

CHAPTER III

MATERIALS AND EXPERIMENTAL WORK

3.1 Introduction

This chapter outlines the materials and experimental research works carried out in order to achieve the objectives of this study. Moreover, experimental procedures were grouped into two parts:

1. Treatment by zeolite
2. Preparation of fracturing fluids

3.2 Materials

The samples used in this study were:

1. Produced from water Heglig oil field
2. Natural zeolite from Wadkally(Elgadarf state Eastern Sudan)
3. Two types of cellulose derivatives Hydroxyethyl Cellulose (HEC) and Carboxymethyl Hydroxyethyl Cellulose (CMHEC).

3.2.1 Produced Water from Heglig Oil Field

Sample collection: Produced water samples were obtained from the Heglig oil field. Sample has been taken from two different ponds, the first Ponds presents the untreated water, while the second pond presents the water after the final field treatments with bioremediation project. Sample were taken using sterile bucket and stored in sterile containers of different sizes (1 litter and half litter) and has been kept in 4 degree. This water have been experimentally measured before treatment in order to define its components such as total suspended solid (TSS), total dissolved solids (TDS), oil & grease, bacteria and metals. The characterization has been done using methods of testing available in Sudan and Germany, in order to evaluate the compatibility of proposed treated water with hydraulic fracturing additives and formation water, in order to eliminate any problems that may cause by incompatibility.

3.2.2 Natural zeolite from WadkallyElgadarf state (Eastern of Sudan)



Z1 Z2
Fig 3.1 Zeolite Samples: (Z1 is sample No.1 and Z2 is sample No.2)

3.2.3 Two types of cellulose derivatives Hydroxyethyl Cellulose (HEC) and Carboxymethyl Hydroxyethyl Cellulose (CMHEC).

3.3 Experimental Procedures

Two series of experimental works have been conducted for the samples at different times and conditions. The first series were conducted in Sudan using samples of 24 hours life time while the second group was conducted in Germany using samples of 30 days life time.

3.3.1 Water Sampling Preparation

The following tests were conducted to determine the main components and their proportion that could be found.

3.3.1.1 Total Suspended Solids Measurement (TSS)

A volume of produced water measured according to APHA standard methods carefully removed filter from filtration apparatus was done and transfer to an aluminium weighing dish

in order to reduced high dissolved solids then dried for 1h at 103 to 105°C in an oven, cooled in desiccator to balance temperature and weigh and the TSS content was Calculated in ppm (mg/l) as:

$$\text{Total suspended solids mg/L} = \frac{(a-b)*1000}{\text{sample volume ml}} \dots\dots\dots (3. 1)$$

3.3.1.2 Total Dissolved Solids Measurement (TDS)

Total dissolved solids and electric conductivity were measure using Conductivity meter (Jenway 4320), 50 ml for two samples were used.

3.3.1.3 Oil and Grease Measurement

Oil and grease was extracted follows APHA standard methods. A measured volume of the sample (250 ml=V) was introduced into separating funnel with 1.5ml of HCL1:1 was added. 7.5ml of n-Hexane was added to the acidified sample and shake for 2min. when it reaches the equilibrium the organic layer of Oil &Hexane was separated in evaporating dish. Then replicated this step 2 times more and talk all separated all separated organic layer then transferred into a pre-weighed (W1(gm))flask and hexane was evaporated in a water bath at 103 to 105°C for 1h .The flask is reweighed (W2 (gm)) and:

The Oil and grease content is Calculated in ppm (mg/l) as:

$$\frac{a-b}{\text{sample volume (ml)}} * 106 \dots\dots\dots (3.2)$$

3.3.1.4 Bacteria

Hydrocarbon-utilizing bacteria in produced water were obtained by plating out low dilutions (10⁻¹ to 10⁻⁹) of samples onto modified Nutrient agar medium according to [text].

The medium has been used the following, MacConkey broth for identification and Sub culture with nutrient agar with different Media and different concentrations used, (KIA (kliger, iron agar)), Peptone water, medium, Urea medium), to detect the presence of sulphatereduingbacteria (SRB) indicated by H₂S production. The medium was autoclaved for 15 min and incubated at 35 0C to 37 0C for 24hr, 48hrfor two samples respectively.



Fig.3.2 Water Sample No.1 with Macconky Broth Culter after 24hr



Fig 3.3 Water Sample No.2 with Macconkoy Broth after 24hr



Fig 3.4 Water Sample No.1 with Maconky after 48hr



Fig 3.5 Water Sample No.2 with Maconky Broth Cultures after 48 hr

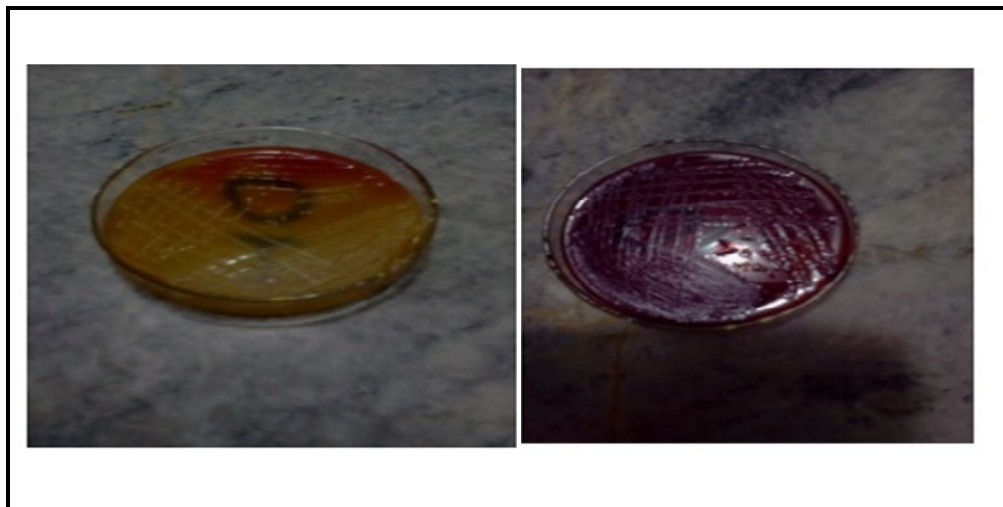


Fig 3.6 Germination Test Dishes

3.3.1.5 Metals

The metals and heavy metals were measured directly by Atomic Adsorption Spectrometry shown in fig (3.9).



Fig 3.7 Atomic Adsorption Spectrometry (AAS)

3.3.2 Zeolite Preparation

The characterization of natural zeolites was analysed by the following steps:

3.3.2.1 X-Ray Diffraction (XRD)

X-ray diffraction patterns for zeolite structure and purity were obtained, using Panan analytical X'Pert³ MRD, Copper K α radiation at 45 kv/ 35 mA ,with a goniometer speed of 2°/ min .In 2 range scanning from 2° 50°.

3.3.2.2 Infrared Spectroscopy

Mixing about 0.05gram of zeolite with 1 gram KBr and grinding till homogenous and passage to 5 tons for 30s, the pellet passage to light. Characterization was performed using an Infrared spectrophotometer FT, IR 84005 Shimadzu, in wavelength 4000 to 400 cm^{-1} .

3.3.2.3 X-ray Fluorescence :

To determine the elemental composition (metal oxide) , used XRF spectrometer Axios max pan analytical (Holland), 9 gram from zeolite with 3 gram sugar grinding to gather in aluminium beach then press to be homogenous put it in the device for 15 min.

3.4 Laboratory Work

Two parts of experimental procedure were done:

1. Preparation and modification of natural zeolite for treatment process
2. Preparation of hydraulic fracturing fluid with HEC and CMHEC

3.4.1 Preparation and modification of natural zeolite for treatment process

Material

To prepare the synthetic solutions the following salts of metal ions were used in the following table:

Table 3.1 Chemical and Its Purity for Elements

Element	Chemical Source and Its Purity
Mg	MgCl ₂ (98.5% purity)
Ca	CaCl ₂ .2H ₂ O(99% purity)
K	KCl
Fe	Fe (NO ₃) ₃ .9H ₂ O
Na	NaNO ₃
NH ₄ Cl	for zeolite modification
HNO ₃ for AAS analysis	(65% ISO.Max)

3.4.1.1 Preparation of Natural Zeolites for Laboratory Experiment

Firstly, natural zeolites have been washed by acid to remove impurities that block the pores, progressively eliminate cations to change into H-form. Zeolite was immersed in HCl 1.0M for 5 hours. Secondly was immersed in sodium chloride for 24 hours to be Na-zeolite. Then grained from 200 to 150 μ surface area, and heated in 100°C for one hour according to (Cho et al., 2013).

In order to achieve high adsorption of metals, 12 g of the zeolite were mixed with 100 ml of 10% HCl, 3es4 the weekend. After washing and decanting several times until the pH was 4.5, it was filtered over vacuum with filter MN 640 m (aschefrei). After that the zeolite was dried at 100°C for 22 h. For the first pre-experiments in order to see, if activation was achieved, zeolite was tested without the calcination step at 450°C for 6h according to (Cho et al., 2013).

3.4.1.2 Zeolite Activation and Modification

10 g of zeolites have been mixed with 100 ml of NH₄Cl solution, 2.0 M and stirred for 24 hours according to (Cho et al., 2013) and . The residual NH₄Cl solution was decanted before the procedure was repeated with fresh NH₄Cl solution, this time over the weekend. The third time of treatment with NH₄Cl solution again lasted 24 h. The suspension was filtered through a filter paper and washed several times with deionized water. When the test for chloride with AgNO₃ was negative, the zeolite was dried in a drying oven for 24 h and subsequently calcinated in a muffle furnace at 450 °C for 6 h in normal atmosphere. The zeolite was then ready to use and will be ((NH₄-zeolite) = (H-zeolite)) and ready for remove metals (Fe, Ca, Mg, K,).

Natural zeolite1 (Zn1) and natural zeolite2 (Zn2) adsorbent were used for removal of dissolved cations in synthetic solutions and produced water.

3.5 Batch Adsorption

For the first experiments, single salt solutions beginning with 50 ppm of the metal with Na-zeolite at pH values of 1, to 9 should be chosen. Different ratios of zeolite concentrations beginning with 0.1 gram to 0.5 gram were used. The experimental was done according to Abreu et al, 2012. Batch adsorption was performed to four types of elements (K, Ca²⁺, Fe²⁺, Mg²⁺) by zeolite and modified zeolite. With particle size 150-200 µm zeolites. The study of Na through this step is not possible because the zeolite has been treated with HCl and subsequently rinsed with NaCl to get a Na-Zeolite.

A stock single salt solution of 500 ppm of each metal was prepared with the salts it's given in Table (3.1). To adjust the desired pH, 10 ml of this stock solution was given into a 100 ml volumetric flask, filled to about ¾ and the pH adjusted with HNO₃ or NH₃ solution to the desired value. Subsequently, the solution was filled to 100 ml with deionized water. 50 ml of this solution was mixed with 0.5 g of zeolite and stirred on a magnetic stirrer for 30 minutes. After stirring, the zeolite was allowed to precipitate and the almost clear solution was filtered through a cellulose acetate membrane filter (0.2 µm pore size). The filtrate was diluted 1:10 for Calcium and 1:100 for Mg. to achieve a maximum concentration of 5 ppm and 0.5 ppm respectively which is appropriate for AAS.

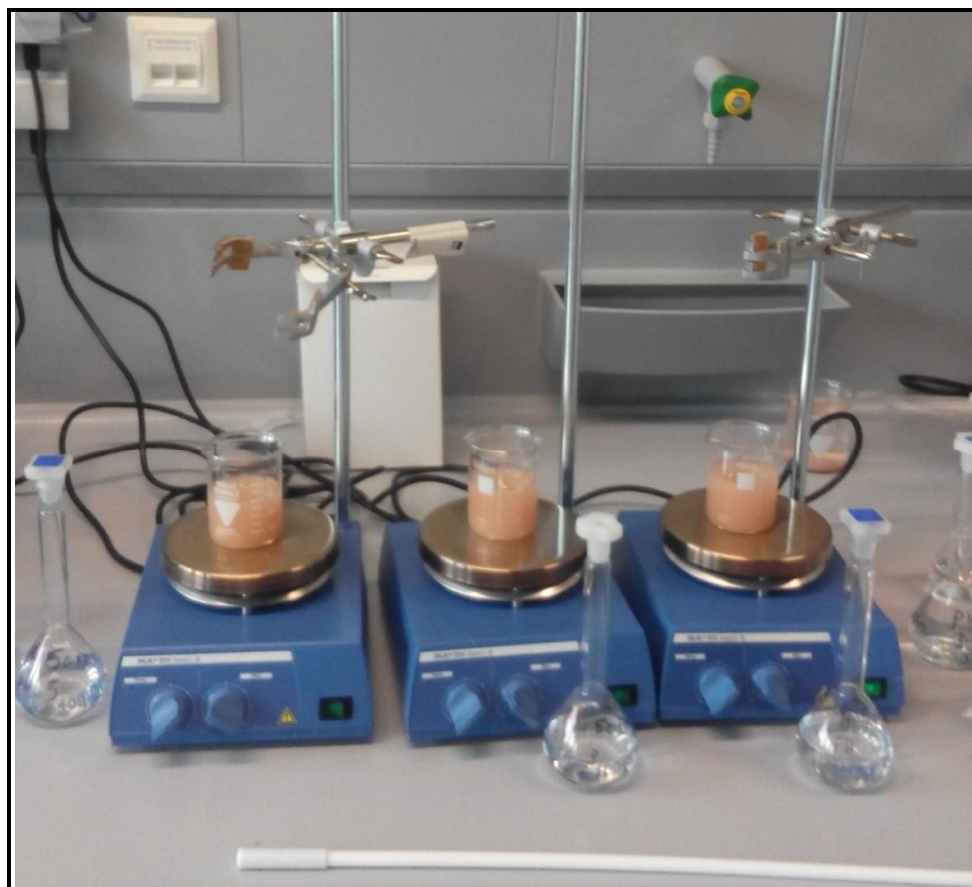


Fig 3.8 Mixing Zeolite with Different Salts by Magnetic Stirrer

3.5.1 Study of pH Effect

To determine the effect of pH on adsorption of metals (K, Na⁺, Ca⁺², Mg⁺² and Fe⁺²) in batch solutions containing concentration 50 ml for each metals and different pH levels was adjusted at 1, 2, 3, 4, 5, 6, 7, 8 and 9 using NH₄OH and HNO₃, before mixing zeolites by (pH meter model 3305 Jenway UK).

3.5.2 Adsorption Capacity and Evaluation of Data:

The removal percentage by zeolite in according to equation:

$$\text{Metal removal\%} = \frac{C_o - C}{C_o} * 100 \dots\dots\dots (3.1)$$

Where C_0 and C are initial and final concentration (mg/l) of the metals ions solution contact with the mass of zeolite, the amount of Mg, K, Ca and Fe adsorbed by zeolite was determined using mass balance equation.

$$q_e = \frac{v(C_0 - C)}{m} \dots\dots\dots (3.2)$$

Where q_e is the metal concentration on the zeolite (mg/l) at equilibrium, C is metal concentration in solution (mg/l) at equilibrium, C_0 is initial metal concentration in solution (mg/l), v is volume of initial metal solution used (ml) and m is mass of zeolite used (g).

Table 3.2 Salt Concentrations for the First Experiments with Zeolite

Species	Atomic or Molar Mass/g	Mass of Salt For 100 ml Of Stock Solution (Mg)
Fe(NO ₃) ₃ *9H ₂ O	403.95	361.6
CaCl ₂ *2H ₂ O	147.02	183.4
MgCl ₂	95.22	195.8
KCl	74.56	95.3
NaNO ₃	85.00	18.8

3.5.3 Adsorption Experiments with Activated Zeolite

50 mg/L solutions of Ca Mg, Fe, K and Na were prepared from the stock solutions with pH values from 1 to 9. Each solution was mixed with 0.5 g zeolite activated following the above given procedure. The protocol of zeolite treatment is also given above.

The adsorption experiments with activated zeolite were done with the same concentrations of single salt solutions it's given in Table (3.1). The formula used for calculation is:

$$\text{Metal (salt)} = \frac{500 \text{ mg/l} * 0,1 \text{ l} * \text{MM (salt)}}{\text{AM (element)}} \dots\dots\dots (3.3)$$

MM=molecular mass

AM=atomic mas

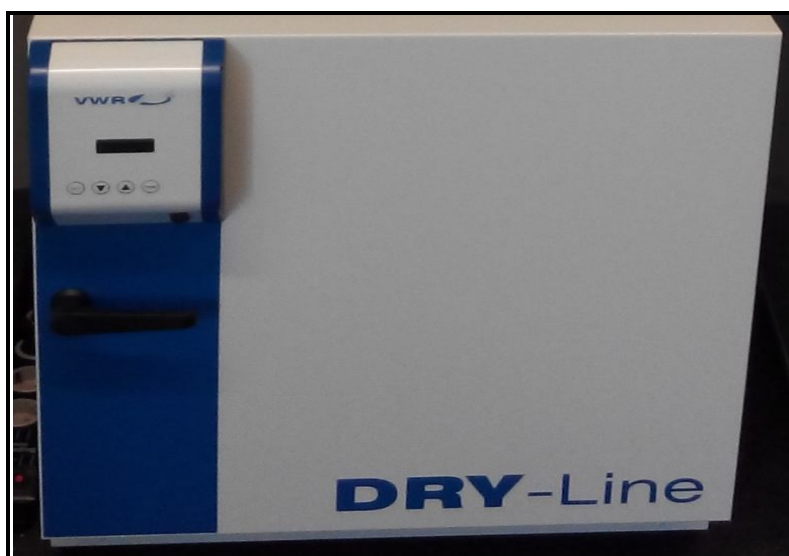


Fig 3.9 Oven for Drying Zeolites Sample



Fig 3.10 Oven for Calcination Zeolite Samples (For 6 Hours)

3.4.2 Preparation of Hydraulic Fracturing Fluid with HEC and CMHEC

During the fracturing fluids process, a viscous non Newtonian fluid was applied to the formation with three major functions:

1. Delivering pressure to create fracture network and geometry within simulated zone.
2. Transporting proppant into the created fracture to maintain fracture conductivity.

3. Control of fluid leak off into the formation by forming a filter cake on the walls of the fracture.

3.4.2.1 Preparation of Polymer Solution

Firstly, a preferred procedure of the study, an aqueous fracturing fluid is first prepared by blending a hydratable polymer into an aqueous fluid. The aqueous fluid could be distilled Water, untreated produced water, treated produced water (by process conducted in site of the Heglig oil field) and treated one by natural zeolite. In the case of batch mixing, the hydratable polymer and the aqueous fluid are blended for a period of time sufficient to form a hydrated solution.

Two types of hydratable polymers useful in the present study (HEC, CMHEC) may be all of the hydratable were used are well known to those in the Well service industry. Several tests were conducted using four types of water (tap water, untreated water, treated water and treated water by natural zeolite).

3.4.2.2 Rheological Properties and Testing

Out of a hydration study, polymer powder was added to 100mL of different types of water with stirring in a Waring® blender (medium rate that was enough to generate a slight vortex) to make up the desired concentration. According to (Vo et al. 2014). The following series tests were conducted.

1. In the first test, the aqueous solution contained HEC was preparing by adding different concentration of powder ranged from 2.5 to 5 gram per 100ml of tap water in order obtain stock solution. A solution containing buffer for adjusting pH, the quantity of polymer was hydrated (starrier) in 1 liter of untreated produced water for about 30 minutes. The solution was divided in to 200ml aliquots in to beaker glasses. Aliquots were mixed with to 1500 rpm to get vortex. The samples were placed into constant temperature and the viscosities measured by proRheo R 180 rheometer with concentric cylinder.
2. In the second series of the testes, the same polymer concentrations in the first series were used. The aqueous solution prepared according to the same procedure described

in the first series. The tests were conducted at different temperature ranged from 10 to 80 C, with aqueous solutions which were thickened with 2.5-5grams of the HEC cellulose per 100ml of solution, Viscosities were determined with a proRheo R 180 rheometer.

3. In the third series of the testes, the effect of various pH on the viscosity of an aqueous solution thickened with two types of cellulose per 100ml of solution was tested and the procedures were repeated. Lastly, in fourth series of the tests, the effect of shear rates on the viscosity was investigated. All the above procedures were used for the two types of the polymer.

3.6 Viscosity of Fracturing Fluids

Viscosity was measured with the several times to show continue loss of viscosity with time at simulated down hole temperature range from (10 - 80 degree C), and constant shear rates 300/sec. and several time with different pH and constant shear rates, and sometime with different shear rates.

The viscosity of the fracture fluids is very important. The fluid should be viscous enough (normally 50–1000 cp) to create a wide fracture (normally 0.2–1.0 in) and transport the propping agent into the fracture (normally 10s to 100s of feet)(Department of Energy, 2004).

3.7 Crosslinking System of The Polymer

There exists necessity, therefore, for a cross-linking system for water based well fracturing fluids which will increase the viscosity of the well treating fluids by a method which is simple and economical. There also exists necessity for such a cross-linking system which will give a fracturing fluid which is shear stable at normal fracturing pump rates and which is temperature stable at elevated well temperatures.

The cross-linking system of the present study for water based well fracturing fluids comprises a mixture of aluminium ion constituent, with a boron constituent. The boron constituent was selected from the group consisting sodium tetraborate, and mixtures thereof.

The liquid cross-linking system was prepared by first dissolving the boron constituent. Aluminium ions are then added and mixed thoroughly. A water based fracturing fluid can be prepared which comprises water, the cross-linking system described, and a hydratable polymer capable of gelling in the presence of the cross-linking system. The hydratable polymer useful in the present study can be any hydratable cellulose derivatives CMHEC, and HEC. The water based fracturing fluid can be prepared for use by adding four types of water such as deionized water, raw water, treated water in site of the field and treated water by natural zeolites during present study.

Borate crosslinked was used (0.5-2.0) % by weight of polymer according to Patent (US5806597).

The water based fracturing fluid thus was prepared contain about 5 to 7gof hydratable polymer per 100ml of water used for HEC cellulose derivative and most 0.48 per 100ml of water for CMHEC cellulose derivative.

3.8 The Effect of pH

The pH of the two samples of this study is typically greater than about 8. As in the case of the acidic solution, pH of the aqueous solution also varies depending on the intended end use of the aqueous solution. The pH of the aqueous solution is adjusted, when necessary, to the desired level by the addition of an acid or base. Preferably, the pH is adjusted using a dilute acid or base, e.g., dilute hydrochloric acid or dilute sodium hydroxide, respectively. The crosslinking studies were conducted at different pH values. The pH aqueous solution has been adjusted from 6 to about 10.

3.9 The Effect of Shear Rate

The shear rate is the relative velocity of the stationary bob and rotating cup divided by the gap distance. The apparent viscosity is an indication of flow resistance. It changes for different values of shear rate and is given in Pascal second (Pa.s); different shear rates were selected ranged from 300 to 1000 sec⁻¹.

3.10 The Effect of Time

After the hydratable polymer and the water base have been mixed for a time sufficient to form a hydrated gel, a quantity of the cross-linking system is mixed with the hydrated gel, and the apparent viscosity is an indication of flow resistance. It changes for different timesto study a degradation pattern and is given in pascal second (Pa.s).

3.11 The Effect of Temperature

The temperature was changed by heating the water through plate to desire temperature, and the range from 10 to 80 degree C were used.

3.12 Instrument for Rheological Measurements (Viscometer)

In this experiments work, the dynamic rheological measurements were conducted using a. R 180 rheometer with concentric cylinder. The measuring bob radius and its viscosities range in which follow table, the bob radius 2 were used according to ISO standard 2555.

Table 3.3 Measurement system following ISO standard 2555, Rotational speed range: 5 to 1000 min⁻¹.

(Operating instructions, proRheo R 180)

System no.	Bob no.	Viscosity (Pa.s)
61	1	0.01-260
62	2	0.02-105
63	3	0.05-265
64	4	0.1-530
65	5	0.2-1060
66	6	0.4-2650
67	7	1.5-10.600



Fig 3.11 ProRheo R180 Viscometer