkaline minerals which naturally occur in sufficient amounts to be considered efficient in the control and prevention of acid drainage. Silicate minerals and aluminosilicate, such as mica and clay minerals, have some acid consuming ability but are of minor significance relative to the carbonates (EA, 1997).

2.2.1.3 Tertiary Factors

The physical characteristics of the material, how acid generating materials and acid neutralizing mateials take place, waste and hydrologic regime in the surrounding area are some of the tertiary factors which affect the acid drainage. The physical characteristics of the material such as particle size and permeability are very important for the potential of acid generation. Particle size is a fundamental concern because it affects the surface area which is exposed to weathering process. Surface area is inversely proportional to particle size. Very coarse grain material exposes less surface area but they allow water and air to penetrate deeper into the unit, exposing more material to oxidation and finally producing more acid. However, fine grain material may retard and limit air and water flow; but finer grains expose more surface area to oxidation. The relationship between particle size, surface area and oxidation play an important role in acid prediction methods. When material weathers with time, particle size is decreased, exposing more surface area and changing physical characteristics of the unit.

The hydrology of the surrounding mine units is also important in the analysis of acid generation potential. When materal which generates acid occurs below the water table, the slow oxygen diffusion in water slow down the production of acid. This is reflected in the portion of pits or underground workings placed below the water table. Where mine walls and underground workings extend above the water table, the flow of water and oxygen in joints may be a source of acid.

The distribution of mining wastes in units or waste placement, influence the potential of acid generation. For example, the distribution of neutralizing wastes with acid generating wastes may be controlled by the stacking sequence. Calcareous material may be mixed with or placed above the sulphudic wastes to buffer production of acid or supply alkalinity to infiltrating solution prior to contact with wastes which generates acid. An alternative to layering or mixing is encapsulation. This technique provides isolation of acid generating wastes from oxygen and water, thereby decreasing its acid production potential (EPA, 1994).

2.2.2 Prediction and Identification of AMD

Early recognition of the acid drainage potential and the adoption of suitable risk management strategies are the best practice environmental management strategies. The range of factors which affect the rates of the sulphide oxidation and subsequent acid drainage must be thoroughly understood so that best decisions can be made to minimize impacts of acid generating material disposal practices (EA, 1997).

When evaluating the acid generation potential of a rock material, there are two important points that must be considered. The first is how to collect samples from the field for use in analytical testing. The second is which analytic test method should be applied.

Static and kinetic tests are the analytical test methods to assess the acid generation potential of materials. Total acid generating potential and acid neutralizing potential of a sample are determined by static test. Acid generation capacity is calculated as difference of the values or as the ratio of the values. Static tests can not predict the acid generation rate, only predict the potential to produce acid. For the evaluation of sulphide oxidation rate, kinetic tests are carried out. Kinetic tests requires more time and more expensive than static tests. To classify the materials or wastes according to their acid generating potential, data obtained from these tests are used.

Components which affect the total capacity for acid generation include:

- Amount of minerals which generate acid (sulphide minerals)
- Amount of minerals which neutralize acid
- Amount and type of potential contaminants

Components which affect the acid generation rate include:

- Type of sulphide mineral (including crystal form)
- Type of carbonate mineral and other minerals which neutralize acid
- Minerals surface area available for reaction
- Available water and oxygen
- Bacteria

The typical steps to predict the potential of acid generation;

1. The geology and mineralogy description of the area.
2. Collection of samples which represent the compositional variation in the rock area.
3. Selection of static tests or kinetic tests and evaluation of acid formation potential.
4. Evaluation of sampling criteria.
5. Development a model as appropriate.
6. Classification of geological units as acid, non-acid forming or uncertain.

The ability to predict acid generation from mine wastes allows the appropriate control measures to be designed and implemented to either prevent or inhibit the formation of ARD, to contain it, or to achieve a combination of inhibition and containment (EPA, 1994).

2.2.2.1 Sampling

Selection of samples has important implications for subsequent acid prediction testing. Sampling and testing should be concurrent with the evaluation of resource and planning of mine. Samples must be chosen to define the type and volume of the rock materials.

Collection of samples for prediction tests considers geological and environmental factors. Geological factors for the selection of sample are primarily a good understanding of the local geology. This contains information from mines and surrounding areas. This information is important to sampling program and application of the test results. Environmental factors contain consideration of environmental contaminants in the rock materials and climatic variables.

There are many opinions in terms of the number of samples to be collected. One mining company recommends one sample for one million ton or 8-12 samples for each significant rock type. In this situation rock type represent 1 or 2 % of the total volume of the rock. According to The British Columbia AMD Task Force, a minimum number of samples based on the geologic mass unit should be used. They recommended for minimum sample number is 25 for one million geologic unit or 1 sample for 40.000 tons (EPA, 1994).

Sampling of drilling products to determine sulphide and carbonate content should be representative. Samples should be stored in a cool and dry environment to minimize sulphide oxidation prior to testing.

2.2.2.2 Geochemical Static Tests

These are short-term batch laboratory tests that compare the acid generation and the neutralization capacity of a material. The static test is usually the first step in the analysis of acid generation potential. It estimates the balance between the acid generating and acid neutralizing capacity of a sample. There are many test available, including the so-called "acid-base accounting (ABA)" techniques. Each test uses separate methods to determine the capacity of acid generation and neutralization.

The advantages of the static tests are that they are quick and economic to perform and can be reliably used as an initial screening process to separate materials (Hutchison and Ellison, 1992).

2.2.2.2.1 Sobek Test (Acid-Base Accounting Test-ABA)

The acid-base accounting test, a type of static test, was developed to evaluate coal mine waste in 1974 and was modified by Sobek et al. in 1978. The calculation of acid production potential (APP) is given below.

31.25 x percent S = APP

For each mole of sulphur, two moles of acid are produced based on this calculation. Acid production potential unit is tons of acidity for each ton of rock.

Neutralization Potential (NP) is calculated by a fizz test to select the acid strength to use in the next step. With regard to this information, first HCl is added into sample and then sample is boiled until the reaction stops. To determine the acid amount consumed between HCl and sample, the final solution is titrated back to pH 7 with NaOH.

By subtracting the APP from the NP, the net neutralizing potential (NNP) are calculated NNP is a measure of the difference between the neutralizing and acid forming potentials (EPA, 1994).

2.2.2.2.2 Alkaline Production Method

In this test the NP of a waste is evaluated by determining its alkaline production potential. This is accomplished by measuring the amount of hydrochloric acid (20 mL of 0.1M) consumed by 500 mg of the finely ground sample (less than 23 µm) in two hours at room temperature. Acid consumption is determined by back titration of the excess acid to an end point pH of 5.0. AP is determined by the total sulphur content.

The originatory of this technique (Caruccio et al., 1981) calibrated it against the results of longer term kinetic tests and then used it to provide a rapid indication of acid generation potential. The alkaline production potential values obtained for a number of samples from related geological units were plotted against total sulphur contents.

2.2.2.2.3 Hydrogen Peroxide Test

The purpose of the Hydrogen Peroxide Test is to determine the amount of pyrite in a sample. This is done by comparing the rate of chemical oxidation by hydrogen peroxide to a standard curve, prepared by observing the oxidation rates of material with known pyrite content. The rate of chemical oxidation is determined by measuring the rate at which the pH of the reagent in contact with the sample changes (Hutchison and Ellison, 1992).

2.2.2.2.4 Net Acid Production Test

This test was developed by Coastech Research, Inc (1989). This method uses hydrogen peroxide to oxidize the sulphides contained in the waste. All or part of the acid generated by this oxidation is then consumed by the alkaline constituents in the sample. The net amount of acid remaining after the reaction is determined by titration to pH 7.0 and is usually expressed as kg $CaCO_3$ equivalent per ton of waste.

2.2.2.3 Geochemical Kinetic Tests

The tests are conducted to confirm the potential to generate net acidity, determine the rates of sulphide oxidation and neutralization, determine typical constituent concentrations that occur in the acid drainage and evaluate the effectiveness of proposed ARD control and treatment methods. The results of these tests would indicate, for example if the rate of acid generation is significant or negligible, over what period it may be severe and hence over what time period controls would be required.

These are longer term laboratory tests which produce a leachate for analysis and which reflect the rate of acid generation of a material. The tests can provide a measure of the relative rates of acid generation and neutralization.

Kinetic tests, in which a sample is subjected to periodic leaching cycles to simulate weathering, are carried out to determine the acid generation and metal leaching characteristics of the sample. Such tests are carried out to confirm the acid generating potential of a sample as predicted in static testing and/or to predict water quality of resultant drainage. A kinetic test subjects a sample to weathering to provide predictions of relative rates of sulfide oxidation and neutralizing mineral dissolution and water quality. These rates can be used to determine if a sample will produce acidic drainage more accurately than an ABA test. The rates may also be used to predict when a waste pile will begin producing acid drainage. This estimation could be critical for mining operations where waste rock is exposed to field conditions before control measures, such as underwater disposal, can be applied (Hutchison and Ellison, 1992).

2.2.2.3.1 Humidity Cell Test

Humidity Cell Tests determine the acid generation rate (Sobek et al., 1978). Tests are carried out in a chamber resembling a box with ports for air input and output. It is used to provide simple control over air, temperature and moisture while allowing for the removal of oxidation products which are collected and monitored (Figure 2. 1).

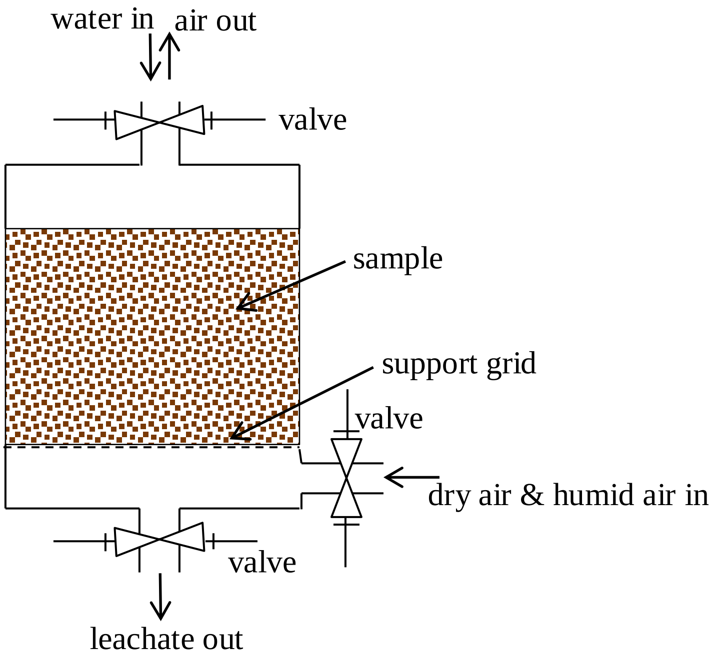


Figure 2. 1 Schematic arrangements of humidity cell

The test procedure involves subjecting a bed of the waste material in a humidity cell to alternating cycles of dry air (3 days), moist air (3 days) and leaching (1 day). The leachate generated is collected and analyzed for a number of parameters, including pH, redox (mV), acidity, alkalinity, sulphate, conductivity and dissolved metals, utilizing the inductively coupled plasma (ICP) techniques. The test is generally run for 10 weeks, although a longer time period might be required to induce sufficient weathering in some samples (Hutchison and Ellison, 1992).

An accelerated-weathering humidity cell apparatus and procedure was developed by Caruccio (1968). Typically, the test involves placing a crushed sample into a vessel, subjecting it to cycles of dry and humidified air, followed by weekly rinses and collection of weathering products. The resultant rinse water volume and chemistry is then related to the rock weight or surface area to determine rates of sulfate production (sulfide oxidation), neutralization and metal release. A cell procedure, as modified by Lawrence (1990), still uses the 7-day cycle of 3 days of humid air but the air is no longer supplied to the upper surface of the sample. Instead, air enters the bottom of a cylindrical cell, passes through a sample (typically 1 kg and crushed to minus 6 mm), and exits through the top. Leaching of the weathering products is conducted on the seventh day with distilled, deionized water and involves trickling water through the sample or flooding the sample then draining.

2.2.2.3.2 Column Test

Column weathering tests are other examples of laboratory kinetic tests. This test involves stacking the waste material in a cylindrical column and allowing water to trickle through at a predetermined pattern to stimulate (Figure 2. 2) (Hutchison and Ellison, 1992).

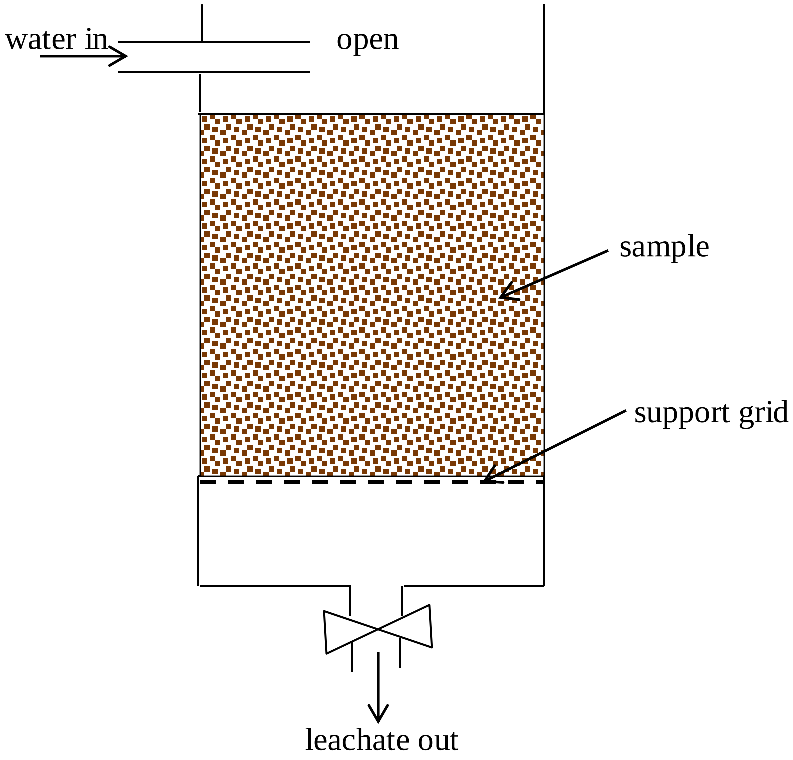


Figure 2. 2 Schematic arrangements of column

Wetting and drying cycles are performed with adding water and then allowing to column to dry. Each cycle may take place over a period from several days to a week or more. Water which is added to the column is collected and analyzed to determine the oxidation rate, sulfate production, metal release and other parameters.

Column test equipment, like humidity cells, is a simple apparatus. Test control options (the effect of bacteria, addition of bacteria and water saturation) can be easily changed. Research results show that field test conditions are accurately represented with column tests filled with tailing materials bigger than 0.5 cm in diameter. High costs and long time required are some disadvantages of column tests (EPA, 1994).

2.2.3 Sulphide Oxidation Management / Acid Mine Drainage Control Strategies

Current most effective environmental management of sulphidic mine wastes needs the assessment of acid generation risk in wastes, the early characterization and classification of the materials and to develop strategies for materials to decrease the oxidation. The best strategy where sulphide oxidation is unavoidable is to isolate higher risk materials. Treating the resulting acid drainage and its effect is less desirable option.

Integration of oxidation and hydrological controls during all mine operation stages from planning of mine to closure of mine and working coordinately to minimize the risk of acid drainage are the best practice management strategies for oxidation of sulphide minerals.

Basically, control strategies need the exclusion of one or more of the inputs that cause oxidation, that is, oxygen, water and sulphide minerals. Where generation of acid drainage cannot be eliminated, it may be treated or its release controlled to a rate that will not significantly affect the receiving environment.

Minimizing acid drainage needs;

- Control of oxidation process and rates of acid generation by regulating water, oxygen and bacteria,
- Control of water percolation through the material to prevent transport or migration of oxidation products from the source,
- Control of acidity and alkalinity balance thus oxidation products and other soluble constituents are precipitated and immobilized within the material.

The most effective control on the rate of oxidation is to decrease availability of oxygen. A cover of low oxygen diffusion restricts water flow through the material thus decreasing the oxidation rate and transportation of product. The most effective environmental management needs site-specific adaptation of local resources and an understanding of the local environment to produce best form of cover.

Water covers and soil covers were used for covers. The most effective control of sulphide oxidation rates is provided by water covers. Soil covers are only as effective as water cover when a cover material proportion remains saturated, which reduces the oxygen diffusion through the cover. However, soil covers has an advantage to reduce the water transportation through the material (EA, 1997).

2.2.3.1 Soil Covers

Soil covers are composed of waste rock or material having low content of sulphide to cover waste materials. They are generally choosed based on specific characteristics like low permeability and rates of compaction. Oxide wastes and clay subsoil are usually used as a cover material. Because of having a high efficiency in water exclusion, synthetic membranes such as geotextile fabrics are used for ore stockpiles to prevent oxidation. Cover materials are selected based on their capacity to decrease water and oxygen availability.

When the pore space of cover is saturated or within about 10% of saturation, control of oxygen is best attained. Soil cover decreases the oxygen transport through the cover.

Soil cover system may have three zones and have the following properties:

- Base zone prevents water flux and provides barrier for diffusion of oxygen, (water retention zone),

- Water reservoir zone retain some portion of water and this zone remains close to saturation,
- Surface zone protects the cover from erosion (barrier zone).

Surface zones are generally used as a barrier zones to provide a growth medium for vegetative cover which helps to prevent erosion (EA, 1997).

2.2.3.2 Water Covers

When sulphidic mine wastes are stored below water, they are not chemically reactive. Water is used as a cover materials having similar objective to soil cover. Water cover decreases the oxygen availability. Due to the lower diffusion coefficient of oxygen in water, the maximum concentration of dissolved oxygen in natural waters is approximately 25 000 times lower than that found in the atmosphere (EA, 1997). The reaction rate is decreased when the oxygen available in water is consumed. The resultant decreased oxygen availability is most effective inhibitor to sulphide oxidation.

Water covers are more readily achieved in temperate climates. Other methods to ensure saturation may be needed in drier climates, for example, establishing a permanent wetland on tailings impoundment surfaces. There are example of minesites in Canada and Sweden where lake environments are being used for tailings and waste rock disposal (EA, 1997).

2.2.3.3 Selective Handling and Isolation of Sulphidic Wastes

Isolation of reactive and higher risk wastes for selective disposal (separately or within unreactive materials) is the main objective of this method.

Geochemical testing are carried out classification and identification of wastes for selective handling and disposal. Figure 2. 3 shows sulphidic waste isolated within a waste stockpile.

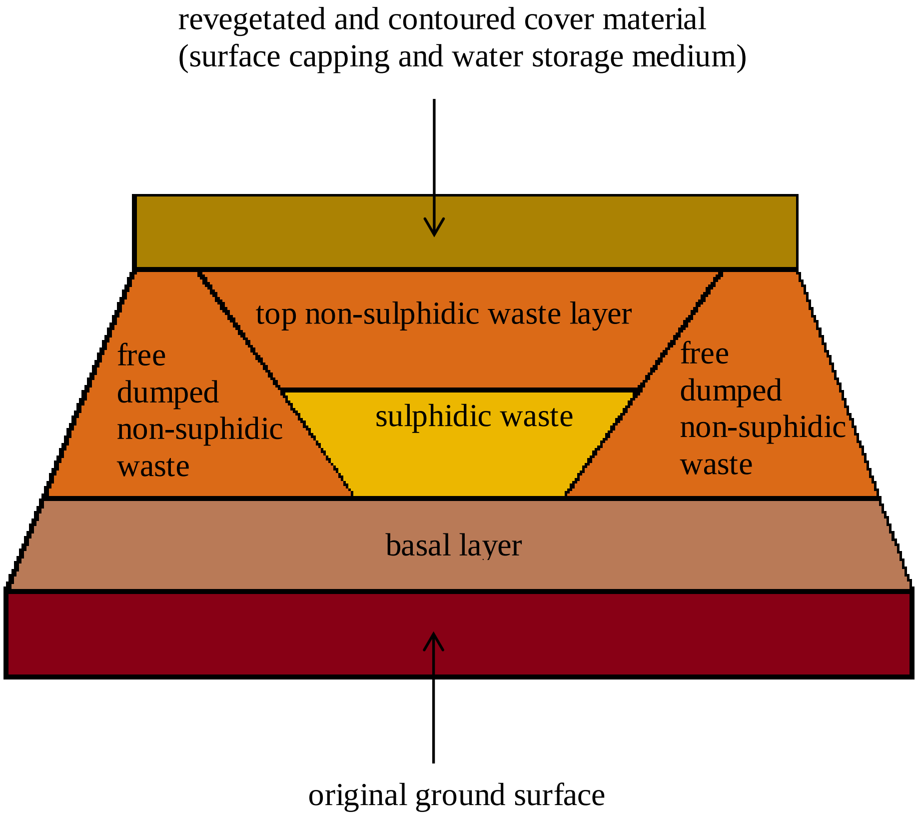


Figure 2. 3 Schematic of isolation strategy

The planning of mine for underground operations include successive backfilling and selective underground disposal of sulphidic wastes, including tailings return underground as sandfill or thickened paste, thus decreasing the amount of acid generating material requiring disposal above ground. Incorporation of cement to bind tailings fill has the advantage of introducing an additional source of alkalinity to the material (EA, 1997).

2.2.3.4 Blending

Blending or mixing of materials is the best method applied with other prevention method when acid consuming and acid generating materials are placed together in waste. The aim of blending is to balance potential of acid generation and alkalinity to reduce potential of acid drainage.

Kiln dust and fly ash supply alkalinity source incorporated into pyritic overburden in the coal industry and reduce the potential of acid drainage (EA, 1997).

2.2.3.5 Bacterial Inhibition

Certain bacteria (acid producing bacteria, APB) like thiobacillus ferrooxidans increase the acid production rate from sulphidic wastes. Bactericides prevent the growth of these microorganisms. They decrease the catalytic role of bacteria in converting Fe^{3+} (ferrous) ion to Fe^{2+} ion under acidic conditions.

Bactericides are only the part of the system to manage the sulphide wastes because this is partially effective and short term solution. They are generally applied to wastes to delay the start of acidic conditions or decrease the cost of secondary treatment (EA, 1997).

2.2.4 Acid Mine Drainage Treatment Strategies

Waste management to reduce the acid drainage production is the preferred option but it is not possible to stop it completely. Treatment of the acidic water is necessary to control off-site environmental effects. A lot of treatment strategies have been developed by the mining industry to decrease the acid drainage potential. These are active and passive treatment strategies (EA, 1997).

2.2.4.1 Active Treatment Systems

The most common strategy for acid drainage treatment is collection and neutralization with alkaline reagents (active treatment process) such as;

- limestone (calcium carbonate),
- hydrated lime (calcium hydroxide),
- quick lime (calcium oxide),
- caustic soda (sodium hydroxide),
- caustic magnesia (magnesium oxide) .

These chemicals increase the pH to acceptable levels, accelerate the rate of chemical oxidation of ferrous iron and decrease the solubility of dissolved metals. Fine metal precipitates (hydroxides) form and then these precipitates are recovered from the solution. The alkaline reagent depends on cost and availability and the pH of the final effluent.

Neutralization is effective and reliable. Relative to passive treatment, active systems require shorter retention times and smaller space. However there are some drawbacks including:

- high capital and operating costs
- it treats the resultant effluent, and
- it produces a precipitate sludge that needs separate disposal (EA, 1997).

2.2.4.2 Passive Treatment Systems

Removal of metals and acidity with active chemical treatment systems of AMD are very expensive and long term liability. Passive treatment systems developed in recent years have many advantages over active treatment systems. Passive treatment systems virtually eliminated the use of chemical addition and energy consumption. The operation and maintenance requirements of passive systems are considerably less than active treatment systems.

The concept behind passive treatment is to allow the naturally occurring chemical and biological reactions that aid in AMD treatment occur in the controlled environment of the treatment system.

The primary passive technologies include:

1. Constructed Aerobic Wetlands
2. Constructed Anaerobic Wetlands
3. Anoxic Limestone Drains (ALD)
4. Successive Alkalinity Producing Systems (SAPS)
5. Limestone Ponds
6. Open Limestone Channel (OLC)

The following information is needed to plan the successful passive treatment systems (Skousen, 1996):

- Low, average and high flow rates
- Iron content and form (Fe^{3+} or Fe^{2+})
- Total acidity
- Total alkalinity
- pH
- Dissolved oxygen content

Figure 2.4 shows the type of passive system for various conditions. In general, aerobic wetlands can treat net alkaline water; ALD can treat water of low Al, Fe^{3+} and dissolved oxygen (DO); SAPS, anaerobic wetlands and OLCs can treat net acidic water with high Al, Fe^{3+} and DO (Skousen, 1996).

2.2.4.2.1 Aerobic Wetlands

Aerobic wetlands treat net-alkaline waters that contain high concentration of iron. They are composed of pond with large surface area and horizontal surface water. The pond is planted with wetland plants. These plants provide more uniform flow and efficient wetland space. Metals can be precipitated after collecting water and providing enough time for residence and aeration with aerobic wetlands.

The acidity and alkalinity balance of water and thus pH are very important since solubility of precipitated metal hydroxide and kinetics of hydrolysis and metal oxidation are affected by pH. Use of aerobic wetlands to remove iron results in decresing pH because of the production of acidity with hydrolysis of iron.

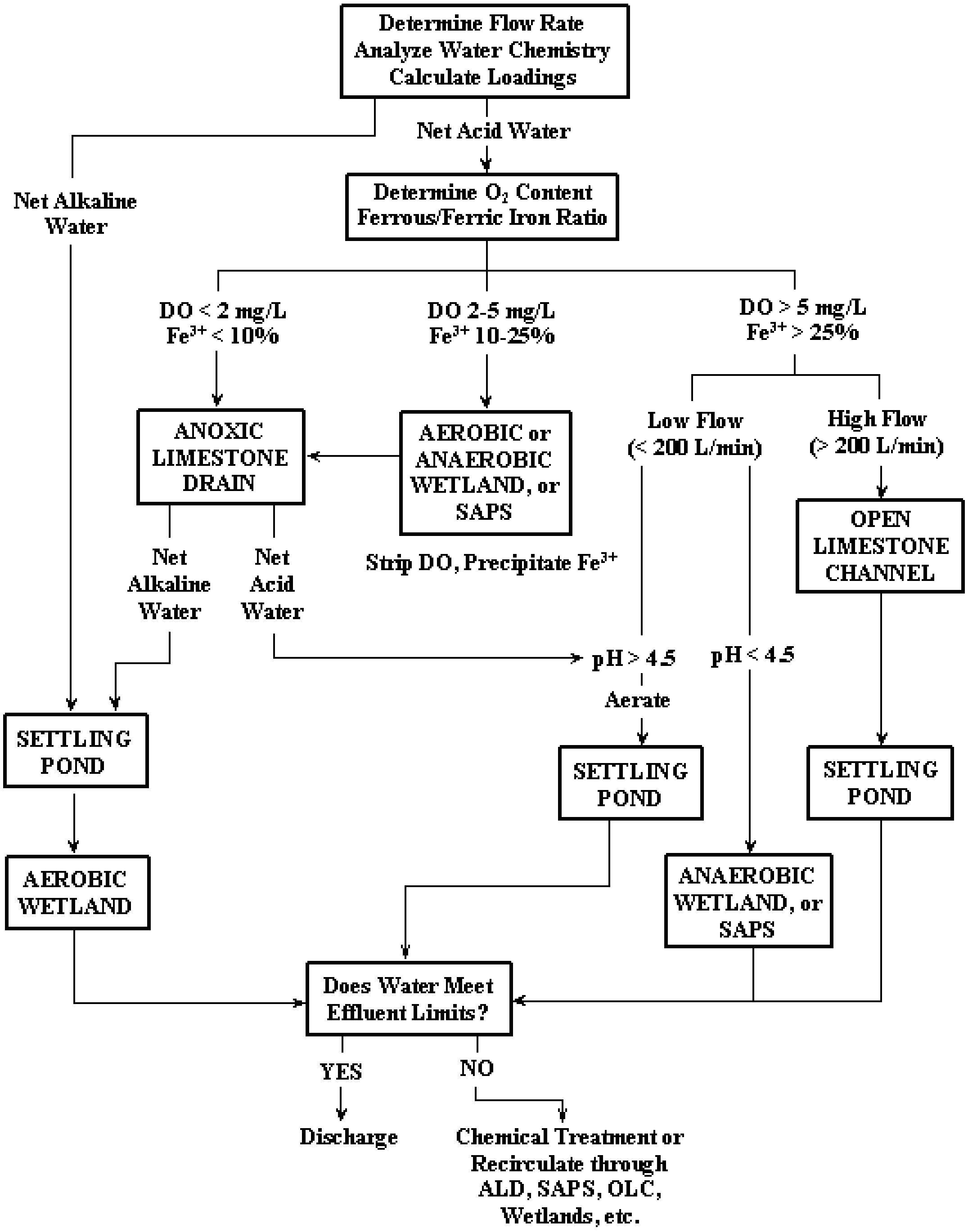


Figure 2. 4 Flowchart for selecting a passive AMD treatment system based on water chemistry and flow (Hedin et al., 1994)

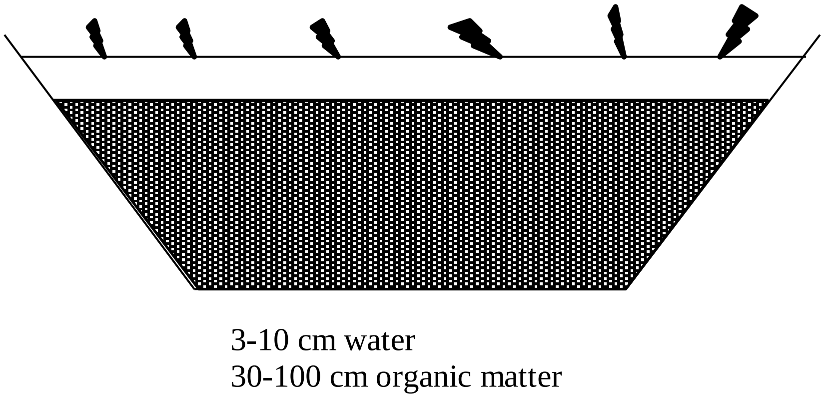


Figure 2. 5 Schematic diagram of aerobic wetland (Skousen, 1996)

2.2.4.2.2 Anerobic Wetlands

Water passage through the organic materials which helps to treatment is encouraged by aerobic wetklands. Wetland system may consist of limestone layer at the bottom or mix the organic material with the limestone. Wetland species are transplanted into organic materials. Aerobic wetlands are used when the water has acidic properties so alkalinity must be produced and introduced to net acidic water before precipitation of dissolved metals.

There are two ways to generate the alkalinity in an aerobic wetland. Certain bacteria use the organic matter (CH_2O) as a carbon source and use sulphate as an electron acceptor for growth.

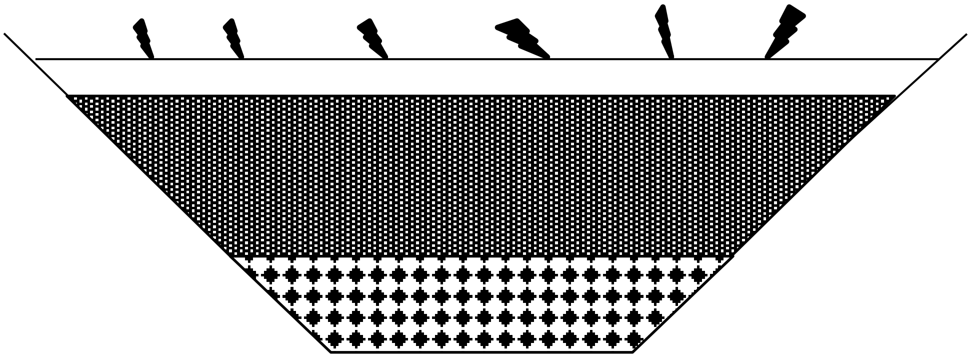
Bicarbonate alkalinity is produced in the conversion of sulphate to hydrogen sulphide:
$SO_4^{2-} + 2\ CH_2O \rightarrow H_2S + 2HCO^{3-}$ (2. 6)

Alkalinity can also be generated as the limestone under the organic material reacts with acidity in the wetland:

$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO^{3-}$ (2. 7)

The limestone continues to react in an anaerobic conditions since ferrous iron is relatively soluble at pH 7 in anoxic environment and $Fe(OH)_3$ does not form and cover the limestone. Ferric iron is formed by the oxidation of ferrous iron and then ferric hydroxide is formed by the hydrolysis of ferric iron. Ferric hydroxide cover the limestone when pH is higher than 3.0. Sulphate reduction with bacteria and dissolution of limestone generate high pH water.

Because of production of alkalinity with anaerobic wetlands, the use of anaerobic wetlands are extended to high Fe, low pH, net acidic, high dissolved oxygen (> 2 mg/L) and poor quality acid mine drainage. Alkalinity production system is very important for the long term acid mine drainage treatment (Skousen, 1996).



3-10 cm water
30-60 cm organic matter
15-30 cm limestone

Figure 2. 6 Schematic diagram of anerobic wetland (Skousen, 1996)

2.2.4.2.3 Anoxic Limestone Drains (ALD)

Anoxic limestone drains (ALD) are buried limestone bed and anoxic water is introduced into bed. The limestone dissolves in acidic water, increase the pH and alkalinity. The limestone does not cover with iron hydoxides in anoxic conditions because ferrous iron does not precipitate as $Fe(OH)_2$ when pH is lower than 6.0.

Duration of treatment is important for anoxic limestone drains in terms of water transportation through the limestone. When Fe^{3+} and Al^{3+} are present, blocking of limestone pores with precipitated aluminium and iron hydroxides are detected. Dissolved oxygen (DO), no Fe^{3+}, Al^{3+} should be present in acid mine drainage for an accepted design. Concentration of oxygen is design limitation for anoxic limestone drains. When the dissolved oxygen concentrations are higher than 1 mg/L, the oxygen must be removed from the water before introduction in a bed. 300 mg/L of alkalinity (as $CaCO_3$) is generated approximately by anoxic limestone drains.

Anoxic limestone drainage utilization is not preferred under the conditions that many source of acid mine drainage is mixed with Fe^{3+}, Fe^{2+} and some dissolved oxygen. Water flow through a organic material to remove oxygen from water and converting ferric iron to ferrous iron are some pretreatment methods for AMD. Then pretreated water is introduced into limestone bed.

To treat specific types of acid mine drainage, anoxic limestone drainage can be used (like wetlands) for a limited period after which this system must be replaced (Skousen, 1996).

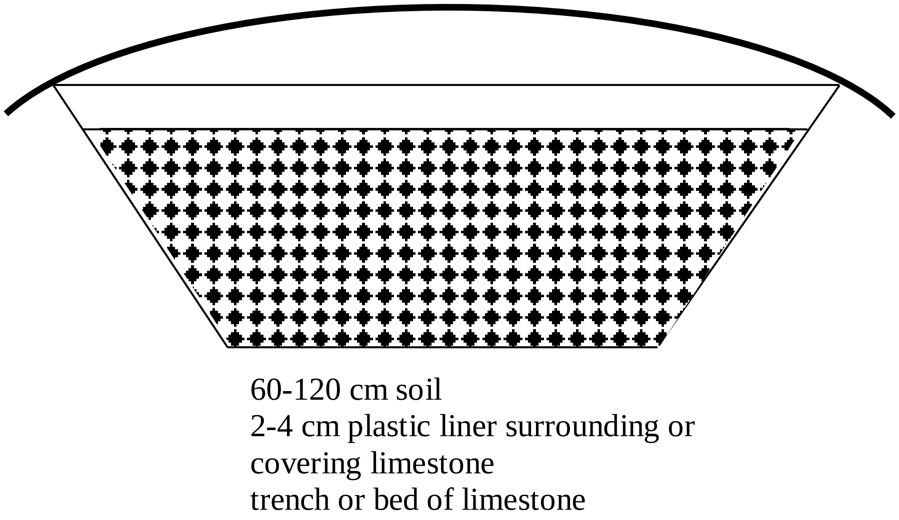


Figure 2. 7 Schematic diagram of anoxic limestone drain system to treat AMD (Skousen, 1996)

2.2.4.2.4 Successive Alkalinity Producing Systems (SAPS) (Vertical Flow Systems)

Successive alkalinity producing system is similar to anaerobic system. However a drainage system is added in the layer of limestone to contact with organic material and limestone.

Organic layer, limestone layer and drainage system are the three main part of the drainage system. Impervious basin is constructed in the system and there is a standpipe in the drainage system to arrange the depth of water. Organic layer and limestone layer is submerged. Two functions are carried out when the acid mine drainage waters flow through the organic layer: Dissolved oxygen in the acid mine drainage is removed by aerobic bacteria which use the organic matter as a sources of energy. Alkalinity is generated by sulphate reducing bacteria in anaerobic zone of organic layer.

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Dissolved sulphate, biodegradable carbon and low dissolved oxygen concentrations are essential for sulphate reduction. An organic layer having the capacity to remove the dissolved oxygen concentration to lower than 1 mg/L is necessary for the prevention limestone armoring. Acidic and anoxic water dissolve the calcium carbonate and alkalinity is produced. The final water is discharged from the standpipe to settling pond to provide neutralization of acid and precipitation of metal prior to discharge (Kepler and McCleary, 1994).

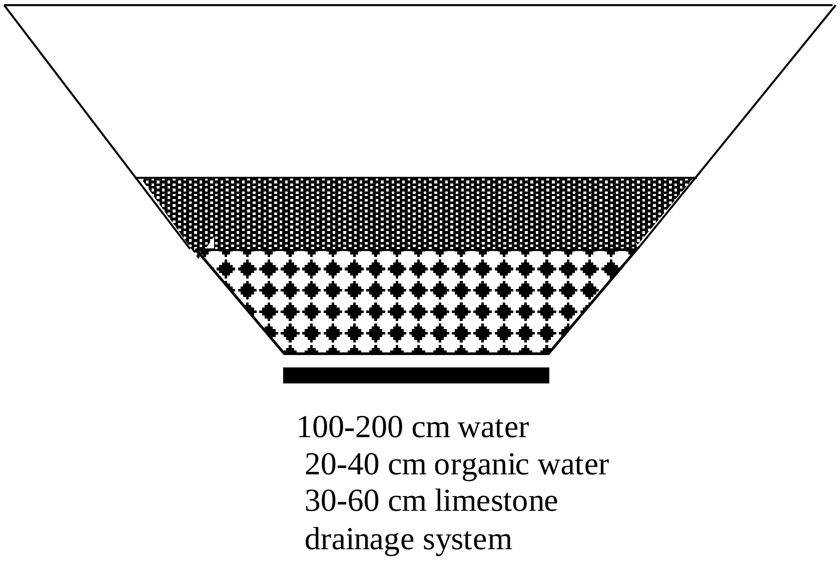


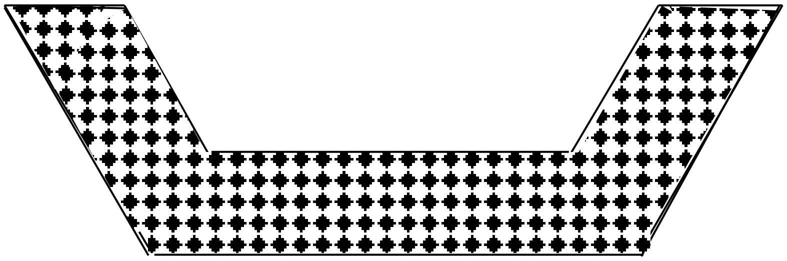
Figure 2. 8 Schematic diagram of vertical flow systems (Skousen, 1996)

2.2.4.2.5 Open Limestone Channel (OLC)

When the acid mine drainage is transported to somewhere before or during treatment, open limestone channel is an effective system to remove iron and generate the alkalinity. Acidic water is introduced to the channel and the AMD is treated by limestone dissolution.

Even though the limestone in such channels typically becomes armored with Fe, recent work has demonstrated that it continues to yield some alkalinity. They are most effective when open limestone channels are placed on slopes of greater than 20% that velocities of flow keep precipitates in suspension and clean the precipitates from the surfaceof limestone.

Open limestone channels can be efficiently used as one element of the passive treatment system. However, they are not relied on using alone for acid mine drainage treatment (Ziemkiewicz et al, 1994).



Small or large sized limestone placed along sides
and in bottom of culverts, diversioms, ditches
or stream channels

Figure 2. 9 Schematic diagram of open limestone channel (Skousen, 1996)

2.3 CALCAREOUS AND ALKALI SOILS

More than 30% of land surface of earth was covered by calcareous soil. These soils are classified by depending on the amount of calcium carbonate present in soil (Chen and Barak, 1982; Marschner, 1995). Calcareous soils have low plant nutrients due to their poor solubility at high pH (e.g. Fe, Mn, Cu, Zn) and the formation of insoluble complexes (Marschner, 1995).

Alkali soils are salt affected soils which is associated with sodium carbonates (Na_2CO_3). Sodium carbonates affect the plant growth adversely. It can react with H_2O to produce CO_2, escaping a gas and sodium hydroxide (Na^+OH^-) which is alkaline and gives high pH values. According to the United States Salinity Laboratory alkaline soils have exchangeable sodium percentage (ESP) more than 15, pH of saturated soils' paste (pHs) more than 8.5 and electrical conductivity of saturation extract (EC) less than 4 dS/m (Richards, 1954)

Exchangeable sodium has an adverse effect on the physical properties of alkali soils. When the amount of exchangeable sodium increases, the soil dispersion increases. This causes to break down the soil aggregates and decrease the soil permeability. The other effect of excess exchangeable percentage is on plant growth through the soil pH. High pH of alkali soil does not affect the plant growth directly but it causes to decrease the availability of some essential micronutrient needed for plant growth. For example, Ca and Mg concentration decreases when the pH increases because of the formation of insoluble $CaCO_3$ and $MgCO_3$.

Alkali soils have poor physical conditions and prone to clay dispersion, formation of impervious soil surface and reduced soil hydraulic conductivities adversely affecting air and water movement and plant growth (Shainberg and Letey, 1984). As a result, production of crop in alkali soil is very poor. These soils can be remedied with adding chemical amendments and leaching to remove excess salts. The successful accomplishment of these two objectives usually results in the conversion of an alkali soil into productive soil (Rao and Burns, 1990).

There are large areas of the world having sodic soils and need attention for these soils to efficient, inexpensive and environmentally feasible amelioration (Qadir et al., 2001). Turkey covers totally 77.797.127 ha area and 35.6 % of the total area (nearly 27.700.000 hectare) is arable land. There is 1.518.749 ha area having the alkalinization-salinization problems in Turkey (Aksoy et al., 2010).

Reclamation and improvement of alkali soil can be achieved by decreasing the ESP to acceptable levels. The level of final ESP depends on the plant type to be grown (Mzezewa et al., 2003).

Chemical amendments used in the reclamation could be put under three categories. Firstly, those supplying soluble calcium salts i.e. gypsum, calcium chloride; secondly, calcium salts of low solubility i.e. ground limestone and thirdly acids and acid formers like sulphur, sulphuric acid and pyrites. The choice of amendments is governed by cost, availability and soil characteristics (Somani, 1994).

Gypsum has been used for a long time and is in fact the most common recommended inorganic amendment. Although $CaCl_2$ is generally too expensive to compete with other amendments, there are situations where it is available as an industrial waste product and could therefore be considered for reclamation. Because of its solubility it gives, initially, high electrolyte levels and high water intake rates which make it a more efficient amendment than gypsum for high ESP soils. With time, however, the slow dissolution of gypsum can be more significant in maintaining the electrolyte effects, especially for soils which do not contain minerals able to release electrolytes into the soil solution. (Shainberg and Gal, 1982). Prather et al. (1978) have suggested that for high ESP soils with low water intake rates, a combination of $CaCl_2$ and gypsum might have quicker and more effective reclamation than gypsum alone.

$CaCO_3$ may be dissolved slowly to contribute Ca, especially in the reclamation of saline sodic soils in which its solubility is enhanced. However, it has generally been considered of doubtful value to add $CaCO_3$ to nonsaline sodic soils because its dissolution is not rapid enough to provide either a worthwhile electrolyte effect or much Ca for exchange, unless an acid or acid-former is applied concurrently. Where $CaCO_3$ is locally available, costs of application may be low enough to consider applying, at the same time, and acid former such as sulfur. It appears, therefore, that the soil and management situations in which $CaCO_3$ alone or in combination with an acid can give economically worthwhile responses, need much closer definition (Shainberg and Gal, 1982)

Sulphur is not only costlier amendment but it is also a slow acting amendment because it must first be oxidized to sulphuric acid by micro-organisms which is a time consuming process. Sulphuric acid has been found to be very effective and quick acting amendment but its high cost and handling hazards limit its wider use by farmers.

The use of pyrite as an amendment is a recent development in the chemical amelioration of alkali soil and has been found to be comparable to that of gypsum. In some areas, the availability of acid waste products arising from mining and industrial activities (including pollution abatement) is increasing markedly. Use of these waste products as soil amendments may provide a safe means of disposal and could greatly influence the economics of any amendment proposal (Somani, 1994).

The objective in reclaiming sodic soils is to ameliorate undesirable physical conditions such as crusting and low hydraulic conductivity which impede infiltration, water storage, seedling emergence and root development (Prather et al., 1978).

2.4 RECLAMATION OF CALCAREOUS AND ALKALI SOILS WITH WASTE PYRITE

The ore processing plants are faced with the problem of disposal of tailings containing pyrite. The pyrite, upon oxidation, releases iron sulfate and sulphuric acid. These compounds can be major sources of stream pollution (Tiwari et al., 1992). Research experiments and field trials on cultivators fields have clearly shown that the pyrites can be effectively utilized for reclaiming alkali soils.

Pyrite can be used for several agricultural purposes, as an acidifier to improve soil structure of alkali soils and as a source of micronutrients essential for plant growth, particularly Fe, Cu, Zn, Mn. Therefore, pyrite can potentially provide a cheaper alternative to fertilizer amendments.

The rate of pyrite oxidation is controlled by the diffusion rate of oxygen into the soil which declines rapidly with depth. In view of this, surface application of pyrite and keeping the soil moist around field capacity is advisable for faster oxidation of pyrite. Aerated condition for 3 weeks markedly improved oxidation of pyrites and promoted alkali amelioration (Somani, 1994).

The oxidation of pyrite leads to the production of sulphuric acid which reacts with native $CaCO_3$ to produce soluble calcium to replace adsorbed sodium from the exchange complex of the alkali soil. The CO_2 evolved during the reaction of H_2SO_4 with carbonates further accentuates dissolution of $CaCO_3$ and facilitates replacement of sodium from the exchange complex and bring down the pH (Johnson and Hallberg, 2004). Sequence of chemical reactions of iron pyrite in soils in the reclamation of alkali soils is given in Figure 2. 10.

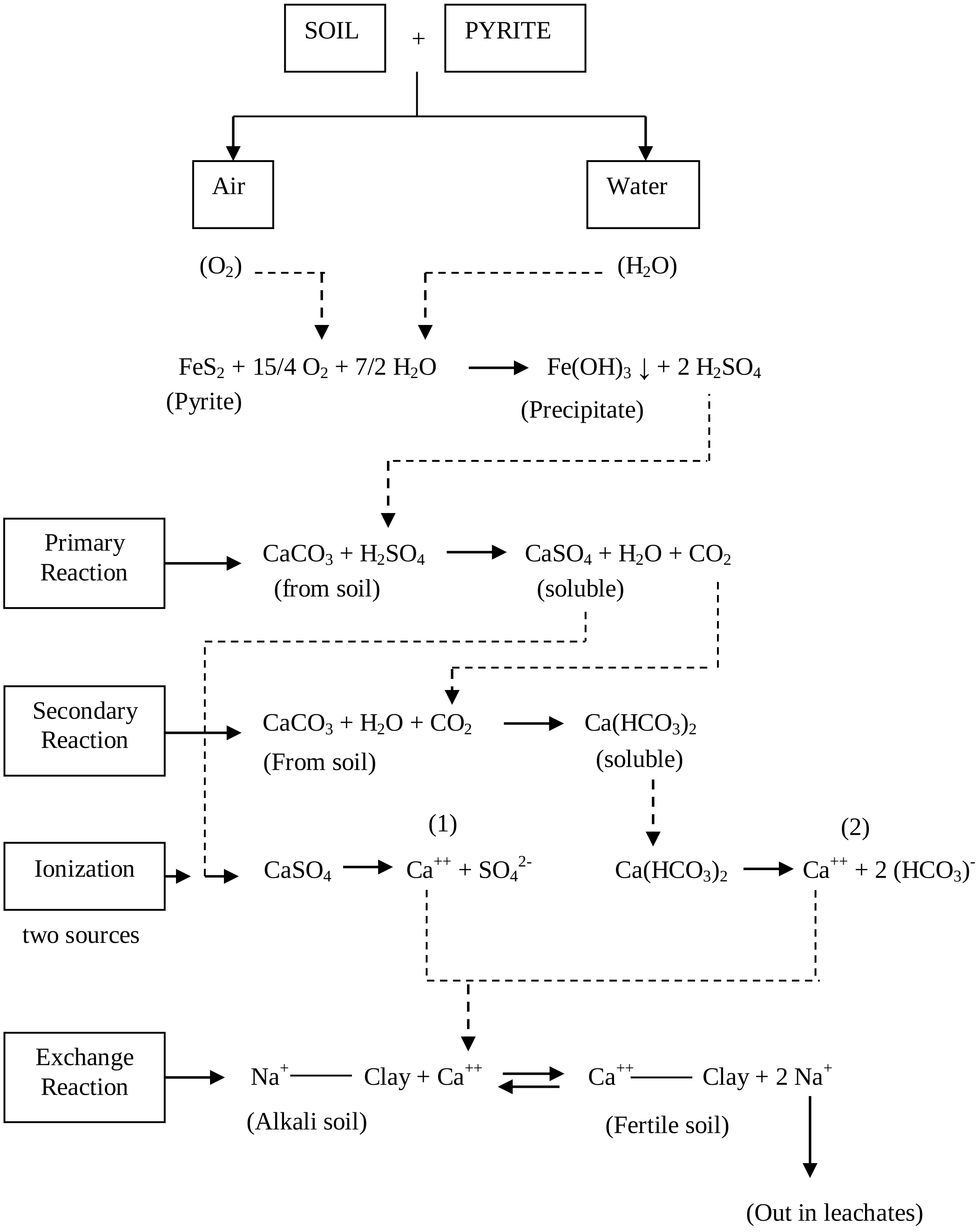


Figure 2. 10 Sequence of chemical reactions of pyrite in soils in the reclamation of alkali soils (Somani, 1994)

Besides improving the calcareous alkali soils by providing soluble calcium from $CaCO_3$ to replace adsorbed sodium and neutralization of the carbonates and bicarbonates of alkali soils, pyrites can also reclaim non-calcareous alkali soils by replacing their adsorbed sodium ion with the hydrogen ion of the sulphuric acid produced with the oxidation of pyrites. The reaction proceeds as shown below:

$$2Na\text{-}Clay + H_2SO_4 \rightarrow 2H\text{-}Clay + Na_2SO_4 \qquad (2.9)$$

The hydrogen clay is known to exhibit good physical conditions. The hydrogen ion acts as a good flocculating agent in the soil.

Sulphuric acid produced by oxidation of pyrite also reacts with the sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) of alkali soils high in pH to produce sodium sulphate (Na_2SO_4) liberating carbon dioxide (CO_2) as shown below:

$$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + 2CO_2 \qquad (2.10)$$

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2 \qquad (2.11)$$

Thus a carbonate-bicarbonates system in soil is converted into sulphate system, which is highly conductive to better soil aggregation and plant growth.

In addition to the beneficial effects of sulphuric acid, the Fe^{2+} ions released with the oxidation of pyrites also act as a proton donar and play an important role in reducing the pH of the soil as indicted by the following reaction (Somani, 1994):

$$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (2.12)$$

All of these reactions help to decrease the pH of the soil which is impermeable, that is not to allow the pass of the water and air through the soil. By these reactions, permeability of alkali soil will increase and soil will have good conditions for agriculture.

Why is it important for Turkey?

In Turkey there is 1.518.749 ha of soil having the alkalinization-salinization problems (Aksoy et al., 2010). On the other hand, 2 million ton of waste pyrite causing acid mine drainage is disposed of as tailing annually. As such, both acid mine drainage (AMD) and alkali soils by themselves are two important problems for Turkey.

Yet, waste pyrite may have beneficial properties when added to certain soils, i.e. calcareous and calcareous-alkali soils therefore it could be used in the remediation of such soils. By doing so, a polluting material can be converted into a useful commodity. Not only environmental hazards will be prevented by this practice, but also economical gains could be realized. This could be a step forward towards “zero waste production” technologies, as well.

CHAPTER 3

MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Soil

Three different types of soils were used in this study. Two of them (calcareous alkali soils-low and high ESP) were obtained from Sarayköy-Ankara; the other was obtained from Gaziantep (calcareous). Soil samples were collected from a depth of 0 to 15 cm at all three sites. These soil samples were air-dried, blended, ground to pass through a 2 mm sieve in the laboratory. Representative samples were stored in plastic bags for analyses.

Table 3. 1 shows the relevant physical and chemical properties of Sarayköy calcareous-alkali soil (low ESP). This soil is classified as nonsaline (EC= 1.27 dS/m), alkali (ESP= 31.29) (Richards, 1954), moderately calcareous (% $CaCO_3$ = 10.50) with low organic matter content (% 1.71) (Ulgen and Yurtsever, 1974). The level of available micronutrients determined by the DTPA method was 2.02 ppm Fe, 0.42 ppm Cu, 0.46

ppm Zn and 6.85 ppm Mn. These levels of Fe, Zn and Mn are classified as marginal for plant growth (Follet and Lindsay, 1970; Lindsay and Norwell, 1978; FAO, 1990). Table 3. 2 shows the heavy metal content of the soil. The heavy metals in the soil were lower than the limit values according to Turkish soil contamination regulation (2001). The clay content of the soil was found to be 54.09%. The X-ray diffractometer of soil indicate a mineralogy consisting of primarily calcite, chlorite, illite, kaolin, plagioclase, smectite and quartz (Figure 3. 1).

Table 3. 1 Physical and chemical properties of Sarayköy calcareous alkali soil (low ESP)

Soil characteristic	Value
Electrical conductivity (dS/m)	1.27
pH	8.76
Bulk density (g/cm^3)	1.28
Cation exchange capacity (me/100 g)	43.04
CaCO3 (%)	10.50
Organic matter (%)	1.71
Boron (ppm)	1.87
Exchangeable cations (%)	
Na	31.29
K	3.83
Ca	51.01
Mg	14.53
DTPA-extractable (ppm)	
Fe	2.02
Cu	0.42
Zn	0.46
Mn	6.85

Table 3. 2 Heavy metal content of Sarayköy calcareous alkali-soil (low ESP)

Element	Concentration/ (mg/kg soil)	Limit values (mg/kg soil)*
Cr	22.07	100
Co	2.33	20
Ni	27.10	75
Cu	16.92	140
Zn	75.34	300
Pb	17.15	300
Mo	1.30	10
Cd	0.14	3
As	2.54	20
Fe (%)	4.24	-

*according to Turkish Soil Contamination Regulation (2001)

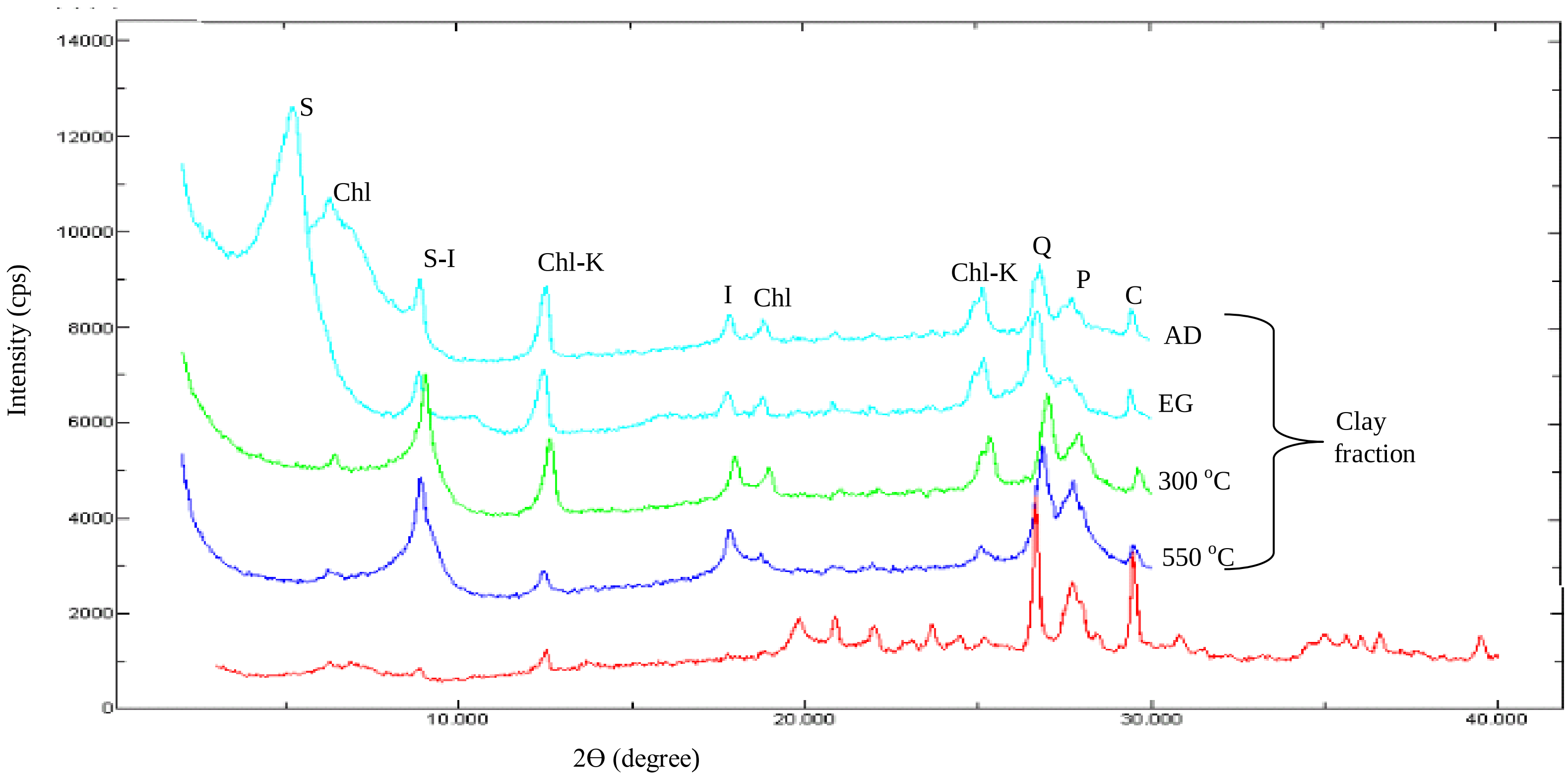


Figure 3. 1 Result of XRD analysis of Saraykoy calcareous-alkali soil (low ESP). C: Calcite, Chl: Chlorite, I: Illite, K: Kaolin, P: Plagioclase, S: Smectite Q: Quartz (AD: Air-dried, EG: Ethylene glycolated, 300 ^{o}C and 550 ^{o}C: Heated in oven at 300 ^{o}C and fried at 550 ^{o}C)

Table 3. 3. shows the relevant physical and chemical properties of Sarayköy calcareous-alkali soil (high ESP). This soil is classified as nonsaline (EC=2.85 dS/m), alkali (ESP= 83.33) (Richards, 1954), moderately calcareous (%$CaCO_3$=9.18) with low organic matter content (% 0.71) and with deficient micronutrients (Fe=1.75 ppm, Zn=0.07 ppm, Mn=3.53 ppm) for plant growth (Follet and Lindsay, 1970; Lindsay and Norwell, 1978; FAO, 1990). The heavy metals in the soil were lower than the limit values according to Turkish soil contamination regulation (2001) (Table 3. 4). The clay content of soil was found to be 56.17%. The X-ray diffractometer indicated a mineralogy consisting of primarily calcite, chlorite, illite, kaolin, plagioclase, smectite and quartz (Figure 3. 2).

Table 3.3 Physical and chemical properties of Sarayköy calcareous-alkali soil(high ESP)

Soil characteristic	Value
Electrical conductivity (dS/m)	2.85
pH	9.27
Bulk density (g/cm^3)	1.22
Cation exchange capacity (me/100 g)	38.52
CaCO3 (%)	9.18
Organic matter (%)	0.71
Boron (ppm)	8.87
Exchangeable cations (%)	
Na	83.33
K	3.06
Ca	10.37
Mg	4.03
DTPA-extractable (ppm)	
Fe	1.75
Cu	0.29
Zn	0.07
Mn	3.53

Table 3. 4 Heavy metal content of Sarayköy calcareous-alkali soil (high ESP)

Element	Concentration (mg/kg soil)	Limit values (mg/kg soil)*
Cr	24.59	100
Co	3.20	20
Ni	20.78	75
Cu	14.40	140
Zn	61.32	300
Pb	20.89	300
Mo	2.19	10
Cd	0.12	3
As	3.09	20
Fe (%)	4.08	-

*according to Turkish Soil Contamination Regulation (2001)

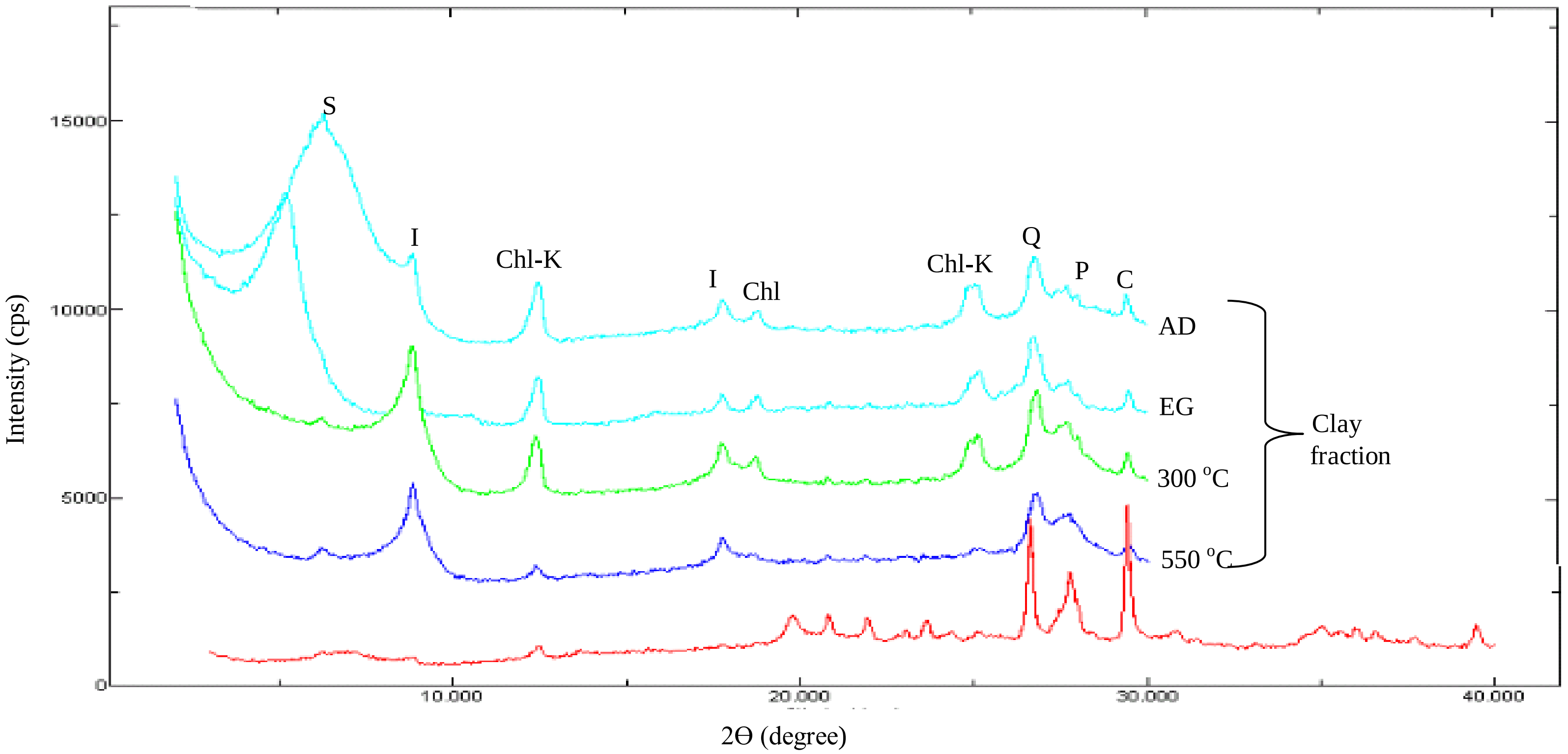


Figure 3. 2 Result of XRD analysis of Saraykoy calcareous-alkali soil (high ESP). C: Calcite, Chl: Chlorite, I: Illite, K: Kaolin, P: Plagioclase, S: Smectite Q: Quartz (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 550 °C: Heated in oven at 300 °C and fried at 550 °C)

Table 3. 5 shows the relevant physical and chemical properties of Gaziantep calcareus soil. This soil is classified as nonsaline (EC= 1.20 dS/m) (Richards, 1954), highly calcareous (% $CaCO_3$ = 33.24) with low organic matter content (% 1.43) (Ulgen and Yurtsever, 1974) and with deficient micronutrients (Fe= 2.10 ppm, Zn= 0.42 ppm, Mn= 9.79 ppm) for plant growth (Follet and Lindsay, 1970; Lindsay and Norwell, 1978; FAO, 1990). The heavy metal content of the soil is below the limits set by the Turkish soil contamination regulation (2001) (Table 3. 6). The clay content of soil was found to be 19.85%. The X-ray diffractometer indicates a mineralogy consisting of primarily illite, chlorite, kaolin, quartz and calcite (Figure 3. 3).

Table 3. 5 Physical and chemical properties of Gaziantep calcareous soil

Soil characteristic	Value
Electrical conductivity (dS/m)	1.20
pH	7.86
Bulk density (g/cm^3)	1.28
Cation exchange capacity (me/100 g)	30.15
CaCO3 (%)	33.24
Organic matter (%)	1.43
Boron (ppm)	1.64
Exchangeable cations (%)	
Na	1.44
K	8.61
Ca	85.34
Mg	4.57
DTPA-extractable (ppm)	
Fe	2.10
Cu	0.35
Zn	0.42
Mn	9.79

Table 3. 6 Heavy metal content of Gaziantep calcareous soil

Element	Concentration (mg/kg soil)	Limit values (mg/kg soil)*
Cr	27.30	100
Co	2.59	20
Ni	21.06	75
Cu	19.49	140
Zn	76.15	300
Pb	14.81	300
Mo	0.93	10
Cd	0.31	3
As	0.74	20
Fe (%)	3.77	-

*according to Turkish Soil Contamination Regulation (2001)

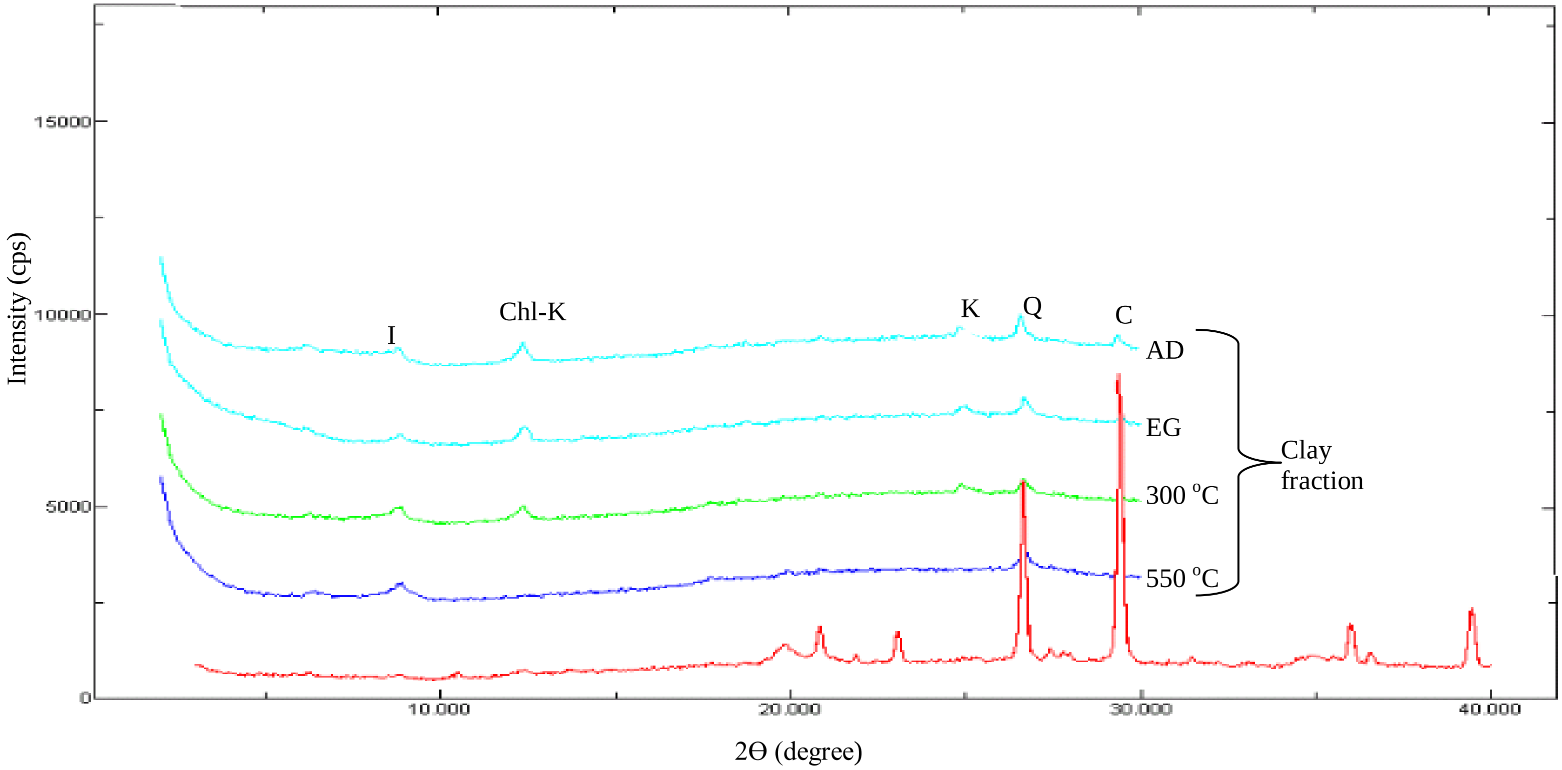


Figure 3. 3 Result of XRD analysis of Gaziantep calcareous soil. C: Calcite, Chl: Chlorite, I: Illite, K: Kaolin, Q: Quartz (AD: Air-dried, EG: Ethylene glycolated, 300 °C and 550 °C: Heated in oven at 300 °C and fried at 550 °C)

3.1.2 Soil Amendments

3.1.2.1 Waste Pyrite

The waste pyrite used as amendment was taken from the tailings stream of Kure Copper Concentration Plant, Turkey. Sulphur content of pyrite was found 44% (TS 1987) corresponding to 83% pyrite. The rest of the waste consists of quartz. Sulphur and heavy metal content of waste pyrite are given in Table 3. 7.

Table 3. 7 Sulphur and heavy metal content of waste pyrite

Element	Concentration (mg/kg pyrite)
Cr	21.22
Co	824
Ni	61.73
Cu	6886
Zn	781.25
Pb	202.54
Mo	<2.40
Cd	<0.54
As	<20
Fe (%)	40.70
S (%)	44.00

3.1.2.2 Sulphuric Acid Produced from Waste Pyrite

The oxidation experiment of waste pyrite was performed by aerating a suspension of 400 g of waste pyrite in 15 l of water placed in a 25 l polypropylene container for 25 days (Figure 3. 4). The suspension was stirred by injecting air through the polyethylene container. Ferric iron (Fe^{3+}) from the oxidation of pyrite precipitates as solid ferric hydroxide and forms sulfuric acid from four H^+ generated for each iron atom initially present as pyrite (3. 1) (Somani, 1994).

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad (3.\ 1)$$

The sulfate concentration of sulphuric acid produced from waste pyrites was calculated to be 10.02 g/L (Richards, 1954). The heavy metal content of sulphuric acid produced from waste pyrite is given in Table 3. 8.

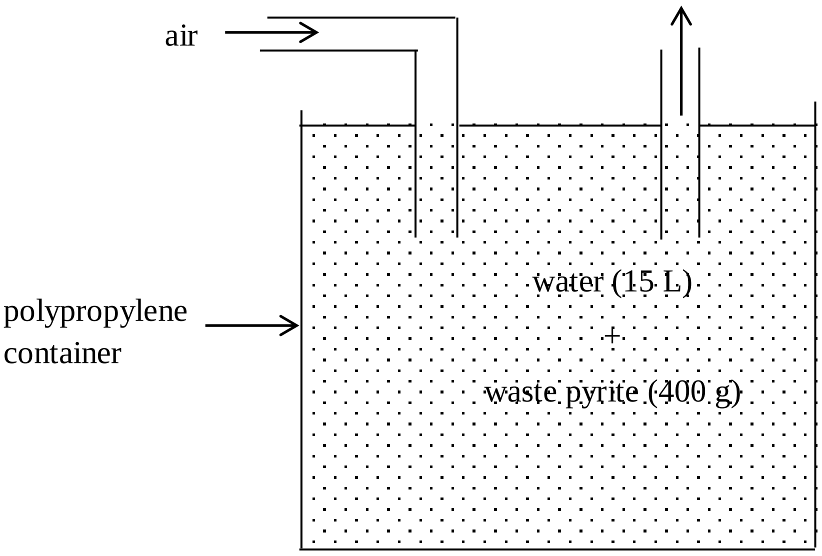


Figure 3. 4 Sulphuric acid production from waste pyrite

Table 3. 8 Metal content of sulphuric acid produced from waste pyrite

Element	Concentration (mg/L)
Cr	0.55
Co	9.10
Ni	0.95
Cu	81
Zn	35.70
Pb	0.86
Mo	<0.0079
Cd	<0.0027
As	2.32
Fe	2286

3.1.2.3 Gypsum

Pure powder gypsum ($CaSO_4.2H_2O$) (Merck, 102161) was used as a reference amendment.

3.1.3 Plant

Seasonal wheat (Ceyhan 99) resistant to disease was used in greenhouse test. Seeds were obtained from Central Research Institute for Field Crops.

3.1.4 Irrigation Water

In this study, METU tap water was used as leaching water in soil columns and well water of Central Research Institute of Soil Fertilizer and Water Resources (CRISFWR) was used for greenhouse test. The characteristics of irrigation waters are given in Table 3. 9.

The quality of tap and well water used in leaching and greenhouse tests were determined by electrical conductivity and sodium adsorption ratio (Figure 3. 5). They take place in C_3-S_1 class. The electrical conductivity of the tap water and well water is 0.85 dS/m (850 μS/cm) and 1.21 ds/m (1210 μS/cm) respectively. They are placed in C_3 class. C_3 (High salinity water): Special management for salinity control may be required and plants with good salts tolerance should be selected. The percolation of soil increased when tap water was used during the leaching process. Wheat used in greenhouse test had a tolerance up to 6 dS/m. Therefore well water is thought to be suitable for the greenhouse test (Table 3.9). The sodium adsorption ratio of the tap water and well water is 1.35 and 1.66 respectively. They are placed in S_1 class. S_1 (low sodium water): It can be used for irrigation on almost all soils (Richards, 1954).

Table 3. 9 The characteristics of irrigation waters

	EC (dS/m)	pH	Cations (mmol$_c$ /L)				Anions (mmol$_c$ /L)				Sodium Adsorption Ratio (SAR)	Classification
			Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CO_3^{2-}	HCO_3^{-}	Cl^{-}	SO_4^{2-}		
METU tap water	0.85	7.65	4.31	1.99	2.39	0.12	-	5.03	1.60	2.18	1.35	C_3-S_1*
CRISFWR well water	1.21	7.14	6.83	3.32	3.70	0.14	-	6.29	2.28	5.42	1.66	C_3-S_1*

*S: sodium adsorption ratio; C: electrical conductivity

(Average of four samples collected two times during irrigation)

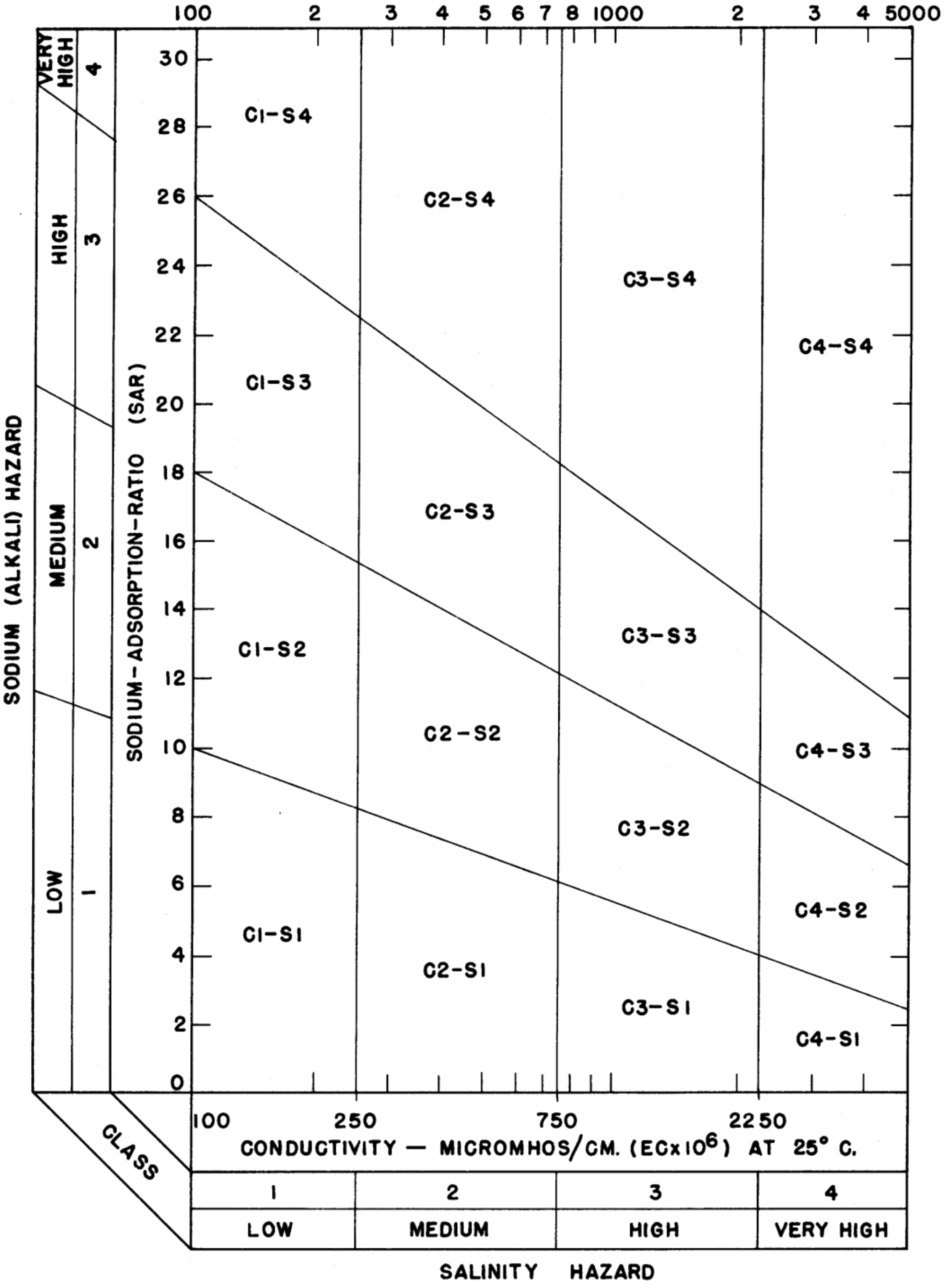


Figure 3. 5 Diagram for the classification of irrigation waters (Richards, 1954)

3.2 METHODS

3.2.1 Laboratory Tests

Laboratory column leaching test were carried out to estimate the amount of leaching needed for removal of excess soluble salts; to determine the response of soils to the addition of gypsum, waste pyrite and sulphuric acid produced from waste pyrite; and to find the changes in soil properties such as pH and ESP after leaching.

3.2.1.1 Leaching Columns

Polyvinyl chloride (PVC) columns were used in the leaching tests (Figure 3.6). A PVC cap was added to the base of each column and holes were drilled on the cap to drain the percolating solution (Figure 3.6.a). Surface of the cap was covered with filter paper to prevent soil loss and to facilitate proper drainage (Figure 3.6.b). This cap was placed in the plug (Figure 3.6.c). Bottom of the plug was drilled and valve was fixed. Polyvinyl chloride (PVC) column was placed on this plug (Figure 3.6.d). The tops of the columns were open to the atmosphere. A 15-cm-height free space was left at the top of the column to facilitate water addition. A schematic representation of the leach column is given in Figure 3. 7.

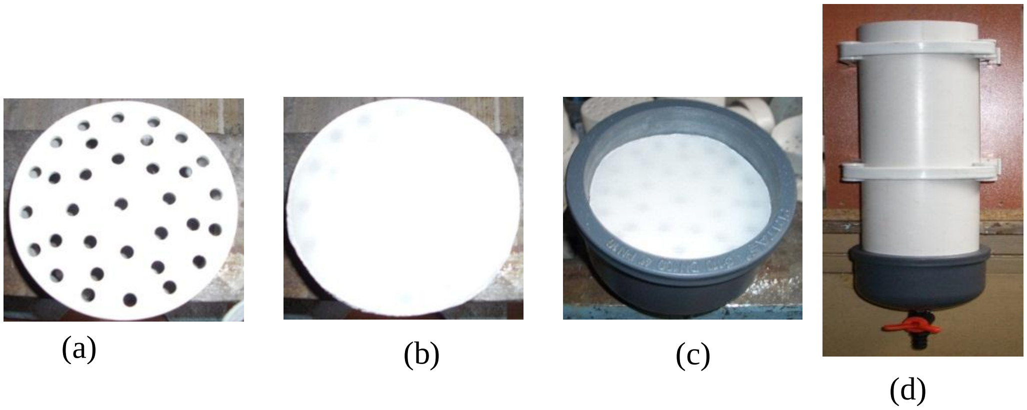

(a) (b) (c) (d)

Figure 3. 6 Set-up of the leaching column

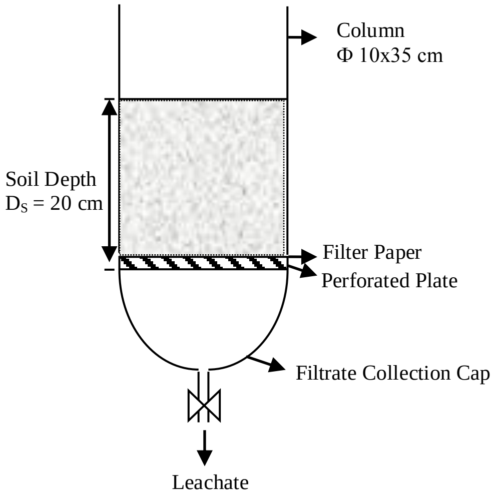


Figure 3. 7 Schematic representation of the column used for the leaching tests

3.2.1.2 Soil Preparation for Leaching Columns

Two Sarayköy calcareous-alkali soils (low and high ESP) and Gaziantep calcareous soil were used in the column studies. Polyvinyl chloride (PVC) columns were hand packed with air-dried and homogenized soils (<2 mm) to a depth of 20 cm. Prior to irrigation, in all treatments except for Sarayköy soil (high ESP), the soil columns were water-saturated from below to prevent air entrapment (Figure 3. 8).

Figure 3. 8 Soil samples in leaching column

The amount of soil for each case was calculated as follows:

Case 1: Sarayköy calcareous-alkali soil (low ESP)

For Sarayköy calcareous-alkali soil (low ESP)-powder waste pyrite;

bulk density = 1.28 g/cm^3
diameter of leaching column = 10 cm
height of soil in column = 20 cm
volume of column = $\Pi r^2 h = 3.14*5^2*20 = 1570$ cm^3
amount of soil used for each column = 1570*1.28 = **2009.6 g**

Case 2: Sarayköy calcareous-alkali soil (high ESP)

For Sarayköy calcareous-alkali soil (high ESP) - powder waste pyrite - sulphuric acid produced from waste pyrite;

bulk density = 1.22 g/cm^3
diameter of leaching column = 10 cm
height of soil in column = 20 cm
volume of column = $\Pi r^2 h = 3.14*5^2*20 = 1570$ cm^3
amount of soil used for each column = 1570*1.22 = **1915.4 g**

Case 3: Gaziantep calcareous soil

For Gaziantep calcareous soil-powder waste pyrite

bulk density = 1.28 g/cm^3
diameter of leaching column = 10 cm
height of soil in column = 20 cm
volume of column = $\Pi r^2 h = 3.14*5^2*20 = 1570$ cm^3
amount of soil used for each column = 1570*1.28 = **2009.6 g**

3.2.1.3 Treatments

The experimental layout was a randomized design with four doses of pyrites and sulphuric acid and one dose of gypsum with four replicates per dose. Gypsum, waste pyrite and sulphuric acid were applied to soil on the basis of gypsum requirement (GR) of the soils (FAO, 1988). The amount of amendments equivalent to GR are given in Table 3. 10.

Table 3. 10 Equivalent doses of amendments for alkali soil reclamation (FAO, 1988)

Amendment	Tons equivalent to 1 ton of 100% gypsum
Gypsum ($CaSO_4.2H_2O$)	1.00
Sulphuric acid (H_2SO_4)	0.57
Pyrite (FeS_2)-30% suphur	0.63

The quantity of gypsum required for decreasing the exchangeable sodium percentage to desired amount was obtained from the following equation (3. 1).

$$GR = (860*10^{-6}) * d_b * Ds * W * (ESP_i-ESP_f) /100 * CEC \qquad \text{Eq.3.1}$$

Where;

GR = gypsum requirement of soil (ton/decare)

d_b = bulk density of soil (g/cm^3)

D_s = soil depth (m)

W = soil width (1 decare=1000m^2)

ESP_i. ESP_f = exchangeable sodium percentage before and after remediation

CEC = cation exchange capacity (me/100 g)

Case 1: Sarayköy calcareous-alkali soil (low ESP)

The minimum amount of pyrite addition level was calculated on the basis of gypsum requirement (GR) to reduce ESP to 10%. Higher levels of pyrite addition were also applied to make up for the possible incomplete pyrite oxidation. Altogether four doses, namely, 19.90 t/ha for gypsum, 8.56 t/ha (Pyrite1=GR), 12.74 t/ha (Pyrite2), 19.11 t/ha (Pyrite3) and 28.03 t/ha (Pyrite4) for waste pyrite were tested.

$$GR = (860*10^{-6})*1.28*0.2*1000*(31-10)/100*43$$
$$= 1.99 \text{ ton/decare} = 0.199 \text{ g/cm}^2$$

Diameter of leaching column = 10 cm

Area of column = $\Pi r^2 = 3.14*5^2 = 78.5 \text{ cm}^2$

Gypsum requirement for each column = 0.199*78.5 = **15.62 g**

1 ton gypsum = 0.63 ton pyrite (30% sulphur) (Table 3. 10)

0.43 tons of pyrite with 44% S (0.63*30/44) discharged from Küre Copper Mine Plant is supposed to use for 1 ton of gypsum. **Pyrite requirement** for each column is **6.72 g** (0.43*15.62) equal to gypsum requirement of each column.

The type and amounts of amendments applied on the soil for remediation for each column and per hectare are shown in Table 3.11.

Table 3. 11 Soil amendments and application rates for Sarayköy calcareous-alkali soil (low ESP)

Soil Amendment	Application rate (g/column)	Application rate (t/ha)
Gypsum	15.62	19.90
Pyrite 1(=GR)*	6.72	8.56
Pyrite 2	10	12.74
Pyrite 3	15	19.11
Pyrite 4	22	28.03

*GR=gypsum requirement of the soil

Case 2: Sarayköy calcareous-alkali soil (high ESP)

The minimum dose of pyrite addition level, 23.74 t/ha (Pyrite1=GR) was calculated on the basis of gypsum requirement (GR), 55.20 t/ha, to reduce ESP to 15%. Higher levels of pyrite addition, namely, 31.96 t/ha (Pyrite2), 39.63 t/ha (Pyrite3) and 44.74 t/ha (Pyrite4) were also applied to make up for the possible incomplete pyrite oxidation.

For Sarayköy calcareous alkali soil (high ESP)-powder waste pyrite;

$$GR = (860 \cdot 10^{-6}) \cdot 1.22 \cdot 0.2 \cdot 1000 \cdot (83.33-15)/100 \cdot 38.52$$
$$= 5.52 \text{ ton/decare} = 0.55 \text{ g/cm}^2$$

Gypsum requirement for each column = 0.55*78.5 = **43.18 g**

Pyrite requirement for each column is **18.57 g** (0.43*43.18) equal to gypsum requirement of each column.

The type and amounts of amendments applied on the soil for remediation for each column and per hectare are shown in Table 3.12.

Table 3. 12 Soil amendments and application rates for Sarayköy calcareous-alkali soil (high ESP)

Soil Amendment	Application rate (g/column)	Application rate (t/ha)
Gypsum	43.18	55.20
Pyrite 1(=GR)*	18.57	23.74
Pyrite 2	25	31.96
Pyrite 3	31	39.63
Pyrite 4	35	44.74

For Sarayköy calcareous alkali soil (high ESP)-sulphuric acid produced from waste pyrite;

In the application of sulphuric acid produced from waste pyrite, 31.46 t/ha of H_2SO_4 was assumed to be equivalent to 55.20 t/ha of gypsum (FAO, 1988). In this study, 17 t/ha (H_2SO_4-1), 19.62 t/ha (H_2SO_4-2), 23.54 t/ha (H_2SO_4-3), 26.15 t/ha (H_2SO_4-4) and 35.31 t/ha (H_2SO_4-5) of H_2SO_4 were tested to determine the effectiveness of sulphuric acid in the reclamation of the calcareous sodic soil.

1 ton gypsum = 0.57 ton sulphuric acid (Table 3. 10)
[43.18*0.57] 24.61 g of H_2SO_4 and [24.61*96/98] **24.11 g of $SO_4^{=}$** is supposed to use for 43.18 g gypsum ($H_2SO_4 \rightarrow 2H^+ + SO_4^{=}$).

The sulphate content of sulphuric acid produced from waste pyrite is 10.02 g/L. Sulphuric acid amount for each column and per hectare are shown in Table 3. 13.

Table 3. 13 Sulphuric acid amount for each column and per hectare for Sarayköy calcareous-alkali soil (high ESP)

Soil Amendment	**Application rate (cc /column)**	**Application rate (t/ha)**
H_2SO_4-1	1300	17.00
H_2SO_4-2	1500	19.62
H_2SO_4-3	1800	23.54
H_2SO_4-4	2000	26.15
H_2SO_4-5	2700	35.31

Case 3: Gaziantep calcareous soil

The soil was treated with four doses of pyrite, namely, 6.37 t/ha (Pyrite1), 11.46 t/ha (Pyrite2), 17.83 t/ha (Pyrite3) and 25.48 t/ha (Pyrite4) and all treatments were replicated four times. It should be noted that 1 t/ha dose corresponds to 0.39 kg pyrite/ton of soil. The type and amounts of amendments applied on the soil for remediation for each column and per hectare are shown in Table 3. 14.

Table 3. 14 Soil amendments and application rates for Gaziantep calcareous soil

Soil Amendment	Application rate (g/column)	Application rate (t/ha)
Pyrite 1	5	6.37
Pyrite 2	9	11.46
Pyrite 3	14	17.83
Pyrite 4	20	25.48

3.2.1.4 Application of Amendments

Laboratory leaching tests were carried out at uncontrolled room temperature that ranged from 15 to 25^{o}C, in the Laboratory of Department of Mining Engineering, Middle East Technical University. The experimental layout was a randomized design with four doses of pyrites and sulphuric acid and one dose of gypsum with four replicates per dose.

Pyrite undergoes rapid oxidation when they are surface applied on moist soils. Therefore, pyrite of predetermined doses was evenly spread on moist soil surface as thinly as possible. In order to facilitate the oxidation of pyrite and ensure the supply of sufficient oxygen, the soil surface with pyrite was moistened until soaked by water spraying every 24 hours for 5 weeks for Sarayköy soils and for 3 weeks for Gaziantep soil in a similar way to Tiwari and Sharma (1989). Sufficient time was allowed for pyrite to oxidize. Gypsum amendment was blended thoroughly with the soil. Sulphuric acid was applied on the soil.

3.2.1.5 Irrigation and Leaching

Irrigation is the application of water to soil for the purpose of providing a favorable environment for soil and plants. Leaching is the process of dissolving and transporting soluble salts by the downward movement of water through the soil.

After the amendment applications, the columns were leached by ponding method with tap water (EC=1.21 dS/m, SAR=1.66) with a hydraulic head of 10 cm (785 ml water) in the columns at certain intervals. Leaching dissolved and carried the amendments downward and removed the soluble salts. The leachate were collected and analyzed for Na, Ca and SAR to determine the effectiveness of the amendments. The leaching system is shown in Figure 3. 9.

Figure 3. 9 The leaching system

3.2.2 Greenhouse Tests

Greenhouse pot tests were conducted to determine the plant response to leaching and the addition of pyritic tailings at the Central Research Institute of Soil, Fertilizer and Water Resources. Treated and untreated soils were used in the greenhouse tests. 1.5 kg of soil was placed in plastic pots and eight wheat seeds resistant to disease were planted in each pot. After germination only four wheat seeds were left to grow up while the remaining was eradicated. The crop was irrigated with well water (EC = 1.21 dS/m, SAR = 1.66) to bring the moisture to field capacity so as to avoid any leaching of salts. Plants were harvested after 30 days from seeding. They were cut 2 cm above the surface of the soil and washed in 0.05 N HCl for about 30 s. The plants were then successively rinsed with distilled water, dried at 70^{o}C and ground finely for analysis.

3.2.3 Method of Analyses

The samples were air-dried and ground to pass a 2-mm sieve. Soil pH was measured in the saturated soil paste and EC was measured in the saturation extract (Richards, 1954). Dry bulk density of soil was analyzed according to Tuzuner (1990). Cation exchange capacity (CEC) was determined with 1N sodium acetate by flame photometer (Richards, 1954). $CaCO_3$ was measured with 3N hydrochloric acid with Scheibler calcimeter (Tuzuner, 1990). Organic matter was determined with 1N potassium dichromate by titration (Walkey-Black, 1947). Boron was analyzed using carmine solution (Richards, 1954). Soluble cations and anions, and exchangeable cations were determined using the methods outlined in Richards (1954). Fe, Cu, Zn and Mn were measured by atomic absorption spectroscopy (AAS) after extraction using DTPA solution (Lindsay and Norwell, 1978). Total trace elements in soils were determined by digestion with nitric acid using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

ESP was calculated using the formula below (Eq. 3.2), (FAO, 1988):

$$\mathrm{ESP} = \frac{\mathrm{Na_x}}{\mathrm{CEC}} \times 100 \qquad \text{Eq.3.2}$$

Where;

ESP = Exchangeable sodium percentage (%)

$\mathrm{Na_x}$ = Measured exchangeable $\mathrm{Na_x}$ (me/100 g)

CEC = Cation exchangeable capacity (me/100 g)

SAR was determined using the formula below (Eq. 3.3), (FAO, 1988):

$$\mathrm{SAR} = \frac{\mathrm{Na^+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \qquad \text{Eq.3.3}$$

Where;

SAR = Sodium adsorption ratio

$\mathrm{Na^+}$, $\mathrm{Ca^{2+}}$, $\mathrm{Mg^{2+}}$ = Soluble cations (me/l)

X-Ray Powder patterns (XRD) were taken by using Rigaku MiniFlex II Diffractometer with Cu Kα (30 kV, 10 mA, λ=1.54050 Å) radiation. Statistical analyses were performed using MINITAB 15.1 software (Minitab Inc., State College, PA). One-way ANOVA was used to compare the means of parameters among treatments. Where the analyses showed significantly differences at $P<0.05$ or $P<0.01$, Duncan’s multiple range tests were conducted using MSTAT program.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 COLUMN TESTS

Column tests were conducted in order to determine the change in the soil properties upon treatment with gypsum, waste pyrite and sulphuric acid produced from waste pyrite.

4.1.1 Leachate Properties

The leachate from the test columns were analyzed after full cycle (collection of 785 ml leachate for each cycle) of leaching tests. Na and SAR in the leachates of the calcareous-alkali soil and Ca in the leachates of the calcareous soil were measured to evaluate the efficiency of the amendments. After reaching stable SAR value, leaching was terminated and the leached soil was analyzed.

Sulphuric acid solubilizes calcium from the native insoluble calcium carbonate present in the calcareous soils to form soluble calcium sulphate (Somani, 1994). Therefore, the amount of calcium in the leachate increased with application of amendments.

The dissolution of free ions such as Ca^{2+}, Mg^{2+} and H^{+} enhanced removal of Na into the leachate of the calcareous-alkali soil as a result of ion exchange.

Sodium adsorption ratio (SAR) is a ratio of the sodium (detrimental element) to the combination of calcium and magnesium (beneficial elements). In other words, SAR is the measure of the sodicity of soil and shows the efficiency of leaching process on soil remediation. After the leaching, SAR of all the soils was lower than 12. This value separates sodic soil from non-sodic soils (Richards, 1954).

4.1.1.1 Case 1: Sarayköy Calcareous-Alkali Soils (Low ESP)

Soil solution (leachate) was collected taking into account of SAR values of treated soils after 10, 14, 15, 16, 17, 18, 21, 24 and 27 weeks after start of irrigation The maximum amount of sodium leaching is observed in gypsum followed by Pyrite4 dose after nine leaching cycles. Pyrite1and Pyrite2 doses show a similar pattern of leaching and removal of Na in soil (Figure 4. 1).

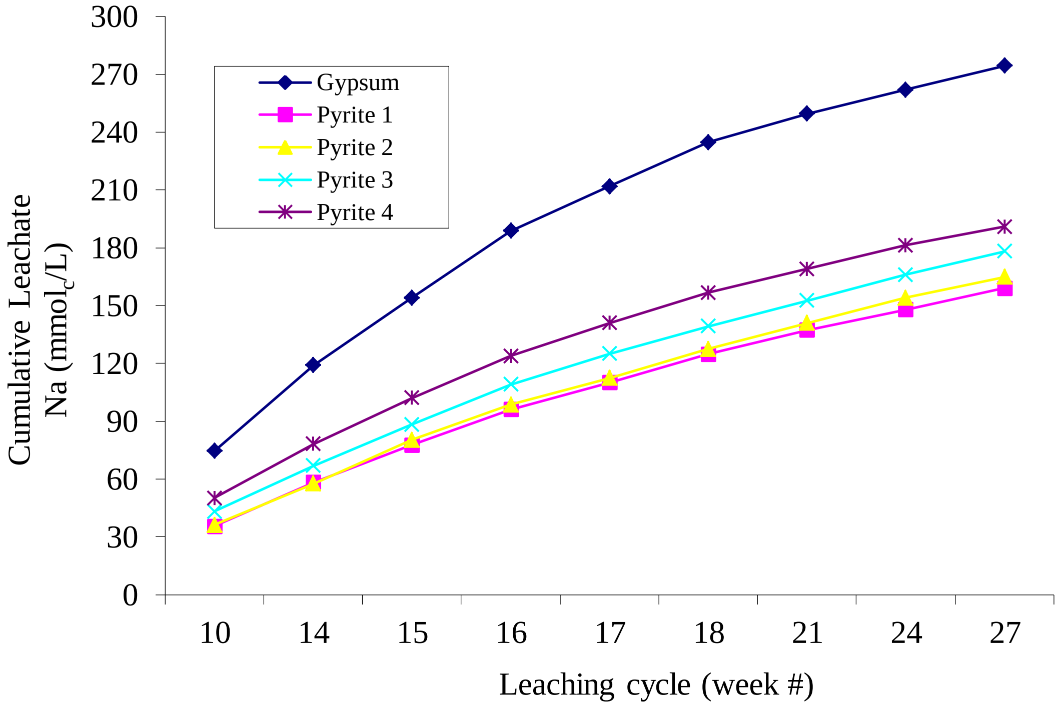


Figure 4. 1 Na in the leachates from Sarayköy calcareous-alkali soil (low ESP) columns treated with gypsum and waste pyrite

Maximum SAR decrement was observed in gypsum followed by Pyrite4, Pyrite3, Pyrite2 and Pyrite1 dose applications, respectively after nine leaching cycles (Figure 4. 2).

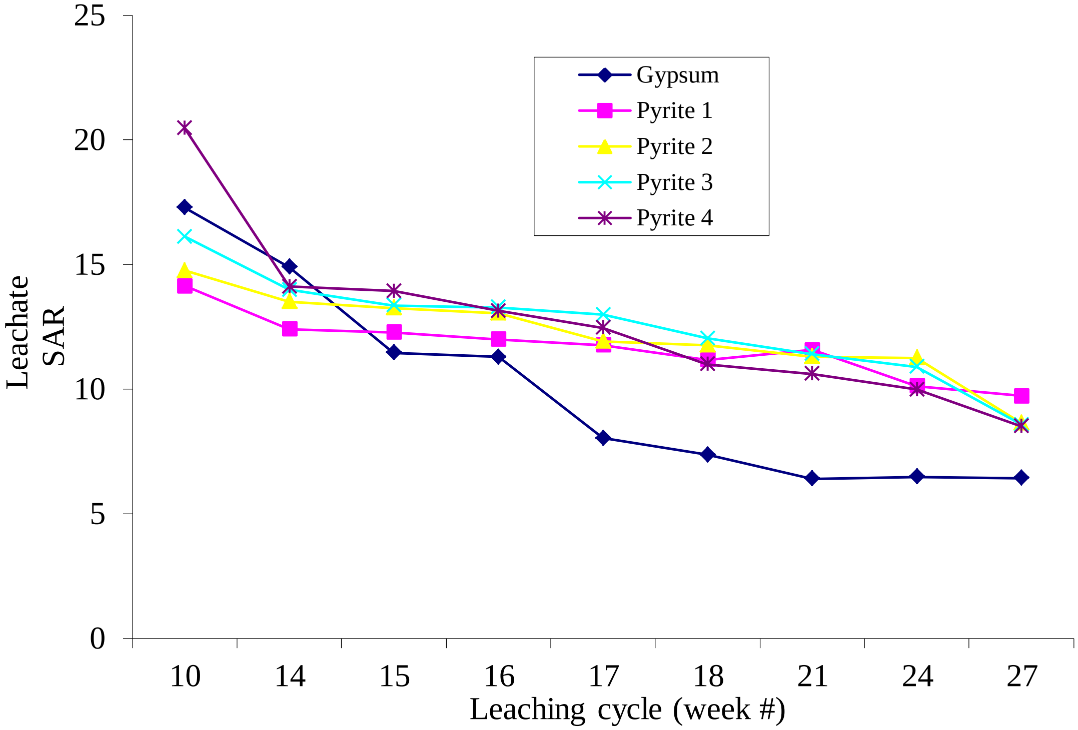


Figure 4. 2 SAR values in the leachates from Sarayköy calcareous-alkali soil (low ESP) columns treated with gypsum and waste pyrite

4.1.1.2 Case 2: Sarayköy Calcareous-Alkali Soils (High ESP)

For the soil treated with waste pyrite, soil solution (leachate) was collected taking into account of SAR values of treated soils after 30, 33, 35, 37, 39, 40, 41 and 42 weeks after start of irrigation. The amount of sodium leaching, 926.17 mmol$_c$/L, was the highest with the Pyrite4 dose; followed by 921.33 mmol$_c$/L with the gypsum application on the last leachate (Figure 4 .3).

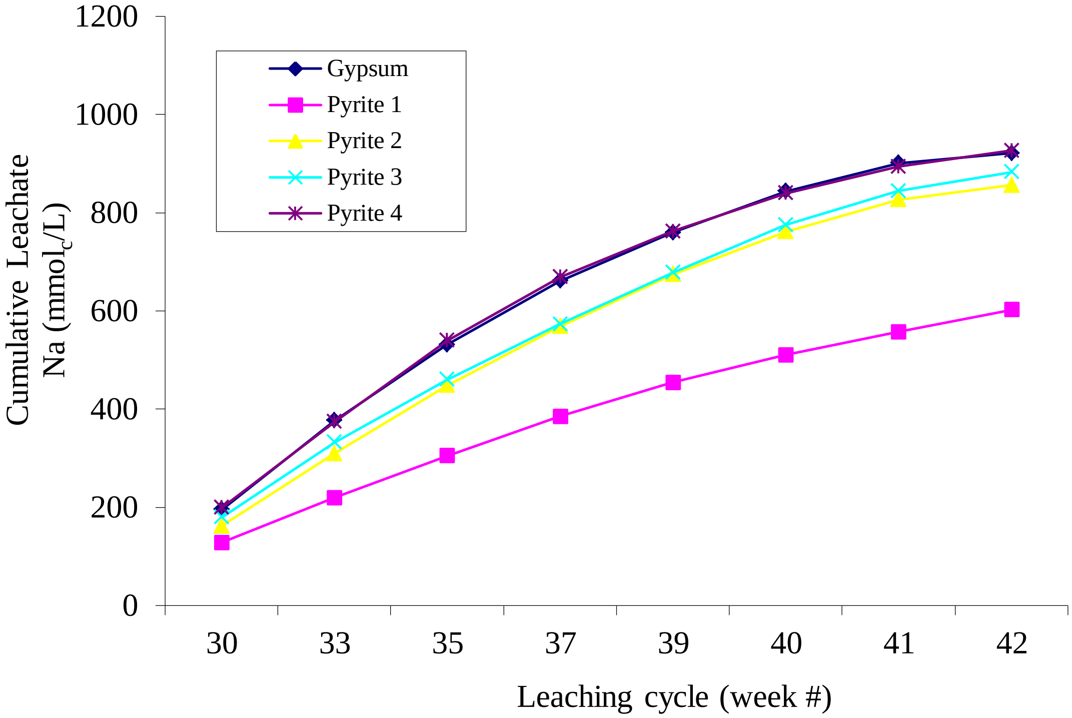


Figure 4. 3 Na in the leachates from Sarayköy calcareous-alkali soil (high ESP) columns treated with gypsum and waste pyrite

For the soil treated with sulphuric acid, leachate was collected after 15, 17, 19, 21, 23, 24, 25 and 26 weeks after the start of irrigation. The highest amount of sodium leaching, 1096.25 mmol$_c$/L, was observed in H_2SO_4-5 application (Figure 4. 4).

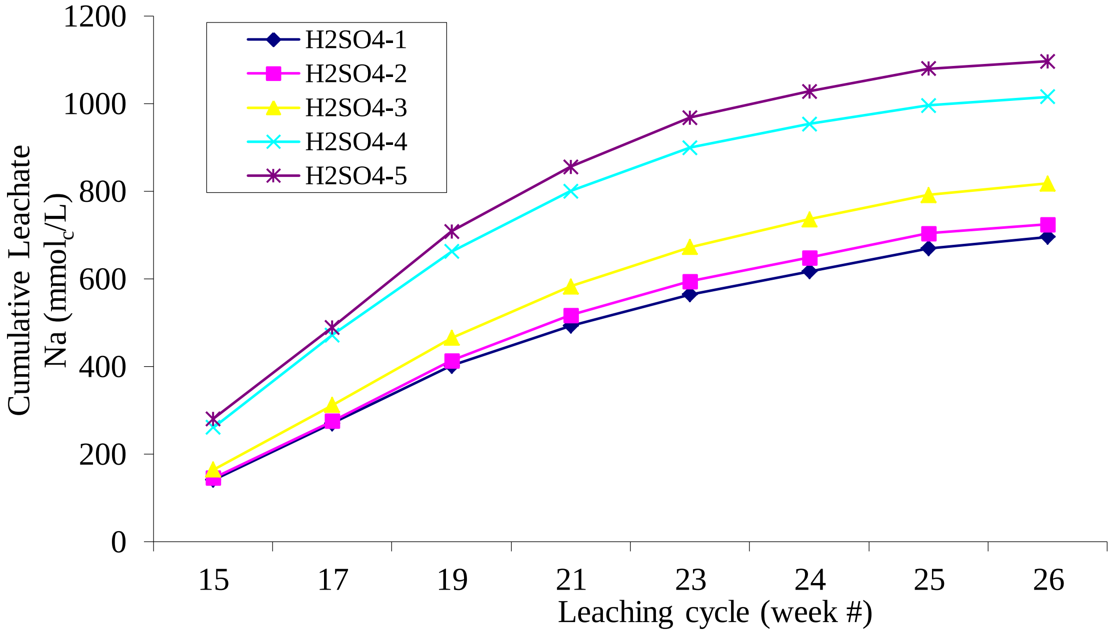


Figure 4. 4 Na in the leachates from Sarayköy calcareous-alkali soil (high ESP) columns treated with sulphuric acid

After eight leaching cycles, SAR of all the soils was lower than 12. For waste pyrite treated soil, SAR value, 6.35, was the lowest with Pyrite4 dose; followed by 6.42 with the gypsum application on the last leachate (Figure 4 .5). For sulphuric acid treated soil, the lowest SAR value, 5.11, was observed in H_2SO_4-5 application (Figure 4. 6).

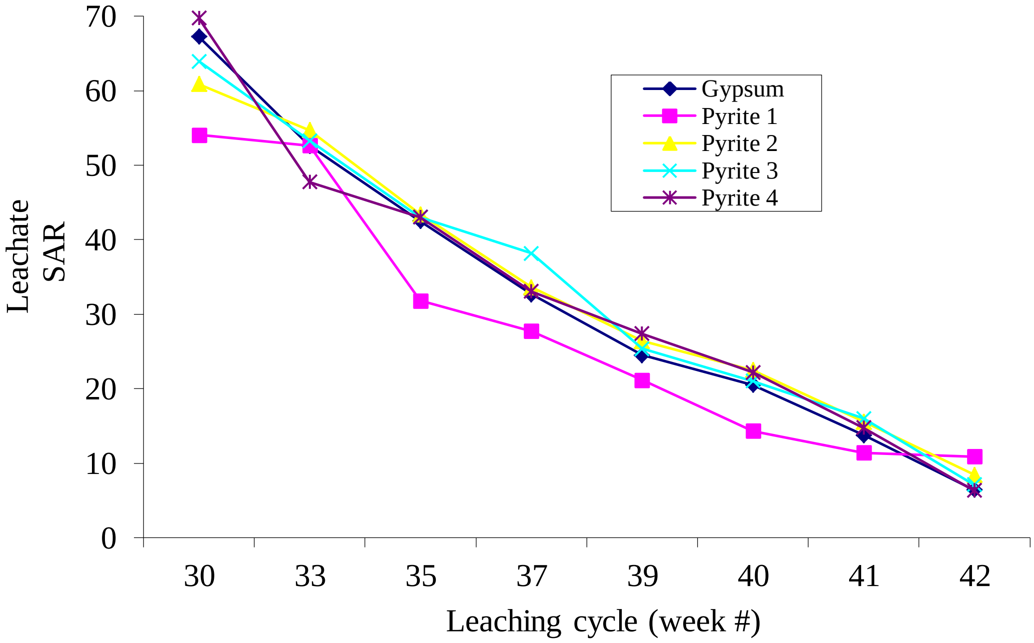


Figure 4. 5 SAR values in the leachates from Sarayköy calcareous-alkali soil (high ESP) columns treated with gypsum and waste pyrite

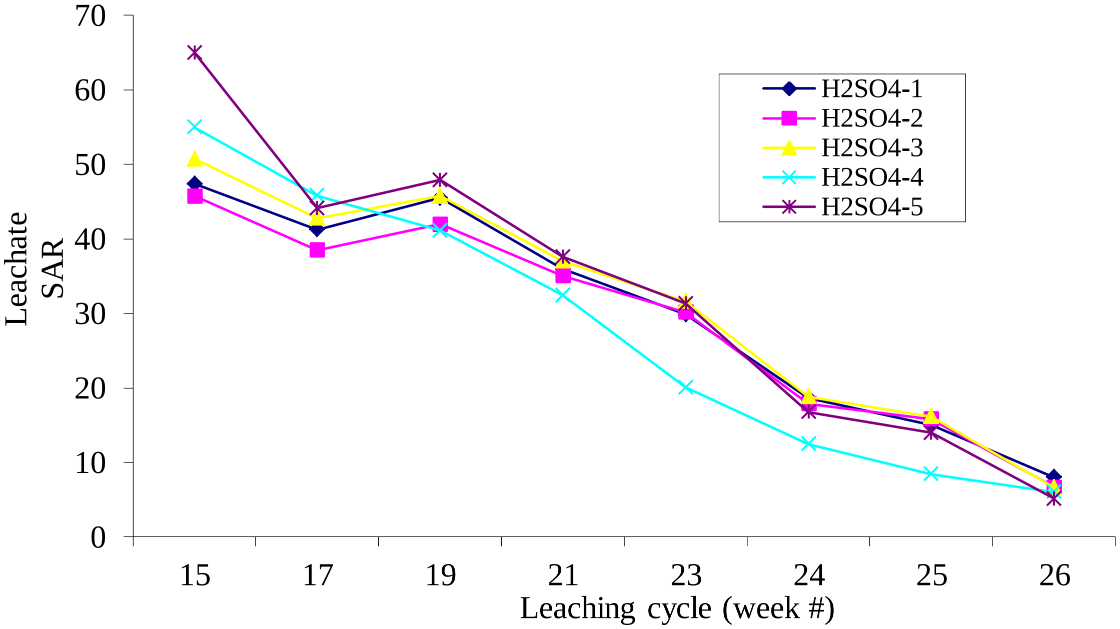


Figure 4. 6 SAR values in the leachates from Sarayköy calcareous-alkali soil (high ESP) columns treated with sulphuric acid

4.1.1.3 Case 3: Gaziantep Calcareous Soils

Soil leachate was collected after 5, 6, 7, 8, 9, 10, 11 and 12 weeks after start of irrigation. The amount of calcium leaching 185.43 $mmol_c/L$, was the highest with the Pyrite4 dose; followed by 172.59 $mmol_c/L$ with the Pyrite3 dose application on the last leachate (Figure 4 .7).

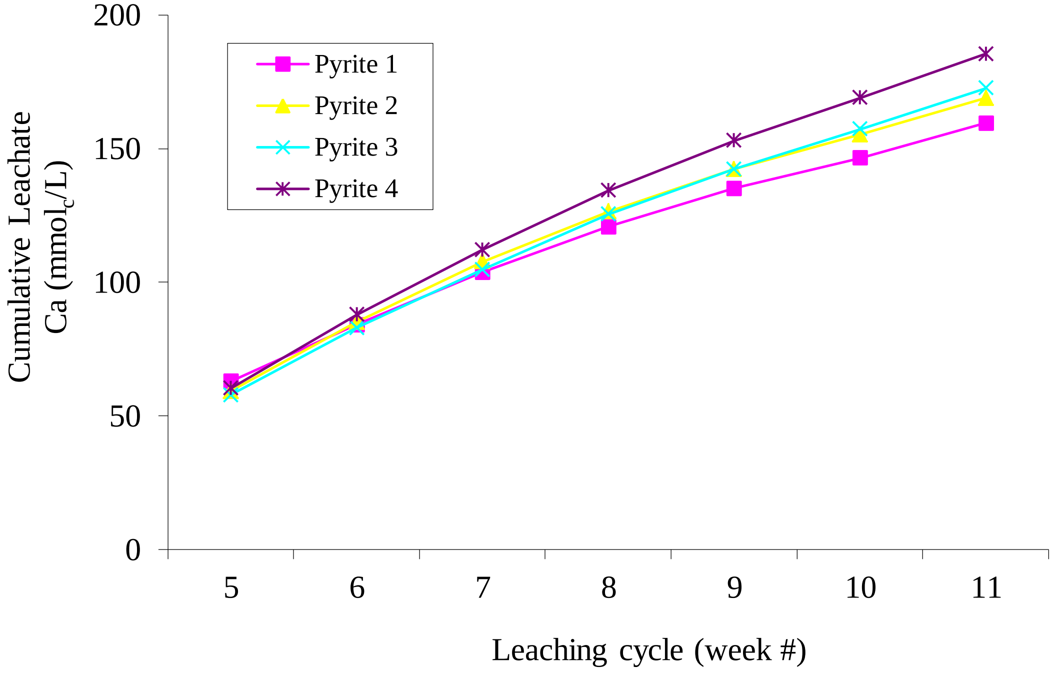


Figure 4. 7 Na in the leachates from Gaziantep calcareous soil columns treated with waste pyrite

4.1.2 Soil Properties After Leaching

4.1.2.1 Case 1: Sarayköy Calcareous-Alkali Soils (Low ESP)

The analysis of the soil before and after treatment with waste pyrite and gypsum are given in Table 4. 1. The treatments of the experiment were replicated four times and the mean values (with standard errors) of the data are presented. The data on soil parameters were statically analyzed using Duncan's multiple comparison tests for testing the significance of differences among treatments. All treatments had a significant effect on ESP, exchangeable Ca, $CaCO_3$, organic matter and boron content at the $P<0.01$ level and pH and EC at the $P<0.05$ level.

As the main purposes of the soil remediation in this study were to bring ESP down to 10 (alkali soils having greater than 15%), it can be seen from the table that this can be accomplished with both waste pyrite and gypsum. The reduction in ESP with pyrite was found to be somewhat lesser. This is probably due to the incomplete decomposition of pyrite. After leaching, the ESP decreased from 31.29 % to 4.85, 10.57, 10.48, 10.25 and 9.62% with the application of gypsum, Pyrite1, Pyrite2, Pyrite3 and Pyrite4 dose applications, respectively.

Although high pH of alkali soil has no direct adverse effect on plant growth, it frequently results in lowering the availability of some essential plant nutrients (FAO, 1988). The pH of the untreated soil was 8.76 slightly higher than threshold value of 8.5 (Richards, 1954). Upon treatment with gypsum and pyrite, the pH values of the soil were reduced down to 7.50-7.75. The decrease in the pH of the soil is due to the replacement of Na^+ during Na^+- Ca^{2+} exchange (Qadir et al., 1996). The electrical conductivity (EC) decreased in the treated soil due to the cation-washing. The starting EC of untreated soil was 1.27 dS/m which is well below the value of 4 dS/m separating non-saline soils from saline soils (Richards, 1954) and it was further reduced below down to 1 dS/m at the end of leaching.

As expected exchangeable calcium percentage in the soil increased with both gypsum and pyrite applications since gypsum itself is a source of calcium ion and acid produced by pyrite leads to the dissolution of $CaCO_3$ which in turn contributes to the availability of exchangeable calcium ions.

The dissolution of $CaCO_3$ is clearly seen in the $CaCO_3$% of the pyrite treated soil. The more the pyrite addition, the more the $CaCO_3$ dissolution and therefore the less the $CaCO_3$% in the treated soil was. $CaCO_3$ dissolution forms carbonic acid (H_2CO_3) which helps to displace the Na^+ and increases Ca^{2+} concentration in the soil solution, thus reclaiming the alkali soil. These findings lead us to infer that the soil is becoming less sodic and more suitable for plant growth. The $CaCO_3$% of the soil decreased from 10.50% to 9.97, 8.40, 7.35, 6.65 and 6.30% with gpysum, Pyrite1, Pyrite2, Pyrite3 and Pyrite4 dose applications, respectively.

Organic content of soil increased under all applications. Soil organic matter content of less than 2% has a low infiltration and low productivity (Ulgen and Yurtsever, 1974). By adding gypsum and increasing dose of waste pyrite, organic matter content in the soil increases significantly ($P < 0.01$) but only with waste pyrite applications the value increases above 2%.

Accumulation of boron in plants at toxic levels may result in plant injury or reduced growth and even death. (FAO, 1988).Limit value of boron is 1.5 ppm in saturated paste extract of soil for sensitive plants according to U.S. Salinity Laboratory (Richards, 1954). At high pH and sodicity, boron is present as highly soluble sodium metaborate which upon addition of pyrite is converted to relatively insoluble calcium metaborate. Gupta and Chandra (1972) observed a marked reduction in the water soluble boron content of a highly sodic soil upon addition of gypsum amendment. Boron decreased to well below 1.5 ppm with the addition of gypsum and waste pyrite.

Table 4. 1 Physical and chemical properties of Sarayköy calcareous-alkali soil (low ESP) before and after gypsum and waste pyrite treatment

Treatments	ESP(**)	pH(*)	EC(*) (dS/m)	Exch. Ca(**) (%)	$CaCO_3$(**) (%)	O.M.(**) (%)	Boron(**) (ppm)
Untreated Soil	31.29	8.76	1.27	51.01	10.50	1.71	1.87
Gypsum	4.85±0.351b	7.50±0.056b	0.78±0.044b	82.70±2.090a	9.97±0.071a	1.95±0.004e	0.47±0.029b
Pyrite 1	10.57±0.287a	7.75±0.045a	0.96±0.040a	71.54±0.651b	8.40±0.143b	2.13±0.008d	0.60±0.026a
Pyrite 2	10.48±0.186a	7.73±0.089a	0.88±0.009ab	72.58±1.270b	7.35±0.143c	2.29±0.003c	0.58±0.025a
Pyrite 3	10.25±0.278a	7.70±0.017a	0.86±0.003b	72.91±1.380b	6.65±0.143d	2.37±0.006b	0.58±0.010a
Pyrite 4	9.62±0.897a	7.60±0.044ab	0.84±0.030b	73.87±1.090b	6.30± 0.00d	2.45±0.002a	0.52±0.007ab

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.05$(*), $P < 0.01$(**) by Duncan's multiple range test

Because waste pyrites were obtained from copper concentration plant, they contain a certain quantity of heavy metals. Therefore, one of the concerns when using waste pyrite as a soil amendment is potential toxicity of the heavy metals to soils and plants. The heavy metal content of soil after leaching with maximum dose of pyrite application (Pyrite 4) to leaching columns and the maximum acceptable concentration for heavy metal concentration according to Turkish Soil Contamination Regulation (2001) are given in Table 4. 2. It was found that all values were within the tolerance limit of soil according to Turkish soil contamination regulation (2001).

Table 4. 2 Heavy metal content of Sarayköy calcareous-alkali soil (low ESP) after treated with Pyrite4 dose (maximum dose)

Element	Untreated soil (mg/kg soil)	Pyrite4 treatment (mg/kg soil)	Limit values (mg/kg soil)*
Cr	22.07	41.74	100
Co	2.33	14.38	20
Ni	27.10	38.80	75
Cu	16.92	115	140
Zn	75.34	109.20	300
Pb	17.15	25.57	300
Mo	1.30	1.83	10
Cd	0.14	0.35	3
As	2.54	7.31	20
Fe (%)	4.24	7.11	-

*according to Turkish Soil Contamination Regulation (2001)

In terms of the essential micronutrient needed for plant growth, it was observed that all the micronutrient into soil increased with waste pyrite application (Table 4. 3). The levels of the micronutrients after the pyrite treatments can be classified sufficient for plant growth (Follet and Lindsay, 1970; Lindsay and Norvell, 1978; FAO, 1990).

Table 4. 3 Essential micronutrient content of Sarayköy calcareous-alkali soil (low ESP) for plant growth

DTPA-extractable	Untreated soil	Pyrite 1	Pyrite 2	Pyrite 3	Pyrite 4	Sufficient level
Fe (ppm)	2.02	7.25±0.163c	7.58±0.264c	8.81±0.302b	10.97±0.177a	> 4.5[1]
Cu (ppm)	0.42	1.11±0.023c	1.25±0.065c	1.52±0.060b	1.97±0.048a	> 0.2[2]
Zn (ppm)	0.46	0.80±0.052c	1.13±0.041b	1.37±0.073a	1.45±0.044a	0.7 - 2.4[3]
Mn (ppm)	6.85	15.07±0.553c	15.31±0.301c	21.15±0.741b	24.68±0.781a	14 – 50[3]

Values represents means ± standart errors, different letters represent statistical differences at the ($P < 0.01$)) by Duncan's multiple range test

[1] Lindsay and Norvell, 1978; [2] Follet and Lindsay, 1970; [3] FAO, 1990

4.1.2.2 Case 2: Sarayköy Calcareous-Alkali Soils (High ESP)

The results indicated that gypsum, all application doses of waste pyrite and sulphuric acid produced from waste pyrite had a significant effect on EC, ESP, exchangeable Ca, $CaCO_3$, organic matter and boron content at the $P<0.01$ level in waste pyrite treated soils (Table 4. 4) and had a significant effect on ESP, exchangeable Ca, $CaCO_3$, organic matter at the $P<0.01$ level and on boron at the $P<0.05$ level in sulphuric acid treated soils (Table 4. 5).

All treatments had the ameliorative potential to lower the soil ESP below 15%. After leaching, ESP decreased from 83.33% down to 15% separating the sodic soils from non-sodic soils. The maximum decrease of ESP was observed in Pyrite4 dose (11.77%) and followed by gypsum (12.26%) applications in waste pyrite treated soil (Table 4. 4) and observed in H_2SO_4-5 (9.33%) and followed by H_2SO_4-4 (9.39%) applications in sulphuric acid treated soil (Table 4. 5).

The pH of untreated soil was 9.27 higher than threshold value of 8.5 (Richards, 1954). Upon treatment the pH values of the soil were reduced to 7.77-7.92 in waste pyrite treated soil and 7.28-7.51 in sulphuric acid treated soils.

The EC decreased in all the treated soil due to the removal of salts by leaching processes. The initial EC of untreated soil was 2.85 dS/m which is well below the value of 4 dS/m separating non-saline soils from saline soils (Richards, 1954) and it was further reduced at the end of leaching (Table 4. 4 and 4. 5).

As expected exchangeable calcium percentage in the soil increased with all gypsum, pyrite and sulphuric acid applications since gypsum itself is a source of calcium ion and acid produced by pyrite leads to the dissolution of $CaCO_3$ which in turn contributes to the availability of exchangeable calcium ions.

The dissolution of $CaCO_3$ is clearly seen in waste pyrite and sulphuric acid treated soils. The more the pyrite and sulphuric acid addition, the more the $CaCO_3$ dissolution and therefore the less the $CaCO_3$% in the soil was left.

Organic content of soils increased after all applications. By adding increasing dose of waste pyrite and sulphuric acid, organic matter content in the soil increased but only with Pyrite3 (2.29%) and Pyrite4 (2.65%) dose of waste pyrite applications the value reached above 2% (Table 4. 4). Boron decreased to well below 1.5 ppm with the all applications due to leaching except for Pyrite1 dose (1.63 ppm) application.

Table 4. 4 Physical and chemical properties of Sarayköy calcareous-alkali soil (high ESP) before and after gypsum and waste pyrite treatment

Treatments	ESP (**)	pH (NS)	EC (**) (dS/m)	Exch. Ca (**) (%)	CaCO3 (**) (%)	O.M. (**) (%)	Boron (**) (ppm)
Untreated Soil	83.33	9.27	2.85	15.37	9.18	0.71	8.87
Gypsum	12.26±0.041c	7.78±0.072	2.05±0.017bc	79.13±0.659a	8.12±0.204a	0.76±0.003d	1.03±0.020c
Pyrite 1	14.92±0.493a	7.92±0.023	2.27±0.016a	76.54±0.57bc	7.59±0.072b	0.84±0.027d	1.63±0.032a
Pyrite 2	14.63±0.15ab	7.87±0.075	2.11±0.023b	74.70±0.210c	7.14±0.047c	1.12±0.046c	1.30±0.011b
Pyrite 3	13.59±0.381b	7.85±0.013	2.09±0.019bc	76.73±0.6abc	6.27±0.052d	2.29±0.007b	1.26±0.079b
Pyrite 4	11.77±0.216c	7.77±0.051	2.02±0.019c	77.41±0.66ab	6.22±0.044d	2.65±0.037a	1.00±0.016c

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$(**) by Duncan’s multiple range test. NS: not significant

Table 4. 5 Physical and chemical properties of Sarayköy calcareous-alkali soil (high ESP) before and after sulphuric acid treatment

Treatments	ESP (**)	pH (NS)	EC (NS) (dS/m)	Exch. Ca (**) (%)	CaCO3 (**) (%)	O.M. (**) (%)	Boron (*) (ppm)
Untreated Soil	83.33	9.27	2.85	15.37	9.18	0.71	8.87
H_2SO_4-1	14.34±0.329a	7.51±0.076	2.06±0.004	76.63±0.261b	8.82±0.000a	1.11±0.000d	1.17±0.033a
H_2SO_4-2	13.65±0.331a	7.46±0.092	2.05±0.006	76.88±1.100b	6.71±0.144b	1.12±0.001d	1.08±0.017ab
H_2SO_4-3	12.16±0.246b	7.42±0.137	2.04±0.006	79.53±0.199a	6.00±0.144c	1.14±0.000c	1.06±0.034ab
H_2SO_4-4	9.39±0.026c	7.34±0.041	2.04±0.002	79.72±0.225a	5.65±0.000c	1.30±0.001b	1.05±0.024ab
H_2SO_4-5	9.33±0.179c	7.28±0.029	2.04±0.012	81.47±0.194a	5.65±0.0.144c	1.54±0.008a	1.00±0.027b

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.05$(*) and $P < 0.01$(**) by Duncan's multiple range test. NS: not significant

The heavy metal content of the soils after treatment with Pyrite4 dose (maximum dose of waste pyrite) and H_2SO_4-5 (maximum dose of H_2SO_4) applications are given in Table 4. 6. It was found that all values are within the tolerance limit of soil according to Turkish Soil Contamination Regulation (2001).

Table 4. 6 Heavy metal content of Sarayköy calcareous-alkali soil (high ESP) after treated with Pyrite4 dose and H_2SO_4-5

Element	Untreated soil (mg/kg soil)	Pyrite4 treatment (mg/kg soil)	H_2SO_4-5 treatment (mg/kg soil)	Limit values (mg/kg soil)*
Cr	24.59	32.40	62.70	100
Co	3.20	16.08	15.70	20
Ni	20.78	33.40	42.50	75
Cu	14.40	128.90	105.50	140
Zn	61.32	94.67	177.36	300
Pb	20.89	35.24	28.28	300
Mo	2.19	3.54	3.11	10
Cd	0.12	0.58	0.45	3
As	3.09	8.99	11.75	20
Fe (%)	4.08	8.04	6.28	-

*according to Turkish Soil Contamination Regulation (2001)

It was observed that all the micronutrient in the soil increased significantly ($P<0.01$) with waste pyrite and sulphuric acid applications (Table 4. 7). The levels of the micronutrients after treatments can be classified sufficient for plant growth except for the iron level with minimum dose of sulphuric acid application, H_2SO_4-1 (Follet and Lindsay, 1970; Lindsay and Norvell, 1978; FAO, 1990).

Table 4. 7 Essential micronutrient content of Sarayköy calcareous-alkali soil (high ESP) for plant growth

	DTPA-extractable	Untreated soil		Pyrite 1	Pyrite 2	Pyrite 3	Pyrite 4	Sufficient level
Waste Pyrite Applications	Fe (ppm)	1.75		8.55±0.094d	10.71±0.218c	14.86±0.402b	19.33±0.257a	> 4.5[1]
	Cu (ppm)	0.29		1.45±0.068d	3.24±0.091c	6.68±0.108b	8.80±0.060a	> 0.2[2]
	Zn (ppm)	0.07		1.70±0.044b	1.94±0.044ab	2.06±0.048a	2.08±0.121a	0.7 - 2.4[3]
	Mn (ppm)	3.53		20.01±0.707cd	28.34±0.877b	22.16±0.795c	35.48±0.538a	14 – 50[3]
	DTPA-extractable	Untreated soil	H_2SO_4-1	H_2SO_4-2	H_2SO_4-3	H_2SO_4-4	H_2SO_4-5	Sufficient level
Sulphuric Acid Applications	Fe (ppm)	1.75	3.61±0.091d	7.36±0.060c	7.25±0.102c	8.12±0.031b	11.07±0.203a	> 4.5[1]
	Cu (ppm)	0.29	3.84±0.037e	8.19±0.063d	9.65±0.060b	9.21±0.037c	9.90±0.056a	> 0.2[2]
	Zn (ppm)	0.07	1.14±0.039c	1.55±0.065b	1.97±0.042a	1.95±0.056a	2.10±0.303a	0.7 - 2.4[3]
	Mn (ppm)	3.53	14.94±0.052d	17.35±0.269c	25.08±0.189b	25.42±0.871b	29.76±0.358a	14 – 50[3]

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$ by Duncan's multiple range test

[1] Lindsay and Norvell, 1978, [2] Follet and Lindsay, 1970, [3] FAO, 1990

4.1.2.3 Case 3: Gaziantep Calcareous Soils

The soil was treated with four doses of pyrite, namely, 6.37 t/ha (Pyrite 1), 11.46 t/ha (Pyrite 2), 17.83 t/ha (Pyrite 3) and 25.48 t/ha (Pyrite 4) and all treatments had a significant effect on $CaCO_3$ and organic matter content (Table 4.8).

Table 4. 8 Relevant properties of Gaziantep calcareous soil before and after treatment

Treatments	$CaCO_3$ (**) (%)	O. M. (**) (%)	Boron (NS) (ppm)
Untreated soil	33.24	1.73	1.64
Pyrite 1	29.04±0.378a	2.54±0.003d	0.46±0.021NS
Pyrite 2	28.69±0.143a	2.64±0.003c	0.44±0.039NS
Pyrite 3	26.24±0.143b	2.73±0.003b	0.43±0.033NS
Pyrite 4	23.79±0.001c	2.78±0.004a	0.42±0.019NS

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$(**) by Duncan's multiple range test. NS: not significant

The $CaCO_3$% was reduced significantly ($P < 0.01$) from 33.24% to 29.04, 28.69, 26.24 and 23.79% with Pyrite1, Pyrite2, Pyrite3 and Pyrite4 dose applications, respectively because of dissolution of $CaCO_3$ with pyrite applications. Organic matter content in the soil increased above 2% under the applications of all doses. Boron decreased to well below 1.5 ppm with the addition of waste pyrite but there is no significant difference among the application doses of pyrite.

The heavy metal content of soil after leaching with maximum dose of pyrite application (Pyrite 4) to leaching columns and the maximum acceptable concentration for heavy metal concentration according to Turkish Soil Contamination Regulation (2001) are given in Table 4. 9. As can be seen from the table, the heavy metal concentration of soil treated with 25.48 t/ha of waste pyrite (Pyrite4) noticably increased. However, the concentrations were lower than the maximum acceptable concentration. It might be concluded that pyrite up to 25.48 t/ha can be added to the test soil with no deleterious risk of heavy metal contamination.

Table 4. 9 Heavy metal content of Gaziantep calcareous soil after treatment with Pyrite4 dose (maximum dose)

Element	Untreated soil (mg/kg soil)	Pyrite4 treatment (mg/kg soil)	Limit values (mg/kg soil)*
Cr	27.30	57.40	100
Co	2.59	13.71	20
Ni	21.06	37.80	75
Cu	19.49	106.60	140
Zn	76.15	154.50	300
Pb	14.81	31.93	300
Mo	0.93	2.47	10
Cd	0.31	1.14	3
As	0.74	4.65	20
Fe (%)	3.77	6.03	-

* according to Turkish Soil Contamination Regulation (2001)

In terms of DTPA-extractable Fe, Cu, Zn and Mn micronutrients essential for plant growth, it was observed that they all increased significantly ($P<0.01$) with the increasing dose of the waste pyrite applied to soil (Table 4. 10). The levels of the micronutrients after the pyrite treatments are sufficient for plant growth (Follet & Lindsay, 1970; Lindsay & Norvell, 1978; FAO, 1990).

Table 4. 10 Essential micronutrient content of Gaziantep calcareous soil for plant growth

DTPA-extractable	Untreated soil	Pyrite 1 (6.37 t/ha)	Pyrite 2 (11.46 t/ha)	Pyrite 3 (17.83 t/ha)	Pyrite 4 (25.48 t/ha)	Sufficient level
Fe (ppm)	2.10	7.22±0.11c	8.77±0.14b	8.90±0.11b	9.85±0.29a	> 4.5[1]
Cu (ppm)	0.35	1.16±0.04c	1.33±0.09c	1.75±0.010b	2.15±0.11a	> 0.2[2]
Zn (ppm)	0.42	1.07±0.06b	1.44±0.09ab	1.48±0.05ab	1.91±0.18a	0.7 - 2.4[3]
Mn (ppm)	9.79	17.31±0.12c	21.83±0.35b	25.40±0.38a	25.44±0.8a	14 – 50[3]

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$ by Duncan’s multiple range test

[1] Lindsay and Norvell, 1978; [2]Follet and Lindsay, 1970; [3] FAO, 1990

4.2 GREENHOUSE TESTS

4.2.1 Dry Matter Yield

Treated soils were used in the greenhouse pot tests to determine the weight of dry matter of the test crop, wheat and to observe visibly how the plant grew on the treated soils.

4.2.1.1 Case 1: Sarayköy Calcareous-Alkali Soils (Low ESP)

Plants were harvested after 30 days from seeding. They were cut 2 cm above the surface of the soil and washed with 0.05 N HCl and then with distilled water. After dried at 70^{o}C, plant was ground and total dry weight was determined. The dry matter production increased significantly ($P<0.01$) with gypsum and waste pyrite applications as compared to the untreated soil (Table 4. 11). More than 100% increase in the dry matter yield was observed in Pyrite2, Pyrite3 and Pyrite4 treated soils.

Table 4. 11 Effect of amendments on dry matter yield for Sarayköy calcareous-alkali soil (low ESP) treated with gypsum and waste pyrite

Treatments	Total Dry Weight (g/pot)
Untreated soil	19.33±0.182a
Gypsum	31.15±0.686b
Pyrite 1	34.65±0.431c
Pyrite 2	40.42±0.356d
Pyrite 3	40.79±0.305d
Pyrite 4	41.87±0.228d

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$ by Duncan’s multiple range test

In terms of length of the wheat, there is a sharp distinction between control group and others in the 30th day. Small wheat growth was observed in control group (Figure 4. 8).

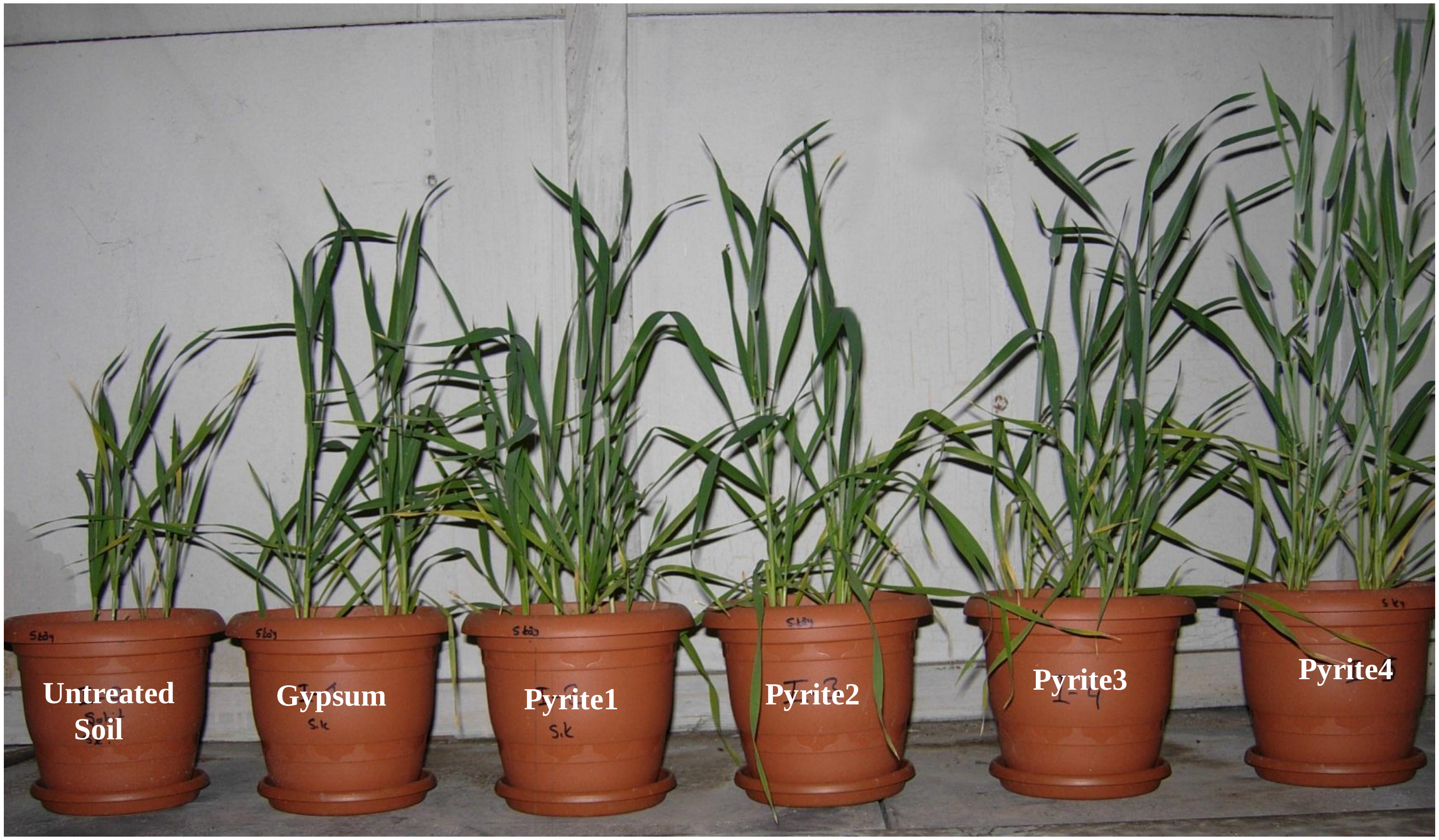


Figure 4. 8 Wheat growth on Sarayköy calcareous-alkali soils (low ESP) treated with gypsum and waste pyrite on the 30th day

4.2.1.2 Case 2: Sarayköy Calcareous-Alkali Soils (High ESP)

The results indicated that the dry matter yield of wheat plant improved significantly with gypsum, waste pyrite and sulphuric acid treated soil as compared with untreated soil ($P < 0.01$) (Table 4. 12 and Table 4. 13). The soils treated with Pyrite 4 dose in waste pyrite applications and 2700 cc dose of H_2SO_4 (H_2SO_4-5) in sulphuric acid applications showed the highest dry matter content (Figure 4. 9 and Figure 4. 10).

Table 4. 12 Effect of amendments on dry matter yield for Sarayköy calcareous-alkali soil (high ESP) treated with gypsum and waste pyrite

Treatments	Total Dry Weight (g/pot)
Untreated Soil	9.98±0.034e
Gypsum	24.03±0.558d
Pyrite 1	25.11±0.144d
Pyrite 2	28.65±0.374c
Pyrite 3	31.67±0.388b
Pyrite 4	35.10±0.129a

Values represents means ± standart errors, different letters represent statistical differences at the ($P < 0.01$) by Duncan's multiple range test.

Table 4. 13 Effect of amendments on dry matter yield for Sarayköy calcareous-alkali soil (high ESP) treated with sulphuric acid

Treatments	Total Dry Weight (g/pot)
Untreated Soil	9.98±0.0342e
H_2SO_4-1	27.35±0.592d
H_2SO_4-2	27.36±0.270d
H_2SO_4-3	29.12±0.295c
H_2SO_4-4	30.57±0.409b
H_2SO_4-5	34.32±0.223a

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$ by Duncan's multiple range test.

Figure 4. 9 Wheat growth on Sarayköy calcareous-alkali soils (high ESP) treated with gypsum and waste pyrite on the 30th day

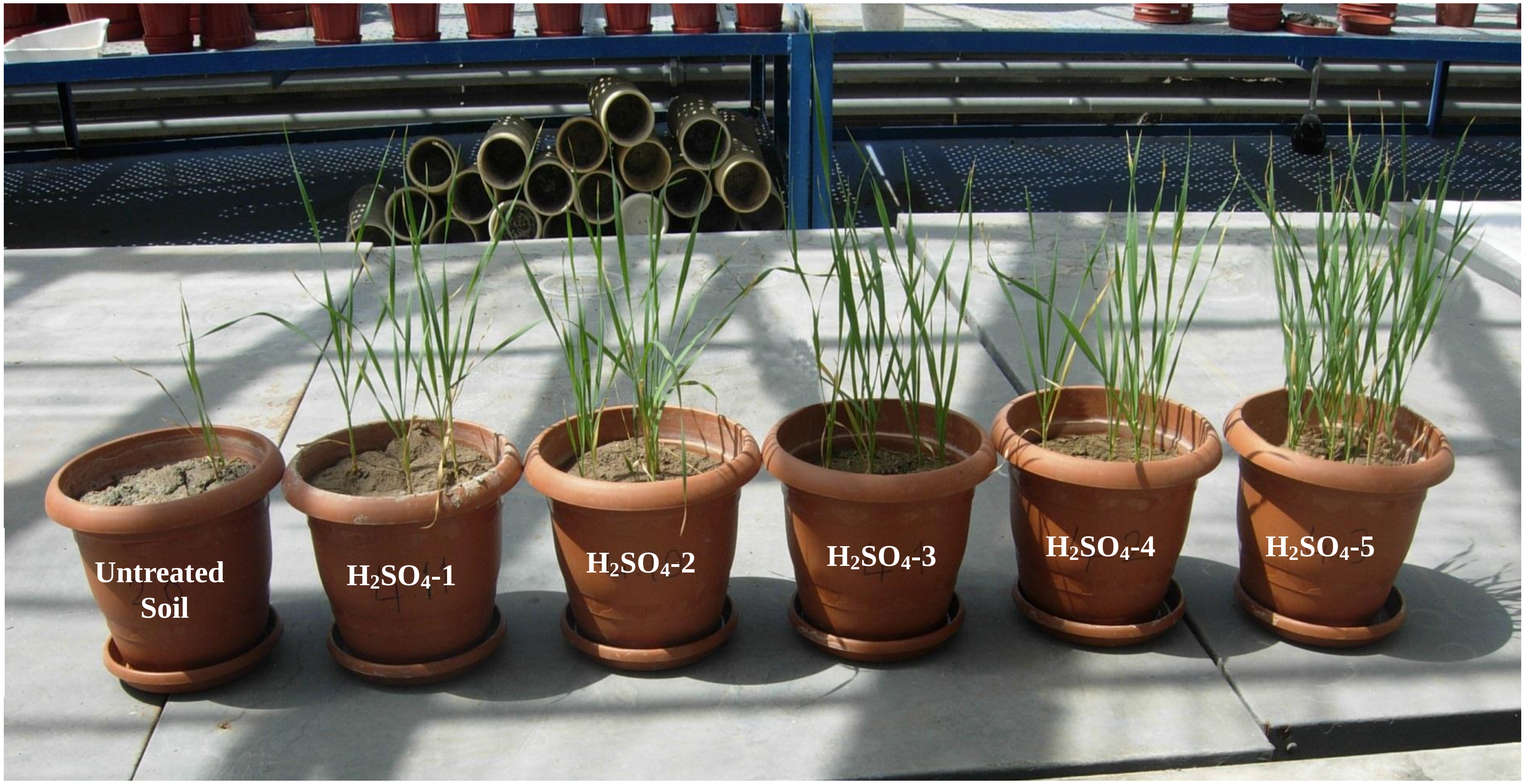


Figure 4. 10 Wheat growth on Sarayköy calcareous-alkali soils (high ESP) treated with sulphuric acid on the 30th day

4.2.1.3 Case 3: Gaziantep Calcareous Soils

The effect of pyrite amendments on dry matter yield given in Table 4. 14 indicate that pyrite addition had a favorable effect on the dry matter yield. It gradually increased from 20.21 g for untreated soil to 31.55 g, 31.92 g, 33.02 g, and 34.72 g per pot for Pyrite 1, Pyrite 2, Pyrite 3 and Pyrite 4 treated soils, respectively. This means that more than 70% increase in the dry matter yield was realized in Pyrite 4 treated soils (Figure 4.11). Similar beneficial effect of pyrites on plant yield of different crops has been reported earlier in India (Kaul et al., 1978; Sinha et al., 1978).

Table 4. 14 Effect of pyrite amendments on dry matter yield for Gaziantep calcareous soil

Treatments	Total Dry Weight (g/pot)
Untreated soil	20.21±1.02a
Pyrite 1	31.55±0.56b
Pyrite 2	31.92±0.54b
Pyrite 3	33.02±1.26b
Pyrite 4	34.72±0.74b

Values represents means ± standart errors, different letters represent statistical differences at the $P < 0.01$ by Duncan’s multiple range test

Figure 4. 11 Wheat growth on Gaziantep calcareous soils treated with waste pyrite on the 30th day

4.2.2 Heavy Metal Content of Wheat

It is necessary to evaluate the metal content in wheat plants when waste pyrite is used as an alkali soil amendment. The most important thing to confirm is whether or not the metal content exceeds the limit value.

4.2.2.1 Case 1: Sarayköy Calcareous-Alkali Soils (Low ESP)

The results, together with the limit values, are given in Table 4. 15. All of the metals in wheat plant increased by applying waste pyrite compared to the untreated soil. However, they all remained below the limit values. The results indicate that the wheat plant did not have any toxicity problems caused by the heavy metals from waste pyrite. These observations agree with those of Banath (1969) who found that high application rates of pyrite did not induce toxicity symptoms on subterranean clover (Trifolium subterranean).

Table 4. 15 The heavy metal content in wheat plant grown in untreated soil and soil treated with Pyrite4 dose and the limit values for Sarayköy calcareous-alkali soil (low ESP)

Element	Wheat grown in untreated soil	Wheat grown in soil treated with Pyrite4 dose	Limit values
Fe (ppm)	1.24	4.84	500 ppm[1]
Zn (ppm)	1.13	5.32	400-500 ppm[2]
Cu (ppm)	2.08	5.16	20-30 ppm[3,4]
Cr (ppb)	11.22	17.94	10 ppm[2]
Ni (ppb)	-	8.26	10 ppm[5,6]
Cd (ppb)	-	-	4 ppm[2]
Co (ppb)	1.21	6.09	10-30 ppm[2]
As (ppb)	14.60	16.17	10-20 ppm[2]

[1]Price and Hendry, 1991; [2]Sener et. al., 1994; [3]Hodenberg and Finck, 1975; [4]Robson and Reuter, 1981; [5]Bollard, 1983; [6]Asher, 1991

4.2.2.2 Case 2: Sarayköy Calcareous-Alkali Soils (High ESP)

The heavy metal content in wheat plant grown in untreated soil and soil treated with Pyrite4 dose and the limit values are given in Table 4. 16. All of the metals in wheat plant increased by applying waste pyrite and sulphuric acid compared to the untreated soil. However, they all remained below the limit values.

Table 4. 16 The heavy metal content in wheat plant grown in untreated soil and soil treated with Pyrite4 dose and H_2SO_4-5 and the limit values for Sarayköy calcareous-alkali soil (high ESP)

Element	Wheat grown in untreated soil	Wheat grown in soil treated with Pyrite4 dose	Wheat grown in soil treated with H_2SO_4-5	Limit values
Fe (ppm)	0.52	1.12	2.04	500 ppm[1]
Zn (ppm)	0.18	0.25	0.35	400-500 ppm[2]
Cu (ppm)	0.12	0.12	0.17	20-30 ppm[3,4]
Cr (ppb)	11.43	16.45	18.77	10 ppm[2]
Ni (ppb)	2.23	23.76	34.78	10 ppm[5,6]
Cd (ppb)	0.88	1.75	2.46	4 ppm[2]
Co (ppb)	2.15	5.47	14.61	10-30 ppm[2]
As (ppb)	11.16	18.75	17.31	10-20 ppm[2]

[1] Price and Hendry, 1991; [2] Sener et al., 1994; [3] Hodenberg and Finch, 1975; [4] Robson and Reuter, 1981; [5] Bollard, 1983; [6] Asher, 1991

4.2.2.3 Case 3: Gaziantep Calcareous Soils

The heavy metal content in wheat increase by applying waste pyrite compared to the untreated soil (Table 4. 17). It was found that all values are within the tolerance limit of soil according to Turkish Soil Contamination Regulation (2001).

Table 4. 17 The heavy metal content in wheat plant grown in untreated soil and soil treated with Pyrite4 dose and the limit values for Gaziantep calcareous soil

Element	Wheat grown in untreated soil	Wheat grown in soil treated with Pyrite4 dose	Limit values
Fe (ppm)	0.13	0.85	500 ppm[1]
Zn (ppm)	0.08	0.44	400-500 ppm[2]
Cu (ppm)	0.03	0.19	20-30 ppm[3,4]
Cr (ppb)	-	22.61	10 ppm[2]
Ni (ppb)	11.77	43.91	10 ppm[5,6]
Cd (ppb)	-	1.36	4 ppm[2]
Co (ppb)	-	28.21	10-30 ppm[2]
As (ppb)	3.80	4.20	10-20 ppm[2]

[1]Price and Hendry, 1991; [2]Sener et. al., 1994; [3]Hodenberg and Finck, 1975; [4]Robson and Reuter, 1981; [5]Bollard, 1983; [6]Asher, 19

CHAPTER 5

CONCLUSIONS

In view of the results obtained in this study, the following conclusions are derived:

- For Sarayköy calcareous-alkali soil (low ESP) 27 weeks was enough to decrease the soil ESP from 31.29% to 9.62% with the application of Pyrite4 dose (28.03 t/ha) and from 31.29% to 4.85% with the application of gypsum of 19.90 t/ha dose. However, the dry matter content increased more than 100% with Pyrite4 dose while 60% increased with gypsum (19.90 t/ha) application to the soil.

- For Sarayköy calcareous-alkali soil (high ESP) the application of waste pyrite with a dose of 44.74 t/ha (Pyrite4) was superior to the gypsum of 55.20 t/ha dose in terms of exchangeable sodium percentage (ESP), availability of essential micronutrients for plant growth and dry matter content in 42 weeks. ESP decreased from 83.33% to 11.77% with the application of Pyrite4 dose (44.74 t/ha) and from 83.33% to 12.26% with the application of gypsum of 55.20 t/ha dose. In addition, application of all the concentrations of the sulphuric acid produced from waste pyrite also increased the availability of essential micronutrients and decreased ESP values. The best values with the sulphuric acid were obtained with a dose of 35.31 t/ha (H_2SO_4-5) in 26 weeks. The soil ESP decreased from 83.33% to 9.33% with the application of H_2SO_4-5 (35.31 t/ha).

- For Gaziantep calcareous soil all pyrite addition level were effective in the availability of essential micronutrient and the dry matter content.The dry matter wheat yield increased with the increasing dose of waste pyrite and highest dry matter yield was obtained in Pyrite4 treated soil.

- The heavy metal content of the soil after all waste pyrite addition level increased relative to their initial levels; but their contents are found below the limit values. Therefore there is no toxicity problem in terms of heavy metal contamination.

To sum up, the application of pyritic tailings to the soil resulted in the increased availability of DTPA-extractable Fe, Cu, Zn and Mn which are essential for plant growth and also resulted in the increased dry matter yield. The pyrite does not appear to lead to pollution or toxical problems in the soil and the plant. Thus, the use of pyrite, by-product or a waste from copper concentration plants, may indeed be a useful amendment and effective fertilizer in calcareous soils and calcareous-alkali soils.

This study showed that if pyrite is applied in a certain dose, it can be efficiently and safely used as a soil amendment and its use in such an application will alleviate the problems in disposal of pyritic materials from mine sites.

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WORK EXPERIENCE

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FOREIGN LANGUAGES English

PUBLICATIONS

BOOKS

Gülsün M., Özün S., Sivrikaya O., Lüle M., **Aydın G**., Kaya R., Acar C., Acar İ., Pekpak E., Sözeri H., Camalan M., Çırak, M., *"Mineral Processing Laboratory Manual",* METU Printing House, Ankara, Turkey, 2010.

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3. The enrichment of low grade hematite ores by gravity and magnetic separation methods.
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1. *“The use of waste pyrite for soil remediation”*. (2010, July). University of British Columbia, Mining Engineering Department, Vancouver, Canada.

SCHOLARSHIPS

1. *“TUBİTAK Yurt Dışı Araştırma Burs Programı Bursu” 2009 - 2010,* Visiting Scholar, University of British Columbia, Mining Engineering Department.