UNIVERSITI
TEKNOLOGI
PETRONAS

FINAL YEAR PROJECT II

Treatment of Acidic Soil Contributed By Carbonaceous Shale

by

AARON SUBASH GEORGE (10363)

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

JANUARY 2010

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

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Approved by,

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TRONOH, PERAK

January 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AARON SUBASH GEORGE (10363)

ABSTRACT

This report basically discusses the research done and basic understanding of the chosen topic, which is **Treatment of Acidic Soil Contributed by Carbonaceous Shale**. The objective of the project is to find the optimum treatment which will be able to treat the acidic soil contributed by carbonaceous shale. The main reason to conduct the study on the shale is due to the soil erosion and landslides that occurs. Leaching process and gas evaporation technique is used to treat the soil. The acidic soil should be treated because it gives a serious impact to the environment and it can also pose a big threat and endanger peoples live. Sulphuric acid due to the oxidation contaminates the underground water. Underground water is the main source of drinking water. Besides that, due to the acidic soil, plants are unable to grow which lead to slope failure. The acidic soil is contributed by the oxidation of pyrite (FeS_2). The challenge in this project is to find the most appropriate method that will be able to suppress the pyrite oxidation which later influences the pH of the soil. Treatment methods using chemicals such as 8-hyroxyquinoline, ammonium gas evaporation, and calcium carbonate will be applied in order to treat the shale. Lab testing will be done by using the carbonaceous shale in order to reduce the acidity by suppressing the oxidation of pyrite. Once the treatment is completed, chemical treatment would be conducted in order to bring down the pH level of the soil. Finally, plants or vegetation will be grown in order to prove that the treatment has worked and the pH of the soil has reduced.

Acknowledgements

I would like to seize this opportunity to thank to all parties who has contributed along the process in completing the project, especially my supervisor AP Askury Abdul Kadir. AP Askury Abdul Kadir was very supportive and he had helped me through out the last eight months of my project duration. My Special acknowledgment to The Department of Chemical Engineering, University technology PETRONAS and its entire staff who has assisted me through out:

1. Dr. Khalik – Fyp II Coordinator
2. Dr.Murugesan
3. All technicians

Besides that, I would like to thank University Technology MALAYSIA (UTM) for providing me the chemicals needed to carry out the project.

Apart from that, I also want to express my appreciation to my beloved parents whose supportive spirit never faded in supporting me to accomplish my project. Lastly, thanks to everyone who has contributed directly or indirectly in completing this task.

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CHAPTER 1
INTRODUCTION

1.1 BACKGROUND OF STUDY

Acidic soil contributed by carbonaceous shale is basically due to pyrite oxidation. Pyrite (FeS_2) is a common mineral found in sedimentary rock and fossils, and its decay is a major problem in the conservation of fossil specimens. Pyrite oxidation, also referred to as pyrite disease or pyrite decay, is identified by a sulphuric acid odor, white crystalline powder, yellow sulphide powder, and/or gray to yellowish microcrystalline mass in and out of specimens. Its presence can be devastating to a geological collection. In the presence of oxygen, pyrite breaks down to ferros sulphate ($FeSO_4$) and sulphur dioxide (SO_2). If water is present, sulphuric acid (H_2SO_4) is also produced and can cause damage to labeling and storage containers. Acid sulfate soils are acidic soil horizons or layers resulting from the aeration of materials that are rich in iron sulfides, primarily pyrite (FeS_2). Potential acid sulfate soils are typically waterlogged soils rich in pyrite that have not been oxidized. Any disturbance which exposes potential acid sulfate soil to the air (oxygen) will lead to the development of extremely acidic, actual acid sulfate soil layers with $pH < 4$. The identification and assessment of the distribution and severity of acid sulfate soil conditions is the first step for land use assessment. However, acid sulfate soils are highly variable and have extremely dynamic characteristics. Also, the source of the acid (sulfides) has a very heterogeneous distribution. These characteristics can make identification in the field and quantification of the problem extremely difficult. Therefore the identification and assessment of acid sulfate soil conditions is highly dependent on appropriate assessment of these soils by survey, field and laboratory analysis and sound interpretation of the results. Oxidation of pyrite, the main source of the acidity, can be described by the following equations.

The initial step in pyrite oxidation is the production of elemental sulfur and ferrous iron II (White and Melville 1993):

$FeS_2 + 1/2O_2 + 2\ H^+ \rightarrow Fe^{2+} + S0_2 + H_2O$ (1)

The sulfur is then oxidized to sulfate and acid (sulfuric acid):

$SO_2 + 3O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+$ (2)

The complete reaction of pyrite to ferrous iron II and sulfate can be written as:

$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}$ (3)

The soluble ferrous ion may then be oxidized further from iron II (ferrous) to iron III (ferric):

$Fe^{2+} + H^+ + 1/4O_2 \rightarrow Fe^{3+} + 1/2H_2O$ (4)

If the pH is greater than 4, the final step is the precipitation of ferric hydroxide and the liberation of more acid in a reaction known as hydrolysis:

$Fe^{3+} + 3H_2O \rightarrow Fe\ (OH)_3 + 3H^+$ (5)

If the pH is less than 4, iron III can remain in solution. The dissolved iron III greatly accelerates the oxidation process of pyrite (by electron transfer) and does not require oxygen to oxidize pyrite.

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + SO_4^{2-}$ (6)

The reaction can result in considerable acid production when existing acid sulfate soils containing iron III are re-flooded or buried under water without lime treatment. This is because oxidation-reduction processes involve electron transfer and do not necessarily need oxygen for oxidation of pyrite to occur as popularly believed. The soluble ferrous iron (Fe2+) can easily be transported downstream where the reaction removes dissolved oxygen from the water during the oxidation process to produce more acid.

$$Fe^{2+} + 1/4O_2 + 3/2\ H_2O \rightarrow FeOOH + 2H^+ \qquad (7)$$

The overall reaction for the complete oxidization of pyrite can be given as Dent (1986):

$$FeS_2 + 15/4O_2 + 7/2\ H_2O \rightarrow Fe\ (OH)_3 + 2SO_4^{2-} + 4H^+ \qquad (8)$$

Due to pyrite oxidation, not only the soil becomes acidic but the soil is decomposed. Plants or vegetation are not able to grow. This is when slope failures occur. The resistance and the strength of the soil can be reinforced by the plant root system. In order to have a plant root system, the pH of the soil need to increased to make it less acidic in order for plants or vegetation to grow.

1.2 PROBLEM STATEMENT

Various researches had been done in order to treat the acidic soil contributed by carbonaceous shale. Acidic soil contributed by pyrite oxidation in carbonaceous shale has a very low pH near 3. An appropriate method need to be implemented in order to treat the acidic soil problem. Due to the high acidity, plants or vegetation are unable to grow. The growth of plants or vegetation is important because the roots of the plant can serve as natural fiber reinforcement and will increase the resistance to slope failures.

1.3 OBJECTIVE AND SCOPE OF STUDY

The main objectives of this research are:

- To find the most effective method to prevent rapid pyrite oxidation or to suppress pyrite oxidation chemically or biologically.
- To find an appropriate treatment to treat acidic soil
- To conduct few experiments to find the appropriate plantation that can grow on a acidic soil condition

1.4 FEASIBILITY OF THE PROJECT WITHIN THE SCOPE AND TIME FRAME.

The scope of work for this project is to investigate the cause and the treatment to treat the acidic soil. Lab testing will be carried out to stop pyrite oxidation and to neutralize the acidic soil. A glasshouse experiment will be conducted to find the appropriate plant or vegetation that would be able to grow on an acidic soil. The project is feasible as there are high chances for the methods tested to produce good results. Previous studies show that some of the methods used in the experiment have given satisfactory results. The time frame for this project is limited. However, good planning and organizing is important in order to complete the project within the time frame given.

CHAPTER 2
LITERATURE REVIEW

2.1 INTRODUCTION

Pyrite (FeS_2) is one of the most widespread and persistent minerals and occurs in sedimentary, metamorphic, and igneous rocks. Pyrite grows in crystalline forms, typically cubic, octahedral, or more rarely pyritohedral (irregular dodecahedral with twelve identical pentagonal faces). The crystal can be several centimeters in diameter for well-grown cubes, or microcrystalline (0.1 to 1.0 µm for the individual microcrystals) (Birker and Kaylor, 1986, and Howie, 1992). Marcasite (FeS_2) is a polymorph of pyrite with orthomorphic form that primarily occurs in sedimentary rocks, and is not as commonly found as pyrite, but it can also be unstable and susceptible to oxidation.

Figure 1: Pyrite

Figure 2: Marcasite

Pyrite oxidation is also known as pyrite 'disease', pyrite 'rot', and pyrite 'decay', and it is caused and accelerated by the presence of oxygen and water. In this condition pyrite undergoes rapid oxidation;

$$4FeS_2 + 13O_2 + 2H_2O \rightarrow 4FeSO_4 + 2H_2SO_4 + 2SO_2$$

Products of oxidation reactions depends on mineral composition of fossils and matrixes associated with oxidizing pyrite or marcasite, but are sulphuric acid and various hydrated sulphates (e.g., ferrous sulphate ($FeSO_4$), copiapite, fibroferrite ($Fe3+(SO_4)(OH)·5(H_2O)$), melanterite ($Fe_2O_4.7H_2O$)) (Wang et. al., 1992).

Figure 3 : Oxidation reaction with various minerals

Pyrite oxidation can also be caused by bacteria, *Thiobacillus ferrooxidans* and *Thiobacillus sp.* but bacterial decay typically occurs above 95% humidity, therefore it is not likely to be a problem in museum collections (Butler, 1994, and Howie, 1992).

Figure 4: Corrosion Damage Caused by Thiobacillus Ferrooxidans and Thiobacillus sp

2.2 Suppression of Pyrite Oxidation by Iron 8 – Hydroxyquinoline (C_9H_7NO)

According to Y.Lan, X.Huang, and B.Deng (2001), one of the important approaches to prevent pyrite oxidation is to create a surface coating on pyrite. In the study conducted, a coating of iron 8 – hydroxyquinoline was formed by leaching pyrite with a 0.10 M H_2O_2/0.0034 M 8-hydroxyquinoline solution; stability of the coated pyrite was tested under various pH and temperature conditions. The results showed that iron 8-hydroxyquinoline coating could significantly suppress further pyrite oxidation by both chemical (H_2O_2) and biological (*e.g., Thiobacillus ferrooxidans*) processes. At pH from 3.0 to 5.0 and temperature from 10–40°C, the amount of $SO4_2$ leached out by 0.10 M H_2O_2 from the coated pyrite samples was 54.8–70.1% less than that from the uncoated controls. The oxidation of pyrite followed a pseudo–zero-order kinetics under the constant concentration of H_2O_2. In the presence of microorganisms, sulfate leached out of the uncoated pyrite in one year accounted for 5.32% of the total pyrite in the system, with a concurrent pH drop to 2.35 under the ambient room temperatures. In contrast, the amount leached out from the coated samples was only 0.15% of the total pyrite and the final pH was 5.48. Thus, the coating decreased the leachability of pyrite by 97% in the inoculated systems. In comparison to the more widely studied iron phosphate coating, the advantage of iron 8-hydroxyquinoline coating was that it inhibited both chemical and biological pyrite oxidation, whereas iron phosphate coating could only inhibit chemical pyrite oxidation.

2.3 Ammonium Gas and Ethanol Amine Thioglycollate Treatment

According Shinya. A and L. Bergwall 1998, ammonium gas and ethanolamine thioglycollate treatments neutralize sulphuric acid and remove ferros sulphate, and are reportedly effective in partly or completely removing oxidation reaction products. Specimens that contain large amounts of pyrite and are in danger of losing morphological information through pyrite oxidation should be molded and cast. Because latex rubber contains ammonium, its use as a molding material can have the added benefit of neutralizing sulphuric acid and ferros sulphate. Although not tested in a controlled scientific experiment, it has been reported that this method was successful in halting the oxidation process in some specimens. Ammonium gas has been successfully used to neutralize sulphuric acid in specimens affected by pyrite decay (Bannister, 1933; Bannister and Sweet, 1943; Birker and Kaylor, 1986; Howie, 1992; Rixon, 1976). Specimens are suspended above a solution of ammonium hydroxide and covered by polyethylene or glass to contain the gas created by evaporation. The RH above the solution can reach 70% but can be lowered to 30% when mixed with polyethylene glycol (PEG) in a 10% (volume to weight) solution. Because porous pyrite will absorb water vapor (resulting in further oxidation) it is important that the ammonium solution be made with a non-aqueous solvent. Use of ethanolamine thioglycollate is useful because it will both neutralize sulphuric acid and remove oxidation products, perhaps more effectively than ammonium gas treatment. Ethanolamine thioglycollate is an alkaline liquid that is soluble in both ethanol and isopropanol; hence the specimen will not be exposed to water during the treatment. Before treatment as much coating as possible should be removed to expose the specimen surface. Two methods are described in the literature (Cornish and Doyle, 1984 and Cornish, 1987):

2.4 Lime (Calcium Carbonate) Treatment

The *in situ* buffering capacity of soil material is the soil's ability to counteract acidity and lowering of the soil pH. The buffering capacity of a soil may include calcium carbonate deposits (eg shell), reaction with the organic fraction (eg peat layer) or cation exchange and reaction with the soil clay fraction (White and Melville 1993). The effectiveness of the buffering capacity however, and the actual pH which is produced in the soil, depends on the types and quantities of clay minerals, the form of the carbonates (fine or coarse) and the rate of oxidation and acid production. The presence of carbonate deposits in excess of potential acidity does not necessarily prevent soil acidification if the carbonates are locked up in shells or as unreactive coarse fragments. It is extremely important to know the *in situ* form of the carbonates for a correct interpretation of analytical results and the identification of appropriate management techniques. It should be noted that normal laboratory preparation methods of grinding the soil affects the fineness and reactivity of shell and may artificially increase the apparent acid neutralizing capacity of a soil.

Finely divided $CaCO_3$ is a source of neutralizing capacity (Dent and Bowman 1993). One mole of CaCO3 will neutralize two moles of acidity (H^+).

1 mole $CaCO_3$ will neutralize 2 moles H^+ (1 mole $CaCO_3$ = 100.0872 g) 1
mole H_2SO_4 is equivalent to 2 moles H^+ (1 mole H_2SO_4 = 98.0795 g)

So, 1 part $CaCO_3$ 1 part H_2SO_4 (by weight)

The reaction of acid produced from pyrite with calcium carbonate results in precipitates of calcium sulfate, usually gypsum, and carbon dioxide.

$$CaCO_3 + 2H^+ + SO_4^{2-} + H_2O \rightarrow CaSO_4.2H_2O + CO_2$$

In most of the acid sulfate soils in Australia, there are insufficient shell deposits, carbonates or natural clay buffering capacity to neutralize the acid produced by pyrite oxidation (White and Melville 1993).

2.5 Plantation and Vegetation according to the pH of the soil

According to New World Truffieres, (2003), the pH value is a measure of the acidity of a soil and is based on a set of numbers from 1 to 10 that are universally recognized. The number 7 has been given to a soil that is neutral. Numbers above 7 indicate an alkaline soil and numbers below 7 indicate an acid soil.

Plants or vegetation planted according to the pH values.

pH of the soil	Plants or vegetation to be planted
Very strong Acid Soil. **pH 3.0 – 4.5**	Melaleuca, lilypilly, sasatras, coachwod, grasses(Axonopus affnis, Veteveria zizaniodes and Brachiaria ruziziensis) and legum (Colologonium mucunoides)
Strong Acid Soil. **pH 5.0 - 5.5**	Plants for acid soil in this range include Parsley, Potato, Tomato, Sweet Potato, Maize, Millet, Oars, Tye, Radish, Azalea, Ferns, Iris, Orchids, Rhododendron, Camellia, Daphne and Boronia.
Moderately Acid Soil. **pH 5.5 - 6.**	Plants for a moderately acid soil include Bean, Brussels Sprouts, Carrot, Choko, Endive, Kohl Rabi, Peanuts, Rhubarb, Soyabean, Crimson Clover, Aster, Begonia, Canna, Daffodil, Jonquil, Larkspur, Petunia, Primrose
Slightly Acid Soil. **pH 6.0 - 6.5**	Plants that prefer this soil include Broccoli, Cabbage, Cauliflower, Cucumber, Egg Plant, Pea, Sweet Corn, Pumpkin, Squash, Turnip, Red Clover, Sweet Clover, White

	Clover, Candytuft, Gladiolus, Iceland Poppy, Pansy, Rose, Snapdragon, Viola, Wallflower, Zinnea and Strawberry.
Very Mildly Acid. Soil **pH 6.5 - 7.0**	Plants that favor very mildly acid soil are Asparagus, Beet, Celery, Lettuce, Melons, Onion, Parsnip, Spinach, Lucerne, Carnation, Chrysanthemum, Dahlia, Stock, Sweet Pea and Tulip.(American Journal of Applied Science)

2.6 Reacting an Acidic Solution of cerium IV salt with Pyrite containing Solid

According to United States of Patent

Patent Number: 4,640,692

Date of Patent: Feb 3, 1987

A process for the removal of pyritic sulfur from shale, coal and other carbonaceous material which comprises reacting a pyritic containing solid with acidic cerium IV salt solution. In particular, this relates to a process for the removal of pyritic sulfur from a pyrite containing solid comprising:

a) Reacting a first quantity of an acidic solution of cerium IV salt with a pyrite containing solid, where the molar ration of the cerium IV salt to pyrite is less than stoichiometric requirement to remove all of the pyrite from the solid.
b) Separating said cerium IV salt treated pyrite containing solid from the said reaction mixture, and
c) Reacting the remaining pyrite containing solid with a second quantity of acidic solution of cerium IV salt, where the molar ratio of the cerium IV to pyrite is more than the stoichiometric requirement to remove the remaining pyrite from the solid.

Although, a single treatment of a pyrite-containing solid with an appropriate quantity of an acidic solution of cerium IV salt will effect a measureable reduction in the pyrite, it is preferable to practice the process of the present invention in multiple stages. Thus, a two stage operation is quite effective although 3, 4, 5 or more stages are beneficial to achieve the desired reduction in pyrite contain. In the first stage of a two stage process and in the first and intermediate stages of those processes employing more than two stages, these stages are operated in a fashion distinct from that of the last stage insofar as the relative quantities of the cerium IV salt solution are concerned. Thus, in the initial and any intermediate stages, the ratio of cerium IV salt to pyritic sulfur of the carbonaceous material should always be less than the stoichiometric. While in the last treating step, the ratio should always be greater than stoichiometric. Those skilled in the art will appreciate that the number of stages utilized when practicing the present invention should be determined by carrying out a screening treatments to provide sufficient data to determine the ideal number of stages to be employed so as to achieve the desired pyrite reduction of a given material.

CHAPTER 3
METHODOLOGY

3.1 PROJECT IDENTIFICATION

The sample used for the experiments are taken from Batu Gajah new road. The samples are collected in the form of rock and sand. In order to perform the experiments, the samples need to be grinded into powder form. Thus the samples collected are grinded using the grinder from the civil lab.

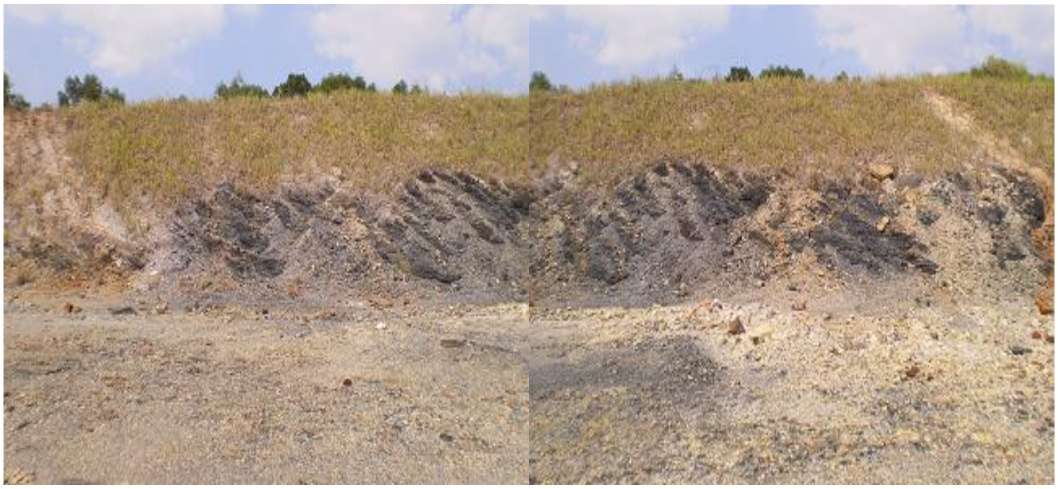

Figure 5: Batu Gajah Road

Figure 6: Rock sample

Figure 7: Grinder

Figure 8: Pots filled with grinded carbonaceous shale

Sample collected was grinded using the grinder above and kept in small flower pots sealed with aluminum foil.

Tests that are going to be conducted for this project:

3.1.1 Suppression of Pyrite Oxidation by 8-Hyroxyquinoline (C_9H_7NO)

a. A fine fraction of carbonaceous shale containing pyrite sample must be prepared.
b. 3 beakers of 300ml of leaching solution must be prepared. The leaching solution must contain 0.10 M H_20_2 and 0.0034M 8-Hydroxyquinoline.

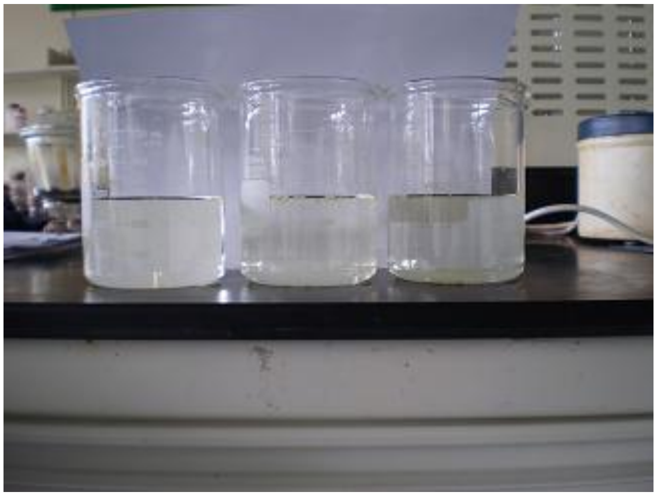

Figure 9: 300ml leaching solution

c. The fine fraction of carbonaceous shale is then added together with the leaching solution into the beaker.

Figure 10: Leaching solution containing carbonaceous shale

d. The solution is stirred well and the beaker is kept into the shaker for 480 minutes (6 hours). During leaching, a coating of iron 8-hydroxyquinoline is expected to form on the pyrite surface because of its extremely low solubility.

Figure 11: Shaker (water bath)

e. After 6 hours, the beaker is removed from the shaker. The solution is then titrated in order to obtain the fine fraction of carbonaceous shale.

Figure 12: Titration

f. The fine fraction is later completely rinsed with distilled water and wrapped in aluminum foil.

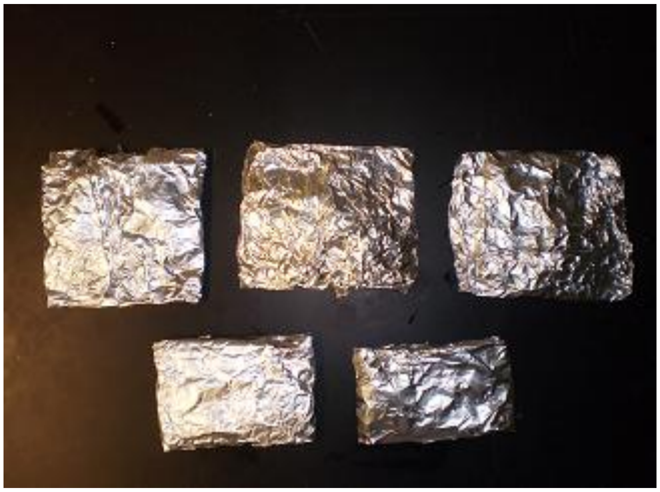

Figure 13: Sample Wrapped in aluminum foil

g. Sample is then dried in the oven at 60 ^{o}C in order to remove water retention (Lin and Xue 1989).

Figure 14: Sample dried in the oven

3.1.2. Ammonium gas treatment

a. 10% volume to weight solution of ammonium hydroxide in polyethylene glycol (PEG) must be made.

Figure 15: 10% w solution of Ammonium Hydroxide

b. A plastic coated metal rack must be placed over the solution and the specimen should be placed on top.

c. The apparatus must be covered with polyethylene or glass to treat the specimen with ammonium vapor.

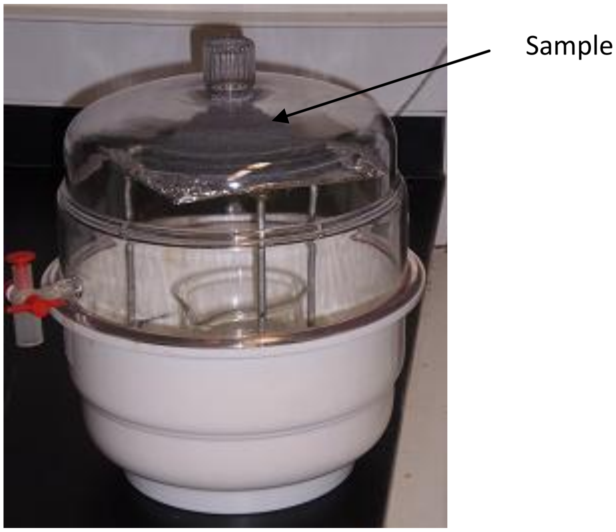

Figure 16: Ammonium Gas Evaporation

d. Treatment is complete when white or yellowish patches on specimen change to rust colored stains.

e. Specimen must be cleaned with alcohol and thoroughly dried.

Figure 17: Sample dried in the oven

3.1.3 Ethanolamine Thioglycollate Treatment

Method 1: Immersion in solution

a. Make 2-5% ethanolamine thioglycollate solution in ethanol or isopropanol.

b. Immerse a specimen in solution for 1-4 hours. Change solution when it becomes dark violet color, otherwise brown insoluble precipitation will stain the specimen.

c. Wash specimen with alcohol.

d. Repeat the process until solution no longer changes its color when specimen is immersed.

Figure 18: Ethanol Amine Thioglycollate Treatment

Method 2: Paste application

a. Make 3-5% ethanolamine thioglycollate solution in ethanol or isopropanol.

b. Mix equal amounts (1:1 ratio) of the solution and sepiolite (magnesium silicate).

c. Apply paste to effected area and cover with polythene or aluminum foil to prevent rapid evaporation.

d. Leave specimen covered for 1-3 hours.

e. Clean and wash specimen with alcohol.

3.1.4 Reacting an Acidic Solution of cerium IV salt with Pyrite containing Solid

Step1: 18.6gms of carbonaceous shale containing pyrite must be mixed with 250ml solution containing 9gms of cerium IV sulfate and 12gms of sulfuric acid. The mixture is then heated to reflux temperature until the deposition of elemental sulfur on the inner surface of the reflux condenser stopped. Heating is then stopped.

Step2: The solution must be cooled to room temperature, be filtered, and the solid recovered by filtration must be washed with deionized water. The solid must be then dried to in a vacuum oven, and its pyrite content is determined.

Step 3: Step 1 and step 2 is continued till the percentage of pyrite contain reaches zero.

3.1.5 Lime (calcium carbonate)

Chemical characteristics must be accurately delineated so that lime application rates are known within plus minus 10 tons $CaCO_3$ /1000 tons of tailings across the treated landscape. The entire depth unit to be amended must be sampled, and analyzed to determine the lime requirement. Samples must be collected at a frequency to adequately characterize the spatial and vertical extent of treatment required. Amendments must be uniformly incorporated throughout the zone to be treated. The lime requirement determined from analytical tests presumes each lime particle applied will be in contact with the soil cation exchange sites and surfaces of sulfide minerals. Since it is impossible to accomplish this goal with surficial applications of lime followed by a tillage procedure, extra lime (25 %) is applied to enhance the opportunity for contact between the lime and every soil particle surface. The amendment materials must be thoroughly mixed into the wastes to assure that sulfide-rich particles are in contact with the amendment. If the materials are not thoroughly mixed, there is potential for acidic hot spots which would diminish the effectiveness of the treatment.

a. Samples are kept in a flower pot after treatment.
b. The weight of the flower pot is obtained using a weighing machine
c. The weight of the samples is then calculated by subtracting the weight of the flower pot from the total weight.
d. Calcium carbonate is then added to the sample in the ratio of 65:1000
e. The sample is then mixed and kept for one week in for the chemical reaction to take place

3.1.6 Glasshouse experiments

Glasshouse experiments will be conducted once pyrite oxidation treatment is done, followed by lime treatment. Appropriate plants or vegetation will be planted according to the pH level of the soil after treatment. Before proceeding with the plantation, the pH of the soil will be tested. Besides that, atomic absorption spectrophotometry will be used to evaluate the content of the soil. Sometimes, plants will not be able to grow due to lack of nutrients and also excessive amount of certain elements. This matter must be taken into account before the plantation process in order to avoid failure of plant growth.

CHAPTER 4
RESULT AND DISCUSSION

Sample has been collected from the site. The sample collected was all in rock form. In order to proceed with the project, the carbonaceous shale should be converted into powder form. The grinding machine in Block J was used to grind the rocks into powder form. As we can see from the literature review, there are 4 methods to suppress pyrite oxidation. From the four methods above, only two methods was carried were carried out, that is suppression of pyrite oxidation by 8-hydroxyquinoline and ammonium gas treatment. The other two methods were not carried out due to unavailability of chemicals and lack of time. nine samples were prepared, three samples for each method, which will accumulate to six samples. The balance three samples were used as control sample or also known as standard samples.

Suppression of pyrite oxidation by 8-Hydroxyquinoline (C_9H_7NO)

300ml of leaching solution containing 0.10M H_2O_2 + 0.0038 M 8 hydroxyquinoline must be prepared. In order to calculate the amount of H_2O_2 to be added, molarity formula was used.

$$\frac{M \text{ x } V}{M_{\text{initial}}} = \text{Amount of } H_2O_2 \text{ to be added}$$

The initial molarity of hydroxide was 0.3M. By using the formula above, the amount of hydroxide needs to be added will be 100ml.

$$\frac{0.1 \text{ x } 300}{0.3} = 100\text{ml of } H_2O_2 \text{ must be added}$$

The amount of 8 hydroxyquinoline needs to be added will be derived from the formula below:

$$\frac{M \times V \times \text{Molar Mass}}{1000_{\text{conversion factor}}} = \text{Amount of 8-Hydroxyquinoline to be added}$$

From the calculation, 0.165 grams of 8-hydroyqunoline must be added to the 300ml solution.

3 Test was conducted in order to check the efficiency of the methods used to treat the soil. The acidity of the soil is contributed by sulfur. Thus, sulfur contain will be used as a benchmark to verify which treatment gives the best results.

a) CHNS (carbon, hydrogen, nitrogen and sulfur) analyzer
b) UV spectrophotometer
c) pH Meter

a) CHNS analyzer used for end product and untreated sample. In order to compare the sulphur contain

Figure 19: CHNS Analyzer

According to The Royal Society of Chemistry 2008

CHNS elemental analyzer provide a means for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. They are capable of handling a wide variety of sample types, including solids, liquids, volatile and viscous samples, in the fields of pharmaceuticals, polymers, chemicals, environment, food and energy.

The analyzer is often constructed in modular form such that they can be set up in a number of different configurations to determine, for example, CHN, CHNS, CNS or N depending on the application. This adaptability allows not only flexibility of operation but also the use of a wide range of sample weights from a fraction of a milligram to several grams (macro-systems.)

In its simplest form, simultaneous CHNS analysis requires high temperature combustion in an oxygen-rich environment and is based on the classical Pregl-Dumas method. This combustion can be carried out under both static conditions i.e. introduction of a set volume of oxygen or dynamic conditions i.e. a constant flow of oxygen for a set period of time. Often, catalysts are also added to the combustion tube in order to aid conversion.

Basic principles

In the combustion process (furnace at ca. 1000^{o}C), carbon is converted to carbon dioxide; hydrogen to water; nitrogen to nitrogen gas/ oxides of nitrogen and sulphur to sulphur dioxide. If other elements such as chlorine are present, they will also be converted to combustion products, such as hydrogen chloride. A variety of absorbents are used to remove these additional combustion products as well as some of the principal elements, sulphur for example, if no determination of these additional elements is required.

The combustion products are swept out of the combustion chamber by inert carrier gas such as helium and passed over heated (about 600^{o} C) high purity copper. This copper can be situated at the base of the combustion chamber or in a separate furnace. The function of this copper is to remove any oxygen not consumed in the initial combustion and to convert any oxides of nitrogen to nitrogen gas. The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen and sulphur dioxide.

Detection of the gases can be carried out in a variety of ways including (i) a GC separation followed by quantification using thermal conductivity detection (ii) a partial separation by GC (‘frontal chromatography’) followed by thermal conductivity detection (CHN but not S) (iii) a series of separate infra-red and thermal conductivity cells for detection of individual compounds. Quantification of the elements requires calibration for each element by using high purity ‘micro-analytical standard’ compounds such as acetanilide and benzoic acid. The results are as below:

Standard Sample of shale without trearment

Sample/Elements	Amount(mg)	C%	H%	N%	S%
1	1.404	1.131	0.520	0.306	0.417
2	1.432	0.985	0.340	0.250	0.427
3	1.582	1.240	0.618	0.265	0.437

Table 1: CHNS results for Standard Sample

Sample Treated by Ammonium Hydroxide

Sample/Elements	Amount(mg)	C%	H%	N%	S%
1	1.478	0.824	0.320	0.471	0.043
2	1.539	0.562	0.250	0.468	0.034
3	1.499	0.986	0.318	0.446	0.039

Table 2: CHNS results for Sample Treated by Ammonium Hydroxide

Sample Treated by 8-Hydroxyquinoline

Sample/Elements	Amount(mg)	C%	H%	N%	S%
1	1.506	0.560	0.165	0.499	0.018
2	1.760	0.532	0.174	0.466	0.016
3	1.765	0.545	0.188	0.439	0.019

Table 3: CHNS results for Sample Treated by 8-Hydroxyquinoline

Average

Sample/Elements	Amount(mg)	C%	H%	N%	S%
Standard Sample without treatment	1.473	1.119	0.493	0.274	0.427
Ammonium Hydroxide	1.505	0.791	0.296	0.462	0.039
8-Hydroxyquinoline	1.677	0.546	0.176	0.468	0.018

Table 4: Summary of CHNS results

From the results above, treatment by ammonium hydroxide gas give a 90.9% reduction in sulfur contain while treatment by 8-Hydroxyquinoline gives a 95.8% reduction in sulfur contain. Both methods provide successful results. In term of comparison, 8-hydroxyquinoline method gives a better result.

b) UV spectrophotometer

Figure 20: UV spectrophotometer

According to Wikipedia

A spectrophotometer is a photometer (a device for measuring light intensity) that can measure intensity as a function of the color (or more specifically the wavelength) of light. Important features of spectrophotometers are spectral bandwidth and linear range of absorption measurement. In this experiment, the wavelength of sulfur concentration is taken as a benchmark in order to rate the effectiveness of the experiments conducts. The result is presented in the graph below:

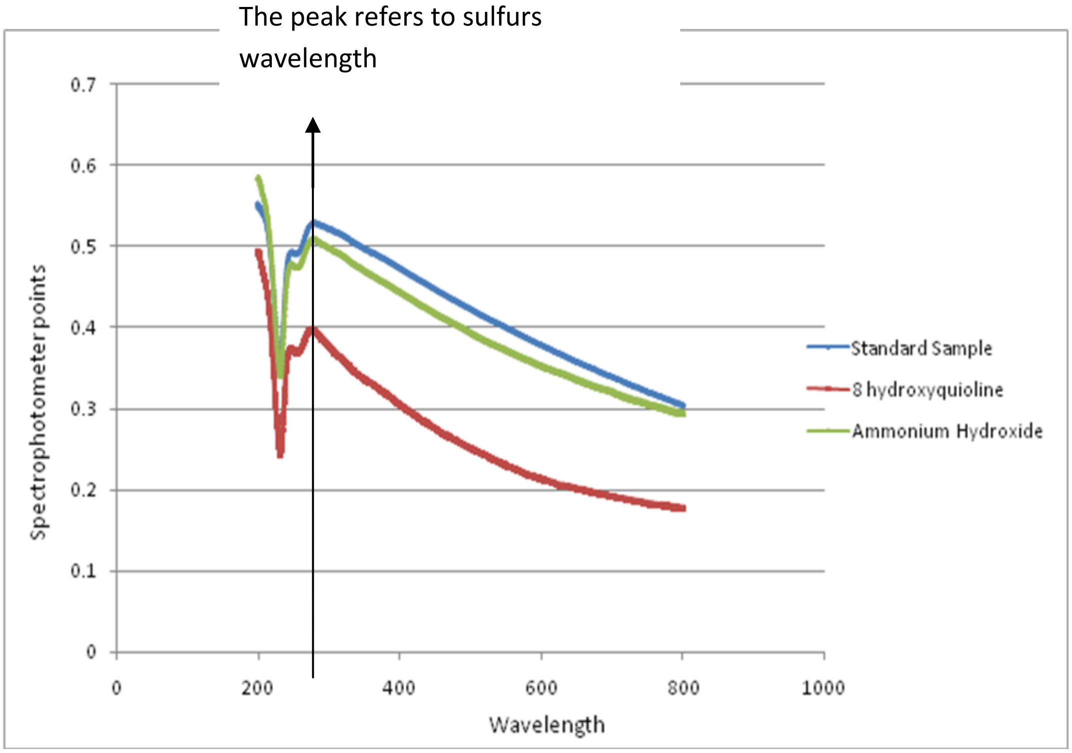
The peak refers to sulfurs wavelength

Figure 21: Spectrophotometer points vs Wavelength

From the graph above, noted that the both treatment method have shown effective results. The sulfur concentration of the soil has reduced vastly after the treatment. In term of comparison, the treatment with 8-Hydroxyquinoline gives a better result with lower concentration of sulfur.

c) **pH meter**

Figure 22: pH Meter

According to Wikipedia

pH meter is an electronic instrument used to measure the pH (acidity or alkalinity) of a liquid (though special probes are sometimes used to measure the pH of semi-solid substances). A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading. The pH probe measures pH as the activity of hydrogen ions surrounding a thin-walled glass bulb at its tip. The probe produces a small voltage (about 0.06 volt per pH unit) that is measured and displayed as pH units by the meter. After executing the treatment, calcium carbonate (lime) was added to the samples in order to increase the pH level. Below is the result before and after treatment:

Samples	pH value
Standard Sample before treatment	3.47
Standard Sample treated with calcium carbonate	7.45
Sample treated by Ammonium Gas + calcium carbonate	8.14
Sample treated by 8-Hydroxyquinoline + calcium carbonate	7.48

Table 5: pH value of Samples

From the table above, we can conclude that calcium carbonate managed to increase the pH value; the soil sample is no more acidic and has a suitable pH value for plant or vegetation to grow.

d) Plant growth

Figure 23: Ladies finger plant

Sample	Plant Growth
Standard Sample before treatment	**No Growth**
Standard Sample treated with calcium carbonate	**2cm growth in a week**
Sample treated by Ammonium Gas + calcium carbonate	**8cm growth in a week**
Sample treated by 8-Hydroxyquinoline + calcium carbonate	**8 cm growth in a week**

Table 6: Plant Growth Analysis

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CHAPTER 5

5.1 CONCLUSION

The objective of the project has been achieved by implementing the methods listed. The reduction of sulfur contains in the soil using both methods have proved that the treatment has been successful. The use of 8-Hydroxyquinoline have given a vast reduction in sulfur contain compared to ammonium gas treatment. In comparison of the both methods used, from the results we can conclude that 8-Hydroxyquinoline does not only give a better result but it is also a more reliable and safer method to be used for treatment. A very small amount of 8- Hydroxyquinoline is used, and it is less hazardous compared to ammonium gas evaporation treatment. In case of leak of ammonium gas, people surrounding will be exposed to great danger.

5.2 Recommendation

From the results obtained, 8-Hydroxyquinoline is an effective and safe method of treatment that can be used in field conditions. There are only two chemicals used in this treatment, that is, 8-Hydroxyquinoline and hydrogen peroxide. The main concern of using these chemicals under field condition is groundwater toxicity. However, 8-Hydroxyquinoline is a strong chelating agent. Chelating agents is used to detoxify poisonous metal agents such as mercury, arsenic, and lead by converting them to a chemically inert form that can be excreted without further interaction with the body. Besides using 8-Hydroxyqunoline as a chelating agent, 8- hydroxyquinoline is also been used for analytical reagents (Hollingshead, 1954) and as antimicrobial agents in medicine, fungicides, and insecticides (Harvey, 1975). It is also used as a preservative in cosmetics and tobacco.

As for hydrogen peroxide (hydrogen dioxide), it is a water molecule with an extra oxygen atom. Hydrogen peroxide (French: Eau Oxygenee) was first reported by the French chemist Louis-Jacques Thenard in 1818. Our upper atmosphere contains an ozone layer. Unstable ozone (03) gives up its extra atom of oxygen to falling rainwater to form hydrogen peroxide (H_20_2). In 1863 Meissner proved its presence in rain water collected during thunderstorms and has been corroborated by other research. Hydrogen peroxide is a naturally occurring compound found in nature (oceans, lakes, rivers, rain and snow) and in all life forms. The human body creates and uses hydrogen peroxide (free radicals) to destroy harmful bacteria, viruses, and fungi.

Ozone (O_3) is created when radiation (ultraviolet light) from the sun interacts with oxygen (O_2) in the atmosphere. O_3 is heavier than O_2 and falls toward the earth. In the lower atmosphere, ozone (O_3) encounters water vapor and forms hydrogen peroxide (H_2O_2). Rain water and snow contain a small percentage of hydrogen peroxide which acts as a natural disinfectant in lakes, rivers and oceans.

Many cities in Europe use ozone and hydrogen peroxide in their drinking waters. Hydrogen peroxide, ozone and ultraviolet light are simple and effective combinations for drinking water sanitation. Ozone and ultraviolet light also works. Some cities in Europe have been purifying their drinking water with ozone since 1901. Ultraviolet light is used to disinfect surgical instruments, bedding, air, skin, body fluids, etc. of viruses and bacteria. Bacterial and viral disinfection with ozone works up to 5000 times faster than chlorine. Many brands of bottled water that you buy in this country have been ozonated for your protection. Hydrogen peroxide is found in all fresh fruits and vegetables, some of it comes from rain water and some of it is manufactured in the photosynthesis process. Eating fresh fruits and vegetables (preferably organic) in their raw state helps get this healing oxygen into our bodies.

Hydrogen peroxide contains one more atom of oxygen than water does. Boiling point: 286° F (141° C) and Freezing point: 12° F (-11° C). Hydrogen Peroxide is a chemical compound that is a colorless, syrupy, oxidizing liquid, capable of reacting explosively with combustibles. When stored under the proper conditions, it is a very stable compound.

Hydrogen Peroxide is used in a water solution as a mild antiseptic, a bleaching agent, an oxidizing agent, and as a laboratory reagent. Hydrogen Peroxide is soluble in alcohol or ether. Commercial Hydrogen Peroxide usually has a small amount of stabilizer (acetanilide) in it. Hydrogen Peroxide is available for household use as a 3% (by weight) water solution; it is used as a mild bleaching agent and medicinally as an antiseptic. Recent studies indicate that Hydrogen Peroxide is toxic to new cells and is not recommended for wound care.

A 3% solution of Hydrogen Peroxide is sometimes called ten volume strength, (one volume of Hydrogen Peroxide releases ten volumes of oxygen when it decomposes). A pint of the food-grade 35% solution contains the equivalent of 130 pints of oxygen. A pint of 3% hydrogen peroxide found at a local drugstore contains 10 pints of oxygen. A pint of the 6% solution, used to bleach hair, contains 20 pints of oxygen. When kept in the absence of light and contaminants, it dismutates (breaks down) very slowly at the rate of about 10% a year. Storing the hydrogen peroxide in the freezer slows this process.

Hydrogen Peroxide is a very powerful unstable oxidant. Hydrogen Peroxide is a natural substance found in trace amounts in rain and snow. Rain combines with ozone (O_3) in the upper atmosphere. When water and ozone mix, the ozone loses one oxygen molecule to the water and hydrogen peroxide is formed. Hydrogen peroxide is very unstable and breaks down readily into water and a single oxygen molecule. Oxygen is stable only when the molecules are paired (O_2). A single oxygen molecule is a strong oxidizing and disinfecting agent.

From, this we can come to conclusion that 8-hydoxyquinoline and hydrogen peroxide, both are safe to be used under field conditions with proper underground water treatment.

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