STUDY OF ZEOLITE IN MITIGATING FORMATION DAMAGE DUE TO INORGANIC SCALING

By

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FINAL PROJECT REPORT

Submitted to the Mechanical Engineering Programme
in Partial Fulfillment of the Requirements
for the Degree
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(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

AP Dr. Ismail Mohd Saaid

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
November 2008

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.

Nur Hasyimah Bt Mohamad Afandi

ABSTRACT

Formation damage causes the reduction of reservoir permeability and therefore reducing the productivity and injectivity of wells. One of the root causes of formation damage is the formation of scale which is either inorganic or organic precipitation. Inorganic scaling can occur in the well tubing and near well bore formations of production and injections wells. Two different types of zeolite which are clinoptilolite and chabazite were used in this study to mitigate the inorganic scaling which causes the formation damage. The objective of this study is to analyze the potential of clinoptilolite and chabazite to remove barium and sodium ions via adsorption. The effect of effective permeability of fluids before and after treatment with zeolite was also investigated. The degree of ions sorption of zeolite will be measured based on the value of the ions concentration measured by Atomic Adsorption Spectrophotometer. Bench Top Permeability System was used to measure the effective permeability of the fluids. The results obtained were analyzed to assess the potential use of zeolite in mitigating the inorganic scale. Results from the present project indicate that both clinoptilolite and chabazite has the capability to adsorp sodium ions. However those types of zeolite do not have the capability to adsorp barium ions. After the zeolite treatment, there were no significant effects that shown the reduction of the effective permeability of the fluids. This study found that raw natural zeolite such as clinoptilolite and chabazite do not exhibit high degree of potential in mitigating the formation of inorganic scales.

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TABLE OF CONTENT

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW AND THEORY

CHAPTER 3: METHODOLOGY

CHAPTER 4: RESULT AND DISCUSSION

CHAPTER 5: CONCLUSION AND RECOMMENDATION

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background

Formation damage is the reduction in permeability in regions near the wellbore. The damage of the formation can lead to reduced production rate of oil and gas, reduced in injection rates of water and gas, increased drawdown or injection pressures and also the reduced ultimate economic recoverable reserves. The damage can occur at any time of the reservoir's life.

The potential for formation damage caused by the use of high density brine during water injection was studied (Baijal *et al.*,1991). The extensive use of water injection for oil recovery and pressure maintenance have led to the problem of scale deposition (A.A.Rocha *et al.*,2001). Due to the precipitation of salt, the effective permeability of the reservoir fluid declined. Characteristics of the precipitate influence the extent of formation damage. In most cases, the precipitate found were carbonate and sulfates, particularly calcium, barium and strontium (P.G.Bedrikovetsky *et al.*,2005). There are limited preventive measures which can be applied in mitigating these salt precipitates (J.Moghadasi *et al.*,2003).

Zeolite can be used to remove and prevent the occurance of the precipitate. Zeolites are hydrated aluminosilicate minerals and have microporous structure. Zeolites have been widely used in metal cation removal from contaminated effluent during water treatment processes (V.J. Inglezakis *et al.*,2006). In this study, two types of zeolite were identified to be used in metal cation adsorption of salt precipitates during formation damage. There are from the chabazite and clinoptilolite type of zeolite.

1.2 Problem Statement

In the oilfield, the use of sea water injection for oil displacement and pressure maintenance as primary oil recovery mechanism lead to the occurrence of sulfate and carbonate scale (J.Moghadasi *et al.*,2003). There is limited method available to remedy the form of scale in the well bore formations (J.Moghadasi *et al.*,2003). Due to this, Zeolite might have the potential to be used in mitigating the inorganic precipitation. Zeolites gain an interest mainly due to their valuable sorption characteristics, ion exchange and chemical properties (D. Caputo and F. Pepe ,2007). Study should be done to evaluate the effectiveness of zeolite in mitigating the inorganic precipitation.

1.3 Objective

1. To identify various type of zeolite that exhibit great sorption capacities towards metal cation.
2. To test the possibility of using zeolite for metal removal in mitigating inorganic scale in formation damage.
3. To assess the effective permeability of the fluids after been treated with zeolite.

1.4 Scope of Work

Based on the objective stated, several experiments related to this study will be conducted were shown in the table in the next page:

Table 1: Experiment for FYP 1&2

Experiment/ Analysis	Purpose
Mineral and Chemical Analysis • X-Ray Diffractometer	Sample characterization based on element and compound percentage
Atomic Adsorption Spectrophotometer (AAS)	Measure the concentration of ions in fluid
Permeability Test • Bench Top Permeability	Measure relative permeability of core sample

From all the experiments above, the results will be discussed with reference to literature review that had been carried out during previous semester. All of these also included in scope of work during the completion of this paper. Other tasks are:

1. Conducting literature review related to inorganic precipitate in formation damage and zeolite that cover all aspects of industry and practical problem;
2. Conducting zeolite ion exchange experiments and characteristic analysises;
3. Discussing all the results done from all the experiments and analysises.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Formation Damage

Formation damage is a term that describes any process causing a reduction in the natural fundamental productivity or injectivity of an oil and gas production, injection or disposal well. It can also be defined as the destruction of the unseen by unavoidable causing an unknown reduction in the unquantifiable. There are four major mechanism of formation damage described by Faruk Civan (2007) which are mechanical, chemical, biological and thermal. These four mechanisms are further narrowed as the following:

1. Fluid-fluid incompatibilities, for example emulsions generated between invading oil based mud filtrate and formation water.
2. Rock-fluid incompatibilities, for example contact of potentially swelling smectite clay or deflocculatable kaolinite clay by nonequilibrium water based fluids with the potential to severely reduce near wellbore permeability.
3. Solids invasion, for example the invasion of weighting agents or drilled solids.
4. Phase trapping/blocking, for example the invasion and entrapment of water based fluids in the near wellbore region of a gas well.
5. Chemical adsorption/wettability alteration, for example emulsifier adsorption changing the wettability and fluid flow characteristics of a formation.
6. Fines migration, for example the internal movement of fine particulates within a rock's pore structure resulting in the bridging and plugging of pore throats.
7. Biological activity, for example the introduction of bacterial agents into the formation during drilling and the subsequent generation of polysacharide polymer slimes which reduce permeability.

Formation damage lead to the reduced in production rates of oil and gas, reduced the injection rates of water or gas, increased the drawdown or injection pressures and also the reduction in ultimate economic recoverable reserves. The damage can occur at almost any time during the life of reservoir. It may occur during drilling operations, completion operations, stimulation operations, and production operations.

Since the formation damage can significantly affect the productivity of any reservoir, sufficient precautions should be exercised to avoid damage during all phases in the life of the well.

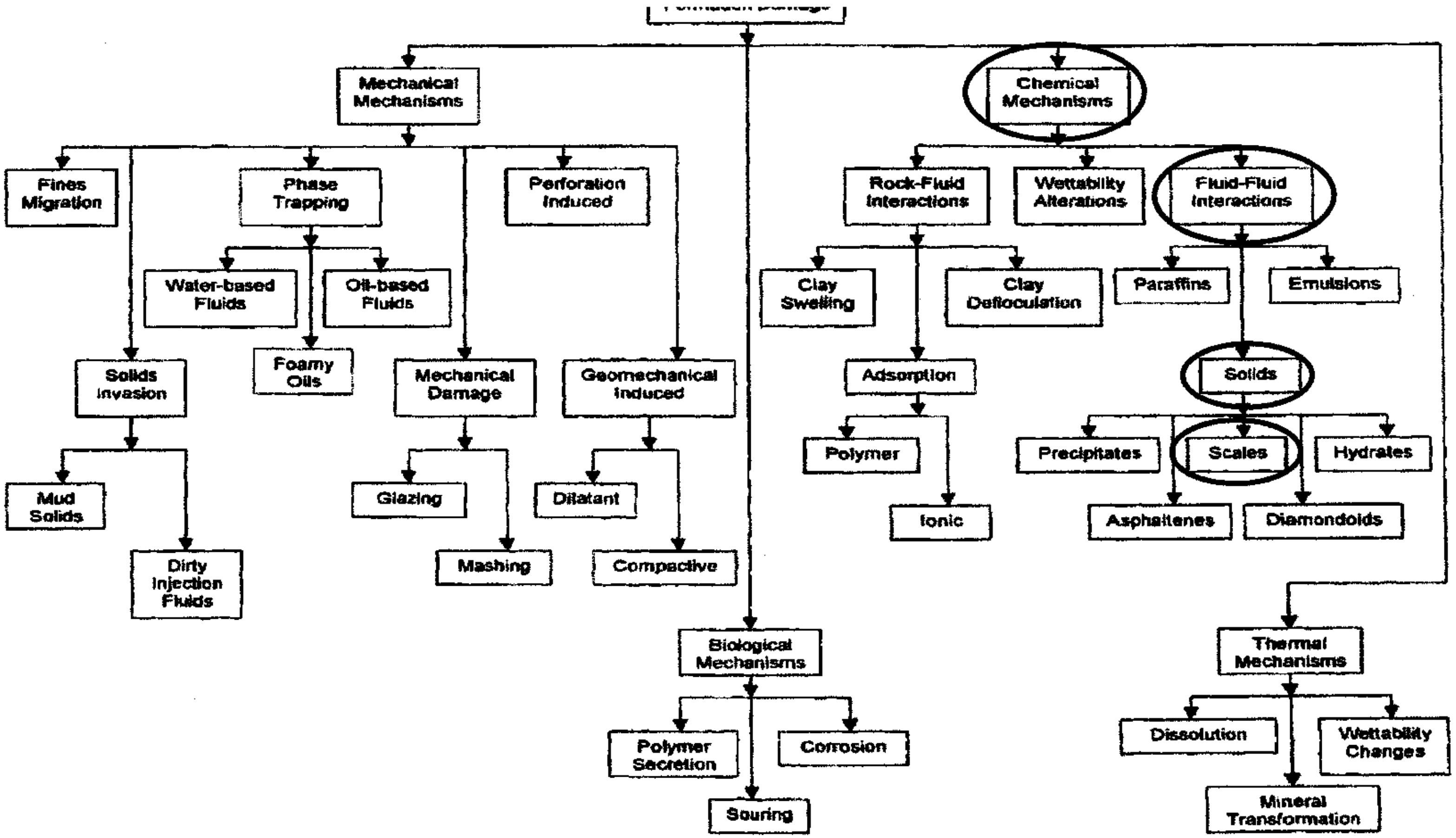


Figure 1: Classification and order of the common formation damage mechanisms (modified after Bennion, ©1999; reprinted by permission of the Canadian Institute of Mining, Metallurgy and Petroleum).

2.2 Scale formation leads to the formation damage

Both organic and inorganic matter can cause permeability reduction in formation damage. Organic damage occurs when there is a change in reservoir temperature and pressure which cause the formation of high viscosity hydrocarbon scale. While the inorganic damage originates from the chemical reactions which entail the release and capture of particulate including in situ fines and precipitates. Water injection processes applied in oilfield for displacement and pressure maintenance has induced the formation of sulfate and carbonate scales of strontium and calcium (J. Moghadasi *et al.*,2003). During the injection process, the fluid is subjected to a high temperature variation. Initially, the water is injected at high temperature; 40°C.The increasing of water depth will be cooling the fluid. For ultra-deep wells; it could arrive to a temperature in order of 3°C. After that, due to the geothermal gradient, the fluid is heated again, arriving to temperature around 115°C for deep reservoir. These high temperature variations increase the amount of salt precipitation (A.A. Rocha *et al.*,2001). There are limited preventive measures available to apply because of the relative hardness and low solubility of these scales (P.G. Bedrikovetsky *et al.*,2005).

Mechanism by which a precipitate reduces permeability includes solids deposition on the pore walls due to attractive forces between the particles and the surfaces of the pore, individual particles blocking pore throats, and several particles bridging across a pore throat (J.Moghadasi *et. al* .,2005).

The change in porosity and plugging of pore throats are two phenomena that can change the permeability of the reservoir to (J.Moghadasi *et. al.*,2005). The growth of clay minerals or the deposition of solid in the pore body causes the change in porosity. Pore throats are the narrow passage that directs the fluid flow through porous media. Once its block, it will reduce the reservoir permeability.

2.3 Mechanism of Solid Plugging

In a typical injection or disposal water contain many different types of solids which are produces water, corrosion products (FeO, FeS,etc), sand, slit, clay, precipitate and scale products, dead or live bacteria, and asphaltenes (Faruk Civan ,2007). The solid should be small enough so that they can pass cleanly into the pore system and significant distance into the formation before they start to bridge and block pore throats.

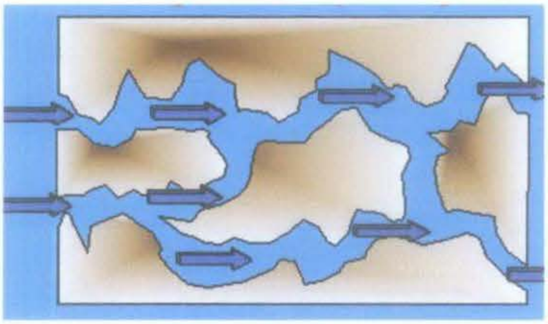


Figure 2: Clean pore system (Faruk Civan ,2007).

If the solids are very small, the solid will remain suspended in the injected fluid even down to very low laminar flow velocities. Long term plugging isn't an issue in this ideal desire condition.

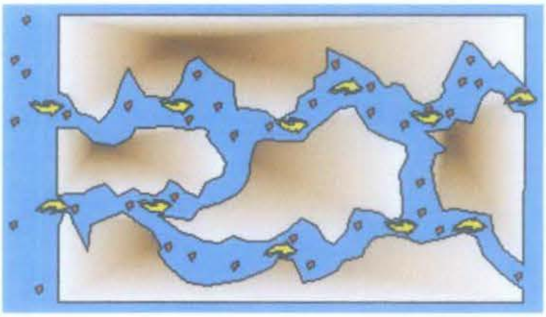


Figure 3: Tiny suspended solid in the pore system (Faruk Civan ,2007).

When the solid getting large, the turbulent flow may remain them in suspension around the injection well. While the solid leave the formation, the velocity will rapidly decrease. Thus, they clog the pore system and form the internal filter cake.

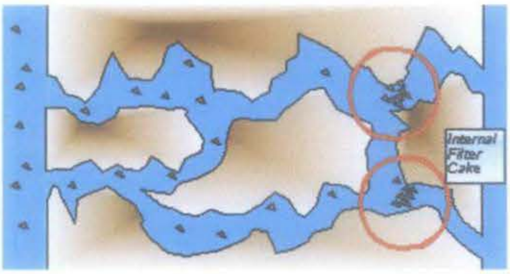


Figure 4: Internal filter cake (Faruk Civan ,2007).

If the solids are larger they will start to block the surface of the formation and form the external filter cake. This can rapidly reduce injectivity.

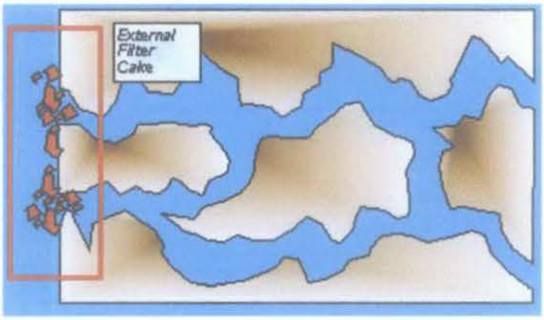


Figure 5: External filter cake (Faruk Civan ,2007).

2.4 Inorganic Precipitation

Inorganic scaling is a process of deposition of scales from aqueous solutions of minerals when they become supersaturated (Faruk Civan., 2007). Scaling is caused essentially by mixing incompatible fluids during well development operations, such as drilling, completion, workover, such as acidizing.

Table 2: Literature review on inorganic scale form in formation damage

Reference	Inorganic scale	Origin
Oddo and Tomson, (1994);	- anhydrate $(CaCO_3)$ - gypsum $(CaSO_4 '2H_2O)$ - hemihydrate $(CaSO_4.1/2H_2O)$ - barite $(BaSO_4)$ - celestite $(SrSO_4)$ - magnesium sulfide $(MgSO_4)$	- Mixing water with brine - Rock and brine interaction
Rege and Fogler, (1989)	- ironhydroxide gel $[Fe(OH)_3)$ - pyrhotite (FeS) - pyrite (FeS_2) - hematite (Fe_2O_3) - magnetite (Fe_3O_4) - siderite $(FeCO_3)$	- acid dissolution - precipitation of iron minerals
Labrid, (1990)	- silicium tetra hydroxide gel $[Si(OH)_4)$	- alkaline dissolution - precipitation of minerals in shaly sandstones such as quartz and kaolinite
Todd et al., (1993)	- polymeric substances	- in-situ gelation

Other inorganic scales that can occur are separation of elemental sulfur (Roberts, 1997); and surfactant precipitation (Arshad and Harwell, 1985).

Compare to other scales carbonate are softer and tend to be acid soluble while for sulfate scale it cannot be dissolved easily in the field due to their relative hardness and low solubility (A.A Rocha *et al.,*2001).

2.5 Brine

Brine or seawater contains a lot of dissolved chemical ions. During water injection processes, this high salinity brine will mix with other reservoir fluid which will result on the formation of certain type of inorganic and organic precipitate. Below are some of the composition and most important chemical species of some dissolved elements in sea water:

Table 3: Elements contains in sea water (Summerhayes, C. P., and Thorpe, S. A., 1996).

Element			
Lithium	Rubidium	Nitrogen	Manganese
Boron	Strontium	Flourine	Iron
Carbon	Cadmiun	Sodium	Nickel
Magnesium	Iodine	Aluminium	Copper
Silicon	Caesium	Phosphorus	Zinc
Sulphur	Barium	Chlorine	Arsenic
Potassium	Mercury	Calcium	Bromine

2.5.1 Brine treatment for water injection

Currently, the brine used undergoes four basic treatment steps before the injection. Firstly particles are removed from the raw seawater using a filter that stops particles down to 35 micron. Then a treatment unit eliminates bacteria as well as zoo-plankton and phytoplankton by means of continuous hyper chlorite dozing and chemical shock dozing. The treated water is then pumped into the reservoir. The treatment processes do not include the removal of metal cation that might further influence the form of inorganic scale during the formation damage.

2.6 Zeolite

Zeolite has attracted the attention to be used in this project due to its well defined intracrytalline structure. It provides large surface area to be used as metal cation exchanger and also can sustain high temperature. More over, natural zeolite is a cost effective material due its low cost.

Zeolites are mainly, though not exclusively, alumina-silica crystalline materials that are widely used in industry for separations and catalysis. A great variety of zeolite architectures exists with channels and cages in the micropore size range, and a wide range of interconnected pore widths and shapes is possible (C.Colella, 2005).

Further variety is added when Si T-atoms are substituted by other species. The substitution of one or more Si, typically by Al, leaves negative charges on the silica-alumina framework that are neutralised by extra-framework ions such as Na^+ or Ca^{2+} (G.Q.Lu and X.S. Zhao,2006).In 1960's, Boenzi and coworkers had done an explorative investigations focused on Cs^+ and Sr^+ removal from aqueous solution simulating radioactive wastewater from nuclear power plants. They used philiptisite-rich tuffs and chabazite tuffs coming from Braccioano lake area. The studies showed the ability of the selected tuffs to removes Sr^+ and especially Cs^+ from water (D.Caputo, F. Pepe,2007). In 1970s, Aiello and Colella proposed the process for removal of Fe^+ and Mn^{2+} which based on the concomitant action of ion exchange and oxidation for iron removal and ion exchange and ion adsorption for manganese removal.

Table 4: List of several studies regarding ion exchange of zeolite

Reference	Purpose	Cation exchange	Types of zeolite used
D. Caputo and F. Pepe (2007)	Predicting the ion exchange and the selectivity of one cation over another.	Pb^{2+}, NH^{+4},Cs^{+}, Ba^{2+}	Chabazite, clinoptilolite, philipsite.
M. Sprynskyy *et al.* (2006)	Study of the selection mechanism of heavy metal adsorption on clinoptilolite	Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}	Clinoptilolite
V.J. Inglezaski *et al.* (2007)	Removal of Pb(II) from aqueous solutions by using clinoptilolite	Pb^{2+}	Clinoptilolite
A.Dyer, M. Zubair (1998)	Study of ion exchange in chabazite	Na^{+}, K^{+}, Rb^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2-}	Chabazite
Cerjan Stefanovic,S.*et al.* (2006)	Structural investigation of Zn(II) sorption in Clinoptilolite tuff from the Vranjska Banja deposit in Serbia	Zn^{2+}	Clinoptilolite
M.A. Stylianou *et al.* (2007)	Removal of Cu(II) in fixed bed and batch reactors using natural zeolite and exfoliated vermicukate as adsorbents	Cu^{2+}	Clinoptilolite

Based on the literature done by various researchers, possible types of zeolite that can be used to mitigate the formation of inorganic scales are clinoptilolite and chabazite. Many researchers favor to use clinoptilolite to adsorp various metal cations contain in contaminate solution while some of them use chabazite as another option.

2.6.1 Clinoptilolite

Clinoptilolite being the most common natural zeolite belongs to the heulandite family or a structural variation of the zeolite mineral group and has the following total chemical formula $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}$-$12H_2O$ (M.Sprynskyy *et al.*,2006). Clinoptilolite has a large amount of pore space, high resistance to extreme temperatures and chemically neutral basic structure. From zeolite species, clinoptilolite has received extensive attention due to its attractive selectivity towards certain metal cations such as Pb(II), Cu(II), and Cd(II) (Inglezaskis,V.J. *et al.*,2006).

Natural zeolites tend to raise the solution acidity. When the H^+ ions are exchanges with the cations initially present in the zeolite there are changes of acidity of the solution. Therefore, during the ion-exchange process, acidity is changing due to H^+ uptake by clinoptilolite, but also due to the uptake of metal cations, which has the tendency to give acidic solutions (V.J.Inglezakis *et al.*,2006). Many studies have devoted to the improvement of the clinoptilolite sorption properties by chemical modification. The chemical treatment of the clinoptilolite increases sorption of the other metals (Sprynskyy,M. *et al.*,2006).

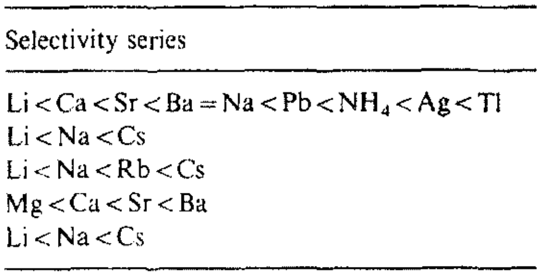
Selectivity Series
Cs>K> Sr = Ba >C >Na >Li
Ca >Rb >K >Na> Sn> Li
Rb> NH4> Ba> Sr >Na> Ca> Fe> Al> Mg> Li
Cs>NH4 >Na
Pb> Ag> Cd= Zn= Cu> Na
Ba> Pb> Cd >Zn> Cu> Na

Figure 6: Selectivity series for ion exchange in clinoptilolite
(Zeolite Austalia Pty.Ltd., 2008)

2.6.2 Chabazite

Chabazite is also known as acadialite and the typical crystal of chabazite is a rhimbohedron. Chabazite has total chemical formula $CaAl_2Si_4O_{12}$-$6H_2O$. Chabazite's structure has a typical zeolite openness that allows large ions and molecules to reside and actually move around inside the overall framework. The structure actually contains open channels that allow water and large ions travel into and out of the crystal structure (Amethyst Galleries,Inc.). Chabazite can act as chemical sieve due to the size of its channel that allows some ions to pass through while blocking other.

A.Dyer and M.Zubair (1998) confirm the potential of Chabazite for the treatment of the aqueous waste streams to remove Cs and Sr.



Selectivity series
$Li < Ca < Sr < Ba = Na < Pb < NH_4 < Ag < Tl$
$Li < Na < Cs$
$Li < Na < Rb < Cs$
$Mg < Ca < Sr < Ba$
$Li < Na < Cs$

Figure 7: Selectivity series for ion exchange in chabazite (A.Dyer and M.Zubair,1998)

2.7 Permeability

Permeability is a measure of the resistance with which a rock opposes the movement of fluid through its pores. Obviously, the larger the pores, the easier the fluid will flow through them, i.e. the higher the permeability of the rock. By and large, larger pores occur in rocks with larger grains and, consequently, permeability is related to grain size. But the relationship is complicated by such effects as: the shape of the pores; the size of the pore throats at the grain contacts; the presence of fine material or secondary mineral growth partially blocking the fluid movement through the pores.

Permeability is measured by actually flowing a fluid through a sample of the rock. It will be obvious that the quality of the sample must be suitable and that, for instance, poorly consolidated rocks will present difficulties. The measuring procedure in fact an experimental version of the Law of Darcy, which describes the flow of fluids through porous media: permeability is computed as the factor ***k*** in Darcy's formula from the measured values of the other parameters. Permeability is expressed in Darcies, but as few reservoir rocks have permeability of more than a fraction of Darcy, the more common unit is the miliDarcy.

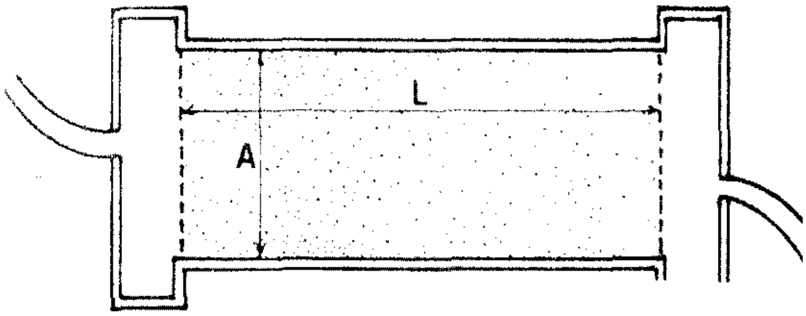


Figure 8: Darcy Test Equipment (Dake, L.P; 1978)

Darcy's Law: $Q=\frac{kA\Delta P}{\mu L}$

Where Q = flow rate

A = cross-sectional area

L = length

ΔP = pressure gradient across length, L

μ = fluid viscosity

k = permeability

CHAPTER 3

METHODOLOGY

3.1 Methodology

The project flow consists of several stages. It begins with the understanding of project background and then translates it into problem statement. Afterward, few objectives that need to be achieved at the end of this project were set. Further step is to develop the structure of the project where planning and scheduling come to pass. During project planning, several interrelated experiments were identified and specific materials needed were ordered and purchased. The experiments were started after getting the material from the supplier. The results from all the experiments are in details discussed in Chapter 4 Result and Discussion.

3.2 Project Flow

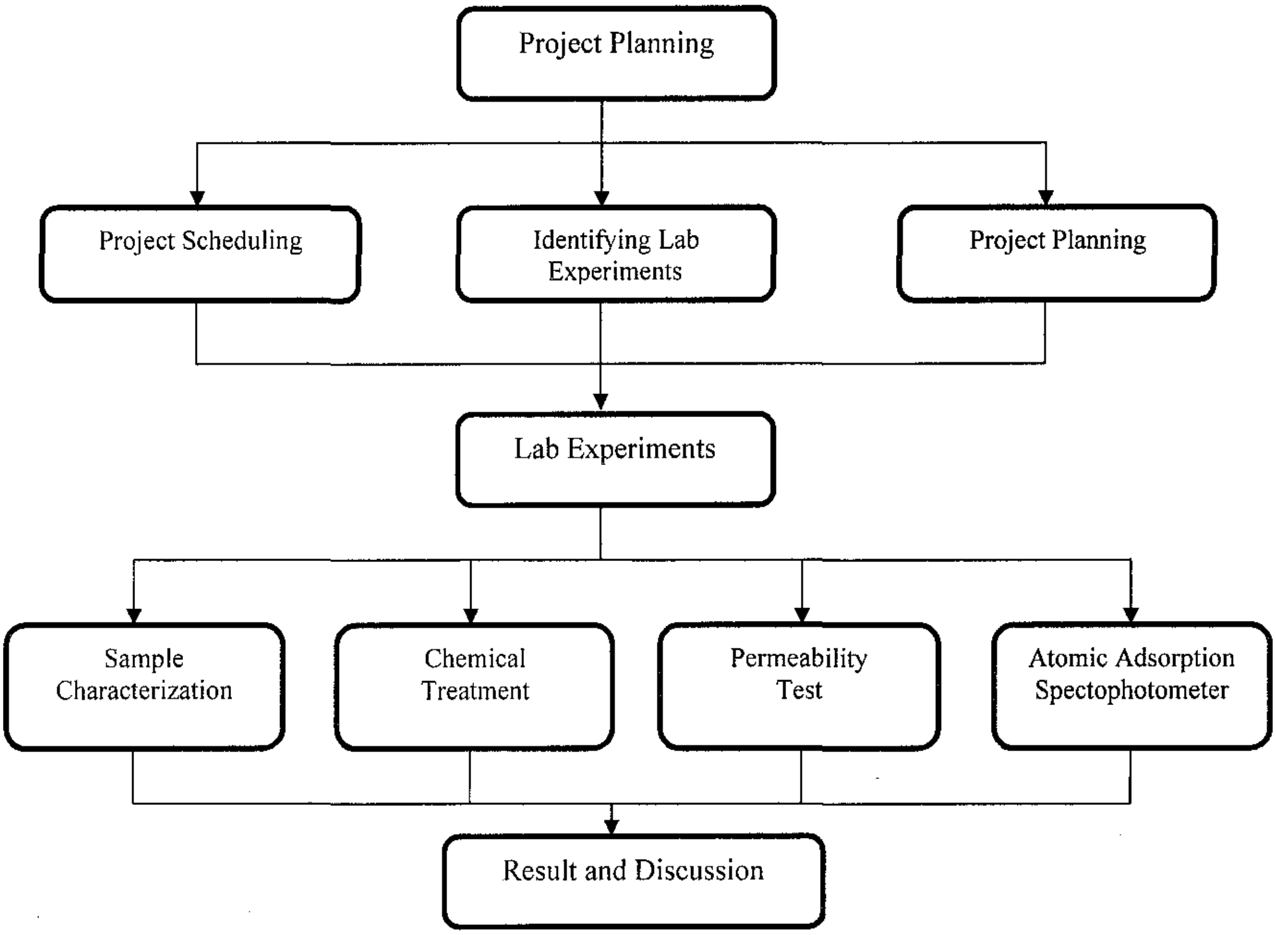


Figure 9: Project Flow

3.3 Project Planning

1. Project Scheduling

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	SW	EW
1	Purchase material	▨	▨	▨	▨												
	-Practical / Laboratory Work	▨	▨	▨	▨												
2	Submission of Progress Report 1					●											
3	Project Work Continue						▨	▨	▨								
	-Practical / Laboratory Work						▨	▨	▨								
4	Submission of Progress Report 2									●							
5	Project Work Continue										▨	▨					
	-Practical / Laboratory Work										▨	▨					
6	Poster Exhibition												●				
7	Submission of Dissertation Final Draft															●	
8	Oral Presentation																●
9	Submisson of Porject Dissertation																●

● Suggested milestone

▨ Process

SW Study Week

EW Exam Week

Figure 10: Project Gantt chart

2. Identify lab experiments

Table 5: List of lab Experiments

Experiment/ Analysis	Purpose
Mineral and Chemical Analysis • X-Ray Diffractometer	Sample characterization based on element and compound percentage
Atomic Adsorption Spectophotometer(AAS)	Measure the concentration of Fluid
Permeability Test • Bench Top Permeability	Measure relative permeability of core sample

3. Lab setup and purchase chemical
    - Lab experiments are conducted at Block 15, Core lab, Block 5&4, Chemical Department, and for the Chemical and Mineral Analysis for XRD and XRF at Block 17, Mechanical Department.
    - Material needed for this project to be completed is natural zeolite, Barium Chloride and Sodium Sulphate.

3.4 Lab Experiments

Several laboratory experiments were run in this project. The chemical solutions were first treated with zeolite. Further, the chemical solution and the zeolite sample were examined to provide information about the change in their mineralogy and the chemical composition.

3.4.1 Zeolite ions exchange experiment

The concern of this experiment is to provide a system for the occurrence of metal ions sorption by natural zeolite. The mixture of barium chloride and sodium sulphate will produce insoluble precipitate of barium sulphate and aqueous solution of sodium chloride. Thus, the sorption of barium or sodium ions by zeolite will help to mitigate the barium sulphate scales. The series of experiments use one day time frame. The manipulating parameters are the type of natural zeolite used.

The procedure of zeolite ions sorption experiment is performed as follows:

1. 30 grams of natural zeolite is accurately weight, placed into a mesh.
2. 1.779 grams of barium chloride is accurately weight, placed into a 1.5 liter beaker and 1 liter of deionised water is added.
3. The barium chloride and the deionised water were stirred until all the barium chloride dissolved.
4. The mesh containing zeolite is placed on top of the 1.5 liter beaker containing the barium chloride aqueous solution.
5. Pump is placed in the 1.5 liter beaker containing the barium chloride aqueous solution.
6. The barium chloride aqueous solution is circulated through the zeolite bed for one day.
7. The 1 to 6 steps is repeated using 6.178 grams of sodium sulphate.

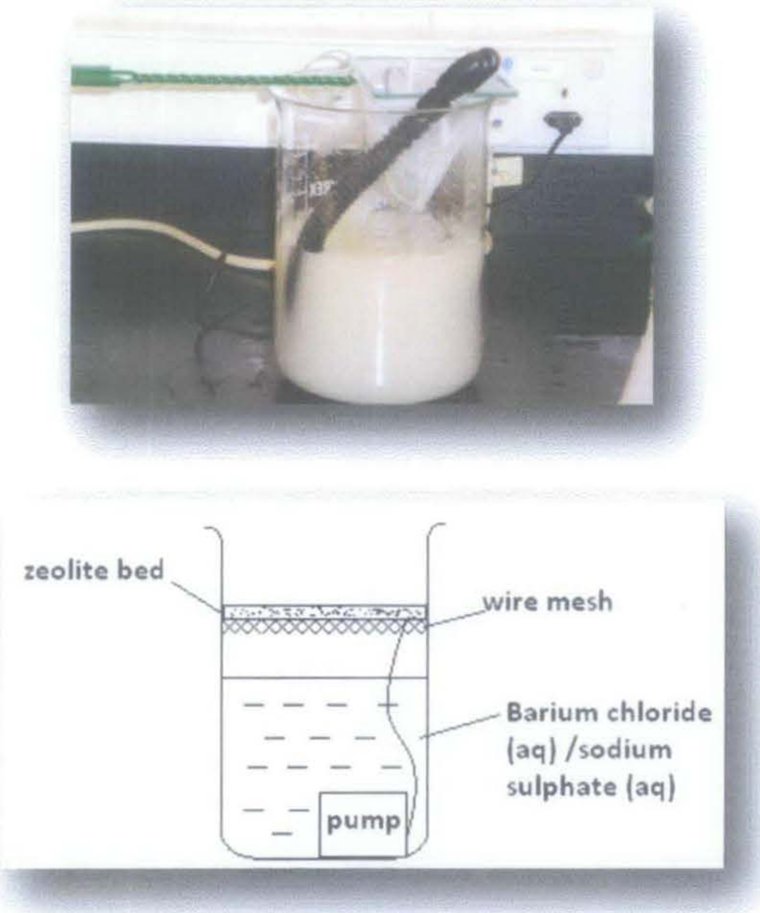


Figure 11: Setup for Zeolite ions exchange experiment

3.4.2 Atomic adsorption spectrophotometer

Figure 12: Atomic adsorption spectrophotometer

The atomic adsorption spectrophotometer is used to measure the ion concentration in the specific chemical solutions. In this study, the interest is to measure the concentration of barium and sodium ions in the barium chloride and sodium sulphate aqueous solution. The equipment will measure the ion concentration base on the standard solution which prepare before the running the equipment. The standards solution uses for barium ions measurement are 2.5 ppm, 5.0 ppm, and 10.0 ppm and the standards solution uses for sodium ions measurement are 0.2 ppm, 0.4 ppm and 0.8 ppm. The barium chloride sample solution has the concentration of 2.5 ppm and the sodium sulphate sample solution has the concentration of 0.8 ppm.

The procedures for the standard solution preparation are as follow:

1. 250 µl, 500 µl, 1000 µl of 1000 ppm standard barium solution is accurately measured, placed in the Erlenmeyer flask.
2. 100 ml deionised water is added and the solution is properly mixed.
3. 5 ml of the standard solution is measured and placed in the test tube.
4. The 1 to 3 steps are repeated using 200 µl, 400 µl, and 800 µl of 1000 ppm standard sodium solution.

3.5.3 Permeability Test

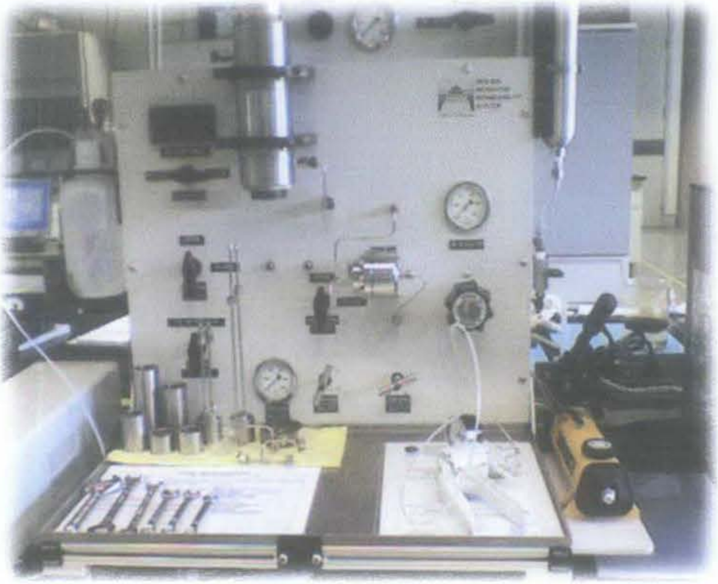


Figure 13 : Bench Top Permeability System

This Bench Top Permeability system is use to measure the permeability of liquid or gas. This equipment can measure both effective and relative permeability of liquid and gas. As in this project we only measure the effective permeability of saturated core. For best result, the core sample should be precision right cylinders with end faces parallel to within +/- 0.01 inches. There are some information and system parameter that user should know before running the test procedure.

1. The sample dimensions
2. The flowing liquid viscosity at ambient and test temperatures
3. The desire start flow rate to use
4. Sample length
5. Sample diameter
6. The fluid content in the sample pore space

Below are the specifications of the equipment:

1. Maximum sleeve pressure
   500 psi
2. Maximum pore pressure
   0-100 psi
3. Core sample length
   1.25" to 3.0"
4. Core sample diameter
   1.0" to 1.5"
5. Confining pressure system
   Pump with gauge bleed and isolate valves
6. Optimal Pumping system
   Constant rate or constant pressure liquid flow sources

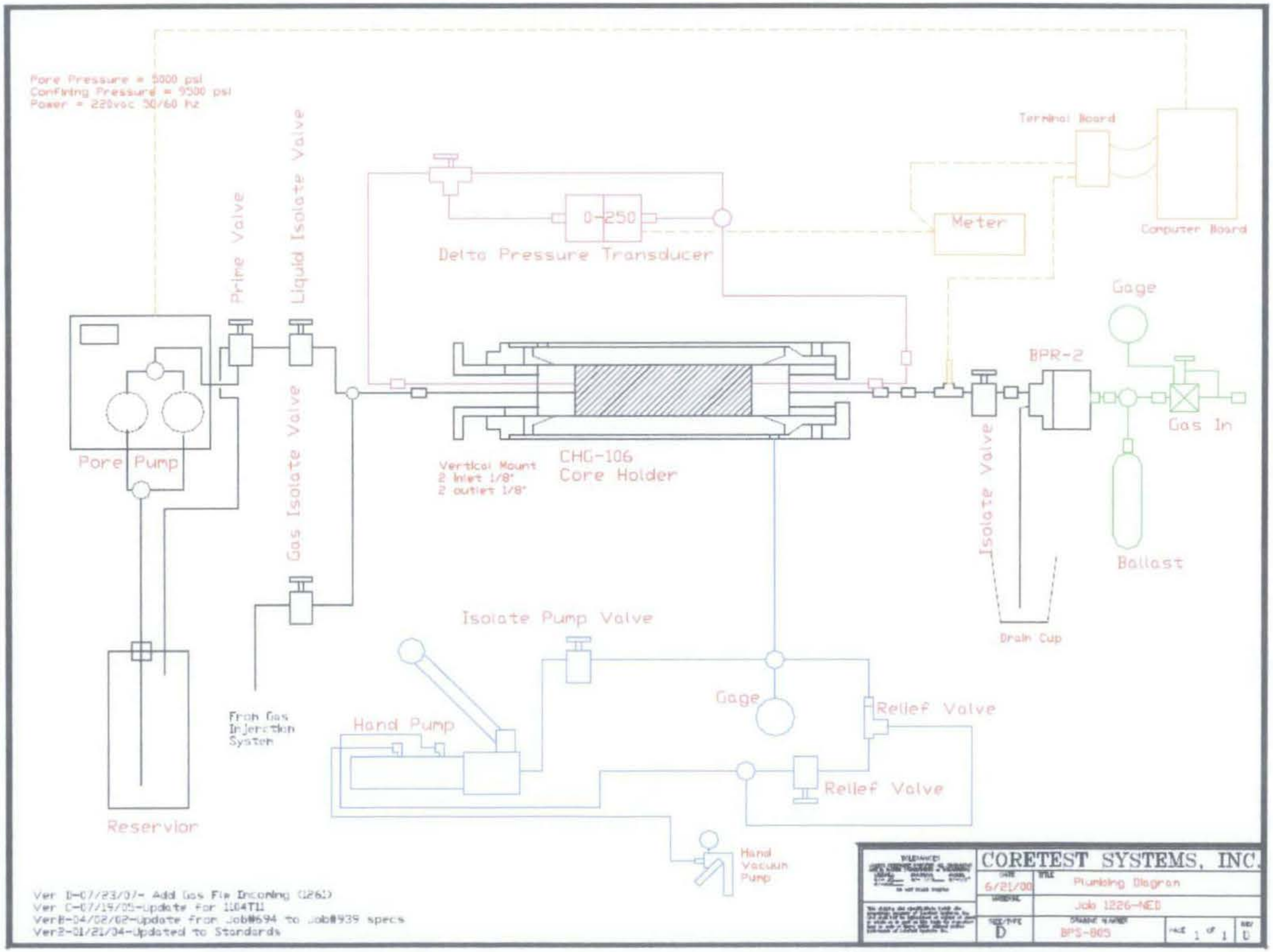


Figure 14: Process Flow diagram for Bench Top Permeability System BPS-805

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result and Discussion

This chapter shows the results obtained from all the experiments done during this project. Three parts of the result are in detailed discussed in the following section. The first part is the result for mineral composition of zeolite before and after the ion exchange process. The second part will explain the result obtained from Atomic Adsorption Spectrophotometer (AAS) and the last part will describe the result obtained from permeability test.

4.2 Mineral composition

4.2.1 Chabazite-50

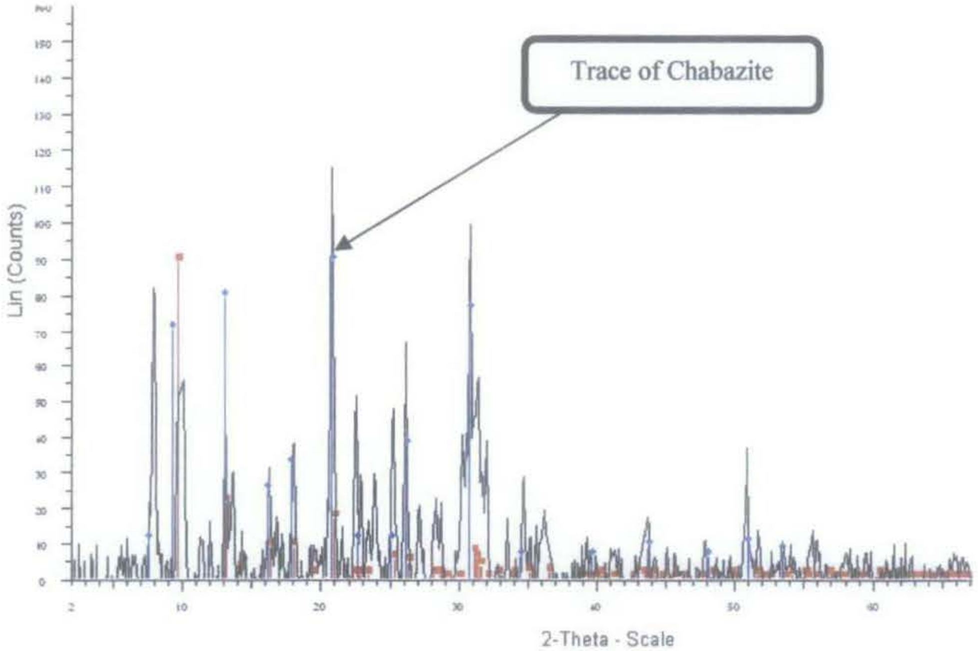


Figure 15: Mineralogy trace of Chabazite-50

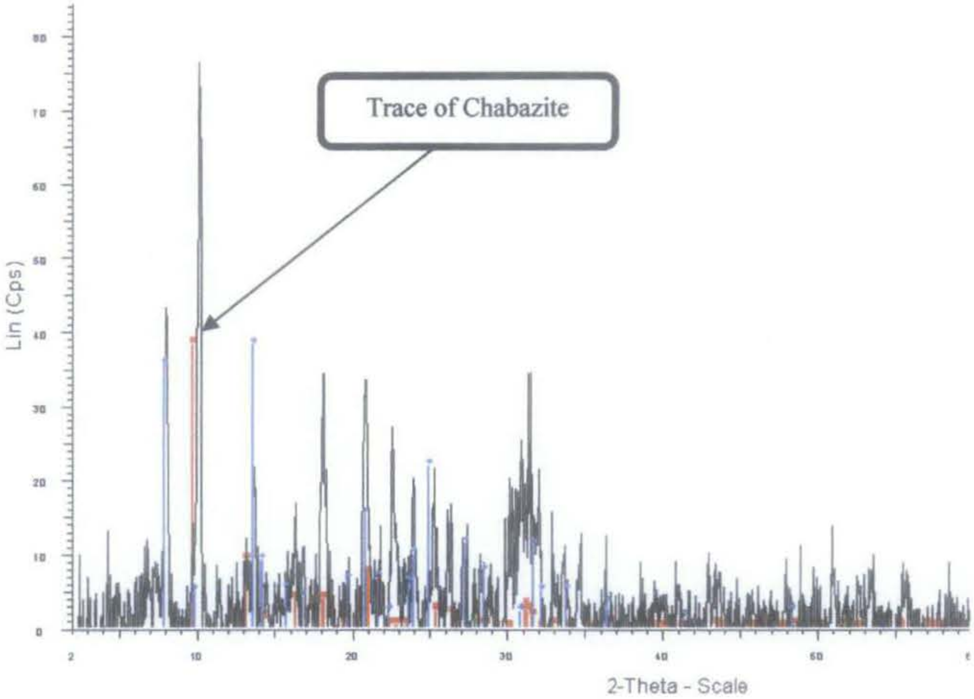


Figure 16: Mineralogy trace of Chabazite-50 after the ion exchange process with barium chloride.

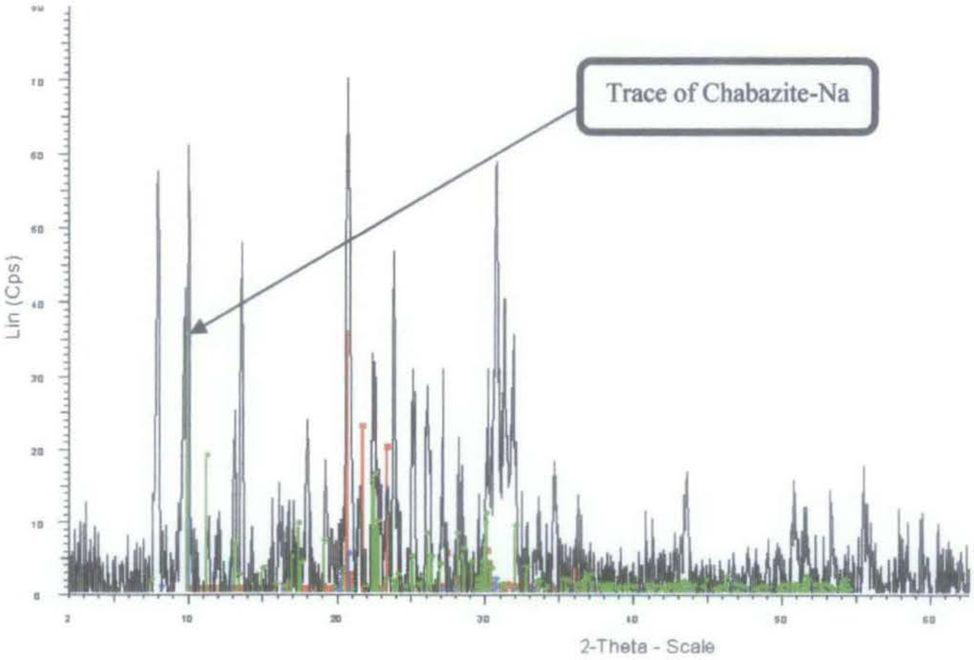


Figure 17: Mineralogy trace of Chabazite-50 after the ion exchange process with sodium sulphate.

Figure 15 shows the mineralogy of chabazite-50 before the adsorption process. The trace of chabazite confirms the properties as receives from the supplier. Figure 16 show that the mineralogy of chabazite-50 after the ion exchanges process by barium chloride. Figure 17 shows the mineralogy of chabazite-50 after the ion exchange process by sodium sulphate. Based on the literature review, chabazite zeolite has the selectivity towards barium and sodium ions. Therefore, after the ion exchange process, the zeolite would probably to have the trace of Chabazite-Ba or Chabazite-Na in its mineralogy. The result in Figure 16 shows the trace of raw chabazite without any added trace of barium ions. While Figure 17 shows some minor trace of chabazite with added sodium ions. Chabazite-50 had shown evidence of adsorbing some sodium ions while unsuccessfully adsorbing barium ions. Comparing the result with the list of selectivity of chabazite in Figure 7 the chabazite should have equal degree of selectivity toward barium and sodium ions. The difference between experimental results and the theory can be caused by the zeolite used in this project which is natural raw zeolite which contains some other impurity elements in it which affects the level of selectivity towards metal ions.

4.2.2 Chabazite-325

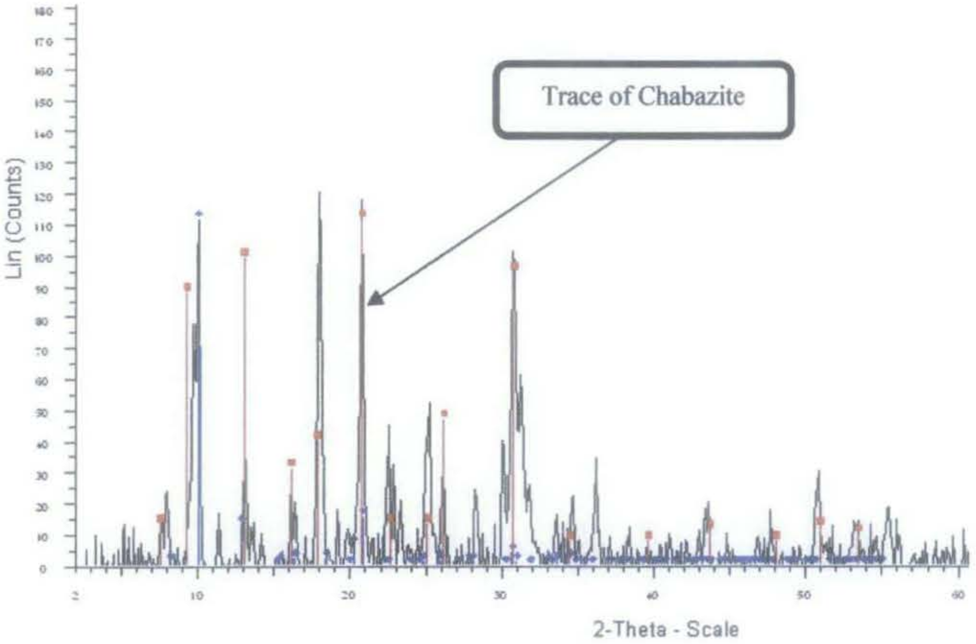


Figure 18: Mineralogy trace of Chabazite-325

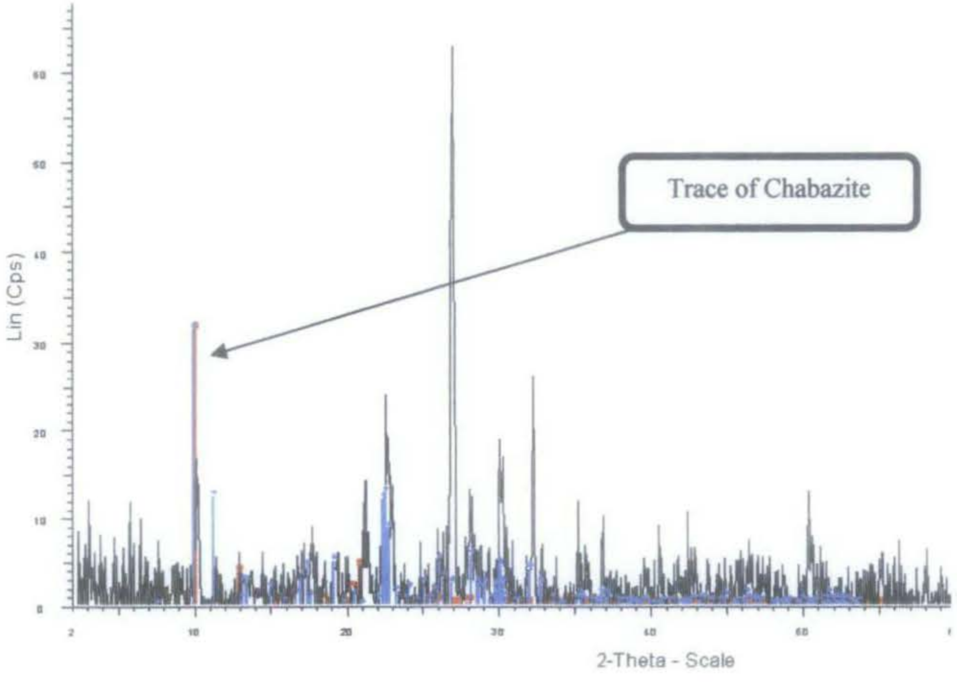


Figure 19: Mineralogy trace of Chabazite-325 after the ion exchange process with barium chloride.

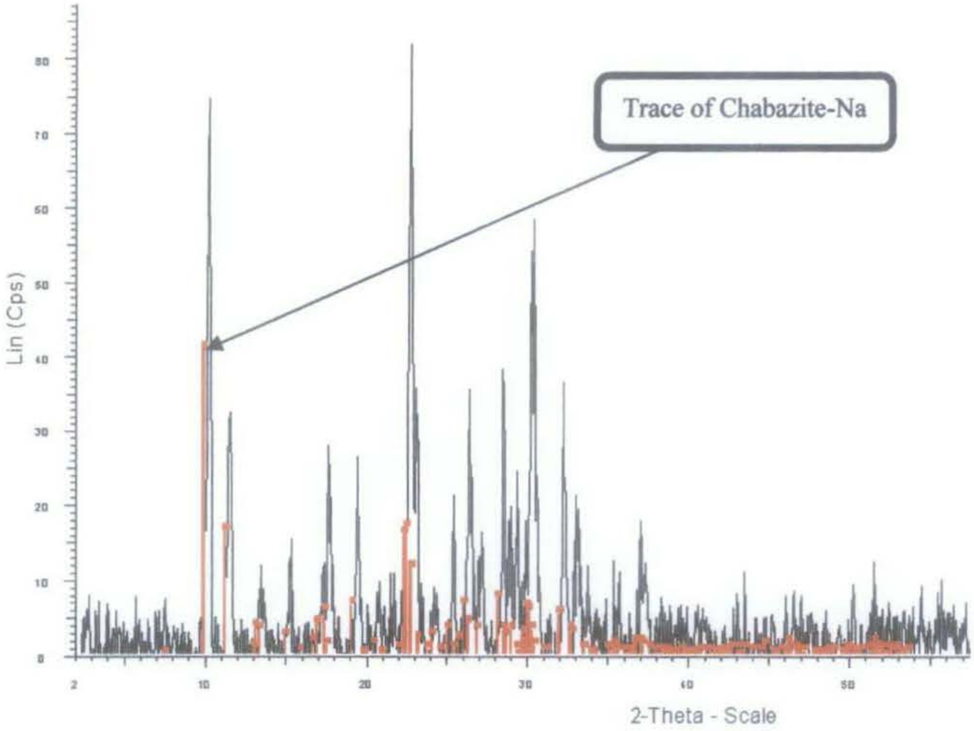
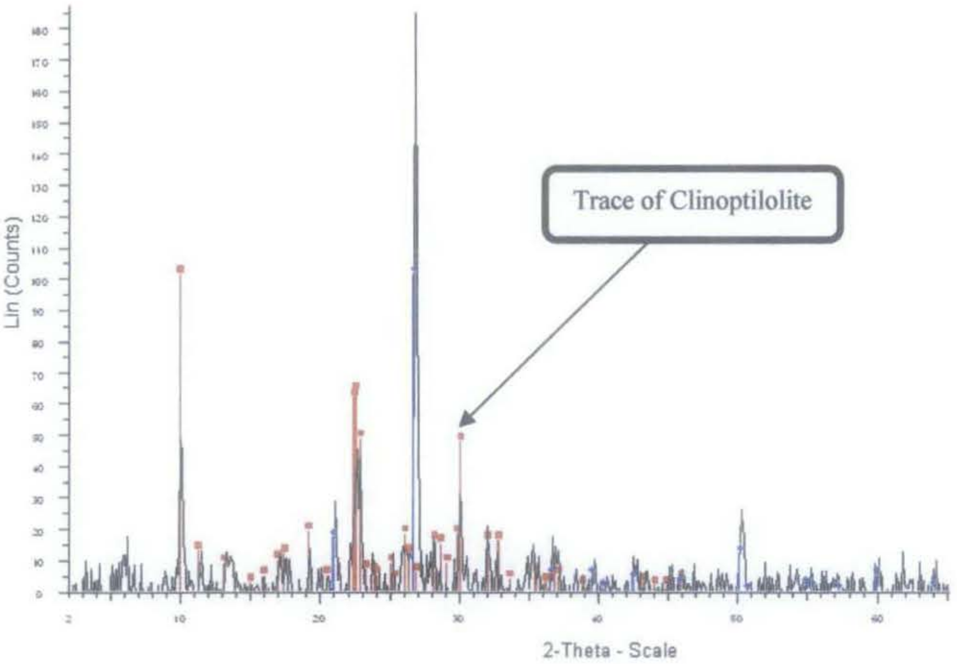


Figure 20: Mineralogy trace of Chabazite-325 after the ion exchange process with sodium sulphate.

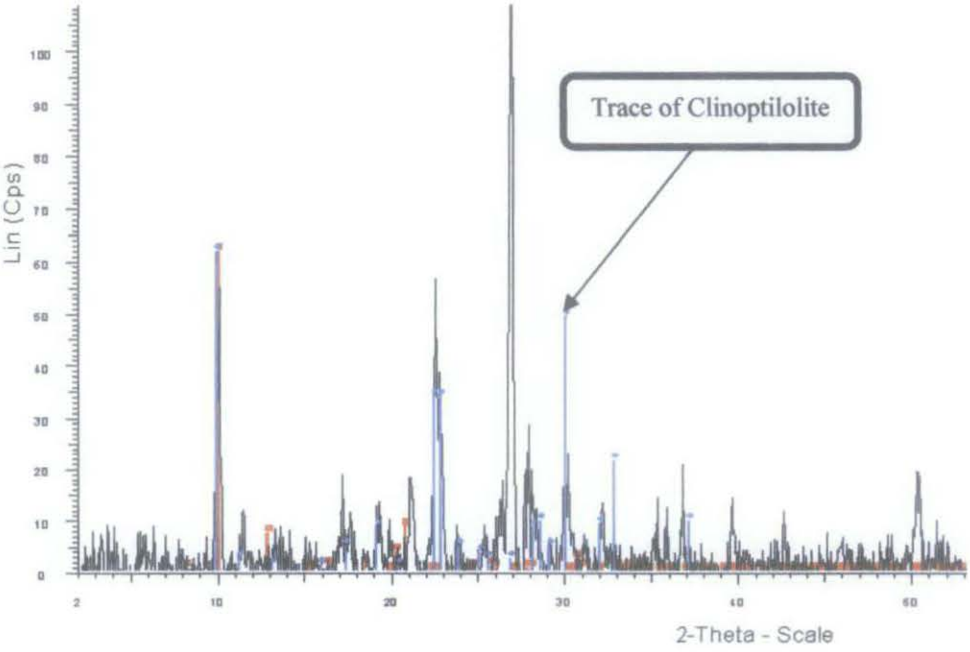
Figure 18 shows the mineralogy of chabazite-325 before the adsorption process. The trace of chabazite confirms the properties as receives from the supplier which when compare to chabazite-50, chabazite-325 have larger grain size. The objective of using the chabazite-325 is to look at the effect of grain size of the natural chabazite on the uptake of barium and sodium ions. Figure 19 show that the mineralogy of chabazite-325 after the ion exchanges process by barium chloride. Figure 20 shows the mineralogy of chabazite-325 after the ion exchange process by sodium sulphate. Figure 19 shows the trace of raw chabazite without any added trace of barium ions. However, Figure 20 shows some minor trace of chabazite with added sodium ions. Comparing with the results from chabazite-50, there is no significant effects of grain size of the chabazite on the uptaken of barium and sodium ions during ions exchange process.

4.2.3 Clinoptilolite 0.1-0.5 mm



Trace of Clinoptilolite

Figure 21: Mineralogy trace of Clinoptilolite 0.1-0.5 mm



Trace of Clinoptilolite

Figure 22: Mineralogy trace of Clinoptilolite 0.1-0.5 mm after the ion exchange process with barium chloride.

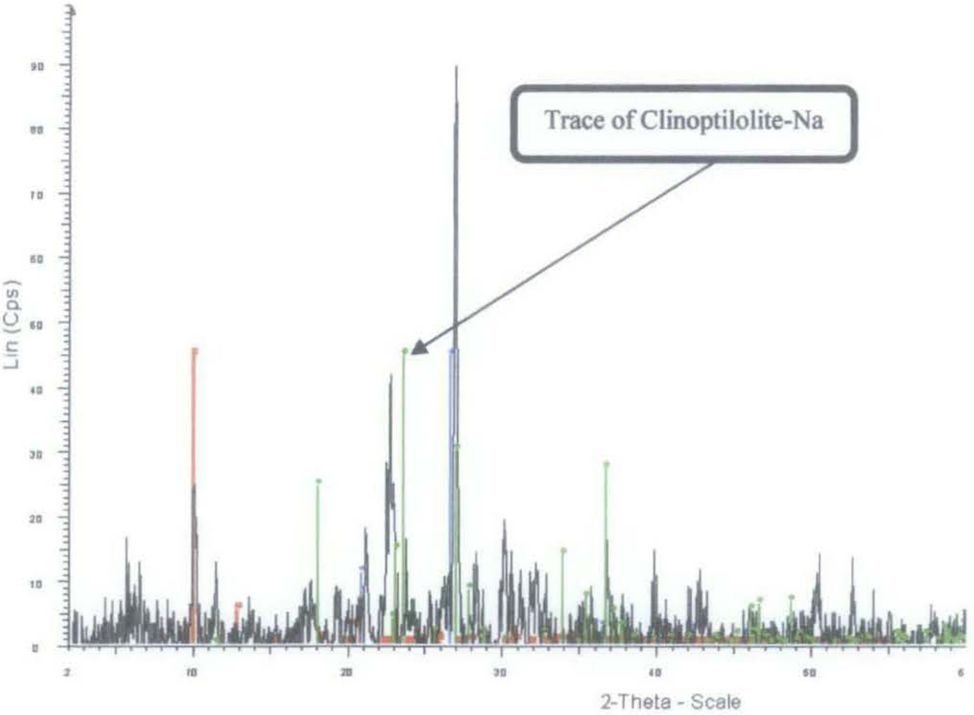


Figure 23: Mineralogy trace of Clinoptilolite 0.1-0.5 mm after the ion exchange process with sodium sulphate.

Figure 21 shows the mineralogy of clinoptilolite 0.1-0.5mm before the adsorption process. The trace of clinoptilolite confirms the properties as receives from the supplier and with grain size of 0.1-0.5 mm. Figure 22 shows that the mineralogy of clinoptilolite 0.1-0.5mm after the ion exchanges process by barium chloride. Figure 23 shows the mineralogy of clinoptilolite 0.1-0.5mm after the ion exchange process by sodium sulphate. The result in Figure 21 shows evidence of clinoptilolite trace with no presence of barium ions in the mineralogy. On the contrary, the result in Figure 23 shows evince of sodium ions in clinoptilolite mineralogy trace. Refer to series of selectivity of clinoptilolite on Figure 6, clinoptilolite exhibit higher degree of selectivity towards barium ions when compare to sodium ions. However, base on the experimental result, clinoptilolite 0.1-0.5 mm unsuccessfully adsorb barium ions which it is contra with the series of selectivity theory. The impurity contains in the raw natural zeolite can be the cause of the contrary.

4.2.4 Clinoptilolite 0.5-1.6mm

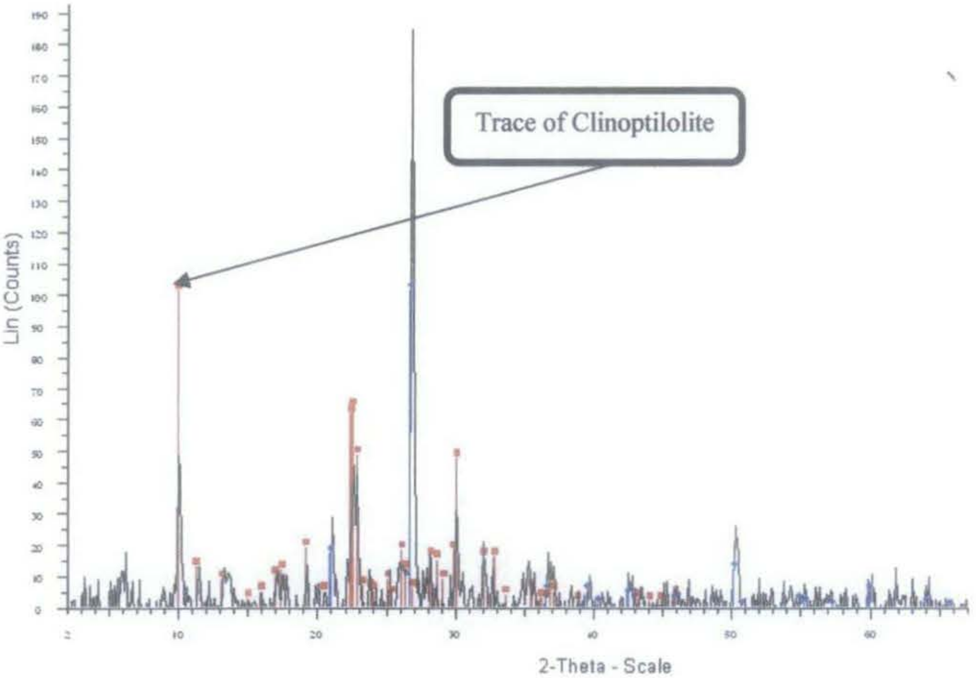


Figure 24: Mineralogy trace of Clinoptilolite 0.5-1.6 mm

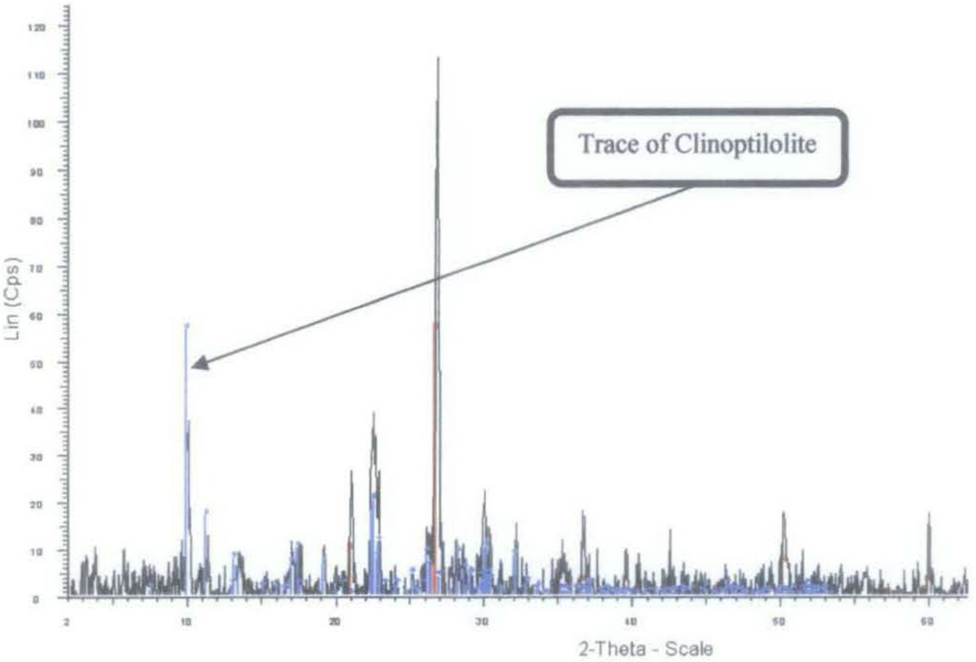


Figure 25: Mineralogy trace of Clinoptilolite 0.5-1.6 mm after the ion exchange process with barium chloride.

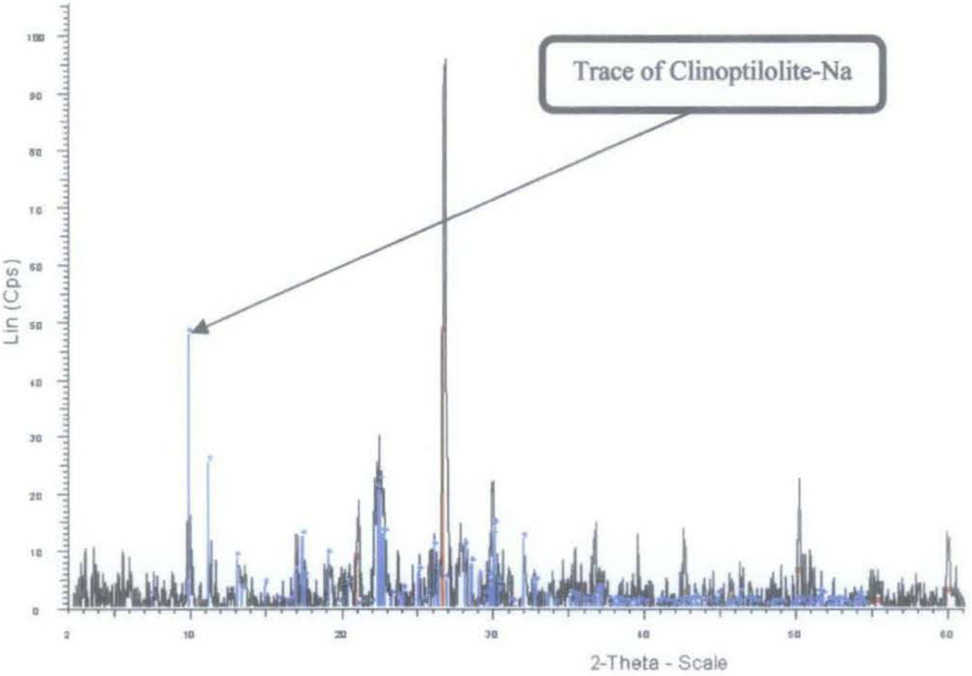


Figure 26: Mineralogy trace of Clinoptilolite 0.5-1.6 mm after the ion exchange process with sodium sulphate.

Figure 24 shows the mineralogy of clinoptilolite 0.5-1.6mm before the adsorption process. The trace of clinoptilolite confirms the properties as receives from the supplier and with grain size of 0.5-1.6mm. This type of clinoptilolite is from the same type of clinoptilolite used in the previous data. They only differ in the grain size. The interest is to look at the effect of using larger particle size of clinoptilolite in ions uptakes during the sorption process. Figure 25 shows that the mineralogy of clinoptilolite 0.5-1.6mm after the ion exchanges process by barium chloride. Figure 26 shows the mineralogy of clinoptilolite 0.5-1.6mm after the ion exchange process by sodium sulphate. Referring to Figure 24, there is no evidence on the presence of bariums ions in the clinoptilolite mineralogy trace. While Figure 26 shows the presence of sodium ions in clinoptilolite mineralogy trace. Comparing the result with the result on clinoptilolite 0.1-0.5 mm, there is no significant effect on barium and sodium ions uptake when the particle size of the clinoptilolite getting larger. Referring on the works of S. Cerjan Stefanovic *et. al.*,(2007) it is proven that clinoptilolite with grain size of 0.1-0.0063 mm enable higher uptake of metal cations. However, in this project, the different in particle size does not exhibit any significant effect towards metals cations uptake. In S. Cerjan Stefanovic *et.*

al., (2007) works, they used pre-treated natural zeolite while the zeolite used in this project is the untreated natural zeolite. By comparing the works by S. Cerjan Stefanovic *et. al.*,(2007). with the result from this experiment, it can be concluded that the pre-treated natural zeolite can exhibit higher metal cations uptakes compare to the untreated natural zeolite.

4.3 Ions Concentration

The specific ions concentration in aqueous solution can be measures using Atomic Adsorption Spectrophotometer (AAS). In this project, sample of Barium Chloride and Sodium Sulphate were run in this equipment to measure the difference in concentration of the solution which had undergone the sorption process and the untreated solution. The AAS will compare the sample solution with the standard solution in order to measure any specific ions concentration.

4.3.1 Ions concentration in Sodium Sulphate Aqueous Solution

Table 6: Concentration of sodium ions in Sodium Sulphate aqueous solution

Sample	Concentration
$NaSO_4$ circulated through 0.5mm-1.6 mm clinoptilolite	0.77
$NaSO_4$ circulated through 0.1mm-0.5mm clinoptilolite	0.83
$NaSO_4$ circulated through 50 chabazite	0.64
$NaSO_4$ circulated through 325 chabazite	0.79
Untreated $NaSO_4$	0.85

Table 6 above show the concentration of sodium ions in Sodium Sulphate aqueous solution measured by AAS. In measuring sodium ions, the standard solution uses are 0.2ppm, 0.4ppm and 0.8 ppm. The sample Sodium Sulphate solution has the concentration of 0.8 ppm. Referring to the above table, the result shows that the solution which has been treated with 50 chabazite has the lowest sodium ions concentration.

While the other sample does not show any big value of different. The small plus and minus value of concentration when compare to the 0.8ppm can be assume as an error while handling and diluting the sample during the preparation.

By comparing the result of XRD and the result obtained from the AAS it is proved that clinoptilolite and chabazite has the ability to uptake the sodium ions. Clinoptilolite with grain size of 0.5-1.6 mm exhibit higher sodium ions sorption when compare to the clinoptilolite with 0.1-0.5 mm grain size. However, for chabazite, the smaller grain size of chabazite exhibit higher sodium ions sorption. The AAS results are all dependent on the accuracy of the standard solution's concentration. The inaccuracy of standard solution's concentration will effect the reading obtains from the equipment. It is difficult to achieve ideal concentration of standard solution because the standards were manually prepared. Thus, there will be some unreliability on the result obtained by the AAS.

4.3.2 Ions concentration in Barium Chloride Aqueous Solution

Table 7: Concentration of barium ions in Barium Chloride aqueous solution

Sample	Concentration
BaCl circulated through 0.5mm-1.6 mm clinoptilolite	2.71
BaCl circulated through 0.1mm-0.5mm clinoptilolite	2.54
BaCl circulated through 50 chabazite	2.41
BaCl circulated through 325 chabazite	2.47
Untreated BaCl	2.63

Table 7 above show the concentration of barium ions in Barium Chloride aqueous solution measured by AAS. The standard solution use in measuring the barium ions are 2.5ppm, 5.0ppm and 10.0 ppm .The sample solution has the concentration of 2.5 ppm. Table 7 shows that the solution which had undergone ion exchange process by 50 chabazite has the lowest value of concentration. The other sample concentration is higher than the 2.5ppm sample solution. This may be caused by the error of the equipment and also while handling and diluting the sample solution.

By comparing the XRD result with the AAS result for the sorption process of barium ions, there are some contrary in both results. Referring to the XRD result, there is no sample of natural zeolite which successfully adsorbing the barium ions from the Barium Sulphate aqueous solution. On the contrary with the results obtained from the AAS, four sample shows that there are sorption process of barium ions occur during ions sorption process. Similar to the sodium standard solutions, barium standard solution were manually prepared. Thus it is difficult to obtain ideal value of standard solution's concentration with no error. During the equipment run, the measurement for barium ions was done for six times before getting the less error data. The AAS has difficulty to detect the barium ions in sample and standard solution. Therefore, there are some possibilities of obtaining unreliable data.

4.4 Permeability Test

In this project the sample solutions that have been circulated through the zeolite bed were then used to saturate the core. The measurements of the core effective permeability were done using the Bench Top Permeability System. The initial effective permeability of the clean cores was first measured. Further, these clean cores were saturated with the sample solutions. Afterward, effective permeability of the saturated cores was measured. By comparing the initial effective permeability with the effective permeability of the saturated core, the difference of effective permeability can be calculated.

The concept of this experiment is, the sample solution of Barium Chloride and Sodium Sulphate that had been circulated through the bed of zeolite will obtained less difference in effective permeability when compare to the untreated solution.

4.4.1 The Effective Permeability

Table 8: Effective permeability

Aqueous Solution	Initial Effective Permeability	Final Effective Permeability
$NaSO_4$ circulated through 0.5mm-1.6 mm clinoptilolite	150 mD	147 mD
$NaSO_4$ circulated through 0.1mm-0.5mm clinoptilolite	160 mD	158 mD
$NaSO_4$ circulated through 50 chabazite	120 mD	116 mD
$NaSO_4$ circulated through 325 Chabazite	150 mD	146 mD
Untreated $NaSO_4$	160 mD	159 mD
BaCl circulated through 0.5mm-1.6 mm clinoptilolite	120 mD	116 mD
BaCl circulated through 0.1mm-0.5mm clinoptilolite	150 mD	147 mD
BaCl circulated through 50 chabazite	160 mD	156 mD
BaCl circulated through 325 Chabazite	120 mD	117 mD
Untreated BaCl	150 mD	148 mD

Table 8 shows the difference of effective permeability between the initial effective permeability and the effective permeability of the saturated core. By referring to the value obtained from untreated $NaSO_4$, the core saturated with treated solution found to have small reduction in their effective permeability. However, those reductions of effective permeability are too small to be considered to have significant effect towards mitigating the permeability reduction in formation damage. By looking at the value of difference of effective permeability for BaCl saturated core, they also shows small difference when compare to value obtained from the core saturated by untreated BaCl. Same as $NaSO_4$, the difference obtained from BaCl saturated core is too small to be considered to have significant effect towards mitigating the permeability reduction in formation damage.

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

The precipitate of inorganic scales is one of the root causes of formation damage. In this project, the focus is to mitigate the formation of barium sulphate which has relative hardness and low solubility. One of the mechanisms that will have the tendency to lead the formation of sulphate precipitate is mixing of two incompatible waters during water injection process, one containing soluble salts of barium and the other containing soluble sulfate. The purpose of this project is to remove barium ion from barium chloride solution and sodium ion from sodium sulphate solution respectively using zeolite bed.

Clinoptilolite and chabazite zeolite have potential in mitigating the formation of barium sulphate scaling. Referring to the results obtained from permeability test and Atomic Adsorption Spectrophotometer, they show small quantity of barium ions had been removed and small value of effective permeability of the core had been reduced. The mineralogy composition results show that both clinoptilolite and chabazite are able to adsorb sodium ions from the sodium sulphate aqueous solution. However, the adsorption of barium ions contains in barium chloride aqueous solution for both clinoptilolite and chabazite is not significant.

5.2 Recommendations

The use of raw natural zeolite does not shows significant potential in mitigating the formation of barium sulphate precipitate. However, the potential use of zeolite can further be studied. In order to have higher metal ions uptake, natural zeolite can undergo pre-treatment to enhance the zeolite exchange capacity. Base on the literature review, zeolite mostly been pre-treated with NaCl and $CaCl_2$ solution.

Based on the work of S. Cerjan Stefanovic et. al.(2007), the suggested methods for zeolite pre-treatment are as follow:

1. Mix 5.0 grams of natural zeolite with 100ml of 2mol/l solutions of NaCl or $CaCl_2$.
2. Stir the mixture for 120 hours by magnetic stirrer at 36 °C.
3. After the treatment, carefully wash the zeolite with distilled water.
4. Dry the zeolite in the oven at 90 °C.

Other then using pre-treated natural zeolite, the usage of synthetic type of zeolite can exhibit higher degree of metal ion sorption because the will be no impurity contains in synthetic zeolite. Further, synthetic zeolites have mineralogy properties because it was manufactured for specific usage. The manufacturers of synthetic zeolite nowadays not only produce the zeolite in a form of solid but also in the form of liquid. Liquid type of zeolite has higher potential to be used in mitigating the formation of scale in the reservoir because they have the possibility to be circulated through the reservoir.

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APPENDICES

APPENDIX 1: CALCULATION OF QUANTITY OF BARIUM CHLORIDE

Quantity of barium chloride in the solution containing 1000 ppm barium ions

Molecular weight of BaCl = 244.28 g

Molecular weight of Cu = 137.327 g

$$Percent\ of\ Ba\ in\ BaCl = \frac{137.327}{244.28} \times 100\%$$

= 56.217 %

$$Concerntration\ of\ Bacl\ o\ give\ 1000\ ppm\ Ba = \frac{100\ \%}{56.217\%} \times 1000\ mg/L$$

= 1.7788 g/L

$$Amount\ of\ BaCl\ in\ 1\ litre\ solution = 1.7788 \frac{g}{L} \times 1L$$

= 1.7788 g

APPENDIX 2: CALCULATION OF QUANTITY OF SODIUM SULPHATE

Quantity of sodium sulphate in the solution containing 1000 ppm sodium ions

Molecular weight of $NaSO_4$ = 142.04 g

Molecular weight of Na = 22.99 g

$$Percent\ of\ Na\ in\ \mathrm{NaSO4} = \frac{22.99}{142.04} \times 100\%$$

$$= 16.186\ \%$$

$$Concerntration\ of\ NaSO4\ to\ give\ 1000\ ppm\ Na = \frac{100\ \%}{16.186\%} \times 1000\ mg/L$$

$$= 6.1783\ \mathrm{g/L}$$

$$Amount\ of\ BaCl\ in\ 1\ litre\ solution = 6.1783\frac{g}{L} \times 1L$$

$$= 6.1783\ \mathrm{g}$$