CHAPTER IV

RESULTS AND DISCUSSIONS

4.1Introduction

This chapter, encompass two parts: part one includes samples analysis and treatment by natural zeolites; while through part two, the effect of temperature, and shearrate sand thepH on hydraulic fracturing fluids properties were investigated. The experimental results have been graphically presented, analysed, and discussed.

4.2 Water Samples Analysis

As discussed previously, the sample has been taken from two different ponds; the first Pond presents the water before any treatment in the field, while the second pond presents the water after the final field treatments with bioremediation project. Table 4.1 presents the summary of the water analysis results for the two samples; which have been measured in both Sudan and German. Although the water samples were selected from the same unit at different times, it was observed that there is a different in the measured values for the metals contents. The results showed a decrease in the total dissolved TDS and TSS value, while high value of sodium and a bit increase in silica and iron.

Table 4.1 Physical and Chemical Properties of Water Sample

Parameters	Raw water mg/l	Treated water mg/l	Acceptable range mg/l	Comments
First Tests (Sudan)				
pH	8.9 - 9.5	8.3-8.6	6-8	Hydration
Oil &grease	250-300	30-50	Zero	Fluid stability
Total dissolved solids (TDS)	2662	3217	300	Hydration
Total suspended solids (TSS)	982	378	Zero	Well plugging
Conductivity (μmhos/cm)	2.7	3.2	-	-
Chloride	20	14	<2-00	Fluid stability
Sodium	575	678	Zero	Scaling
Silica	11.8	11.8	<1	Crossling

Potassium	12.77	14.03	Zero	Scaling
Calcium	7.193	8.190	Zero	Scaling
Heavy Metals(ppm)				
Aluminium (Al)	21.6	0.2871	-	-
Cadmium (Cd)	<0.0009	<0.0009	-	-
Chromium (Cr)	0.0158	<0.0013	-	-
Copper (Cu)	0.0249	0.0249	-	-
Cobalt (Co)	0.0013	0.0013	-	-
Iron (Fe)	12.17	12.17	Zero	Crossling/ hydration
Lead (Pb)	<0.0150	<0.0150	-	-
Manganese (Mn)	0.1052	0.0049	-	-
Nickel (Ni)	0.0155	0.0127	-	-
Zinc (Zn)	0.0660	0.0474	-	-
Boron (Br)	0.01	0.01	Zero	Scaling
Mercury (Hg)	ND	ND	-	-
Phosphorus	<0.001	ND	-	-
Cadmium (Cd)	ND	ND	-	-
Parameters	Raw water mg/l	Treated water mg/l	Acceptable range mg/l	Comments
Second Tests (Germany)				
Conductivity(ms/cm)	2.02	2.56	-	-
Total suspended solids	752	188	Zero	Well plugging
Chloride	29	19	<200	Fluid stability
Silica	17.4	17.4	<1	Crossling
Sodium	520	580	Zero	Scaling
Potassium	12.77	14.03	Zero	Scaling
Calcium	5.2	6.12	Zero	Scaling
Magnesium	1.1	2.3	Zero	Scaling
Hardness	0.175mmole/l	-	Zero	Scaling
Hydrocarbon	6.6	-	-	-
Carbonate	25 mmole/l	-	-	-
Heavy Metals(Ppm)				
Iron (Fe)	19.18	19.18	Zero	Crossli/ hydration

4.3   Zeolites Characterizations

4.3.1   X-Ray Diffraction

The main peaks of the Zeolites for sample 1 (ZN1) were observed at three points: 9.9˚, 22˚and 29.8˚ attributed to type called "STILBITE "the XRD pattern of the sample is presented in Fig (4.1), and themolecular sieve has typical structure with microporous structure, it has Crystal system Monoclinic.

The main peaks of the Zeolites for sample 1(ZN2) were observed at three points: 9.7˚, 19˚ and 21.8˚, attributed to type called "STELLERITE" the XRD pattern of the sample is presented in Fig (4.2), and themolecular sieve has typical structure with microporous structure it has Crystal system Orthorhombic.

4.3.2   Infrared Spectroscopy

Bands around 439 to 442 cm^{-1} showed Si-Al-O, zeolite framework, stretches around 698 and 102 cm^{-1}, OH group was observed at 3448 cm^{-1} in Fig (1) and 3568 cm^{-1} in Fig (2), NH$_4$ group in Fig (2) observed in 1402 cm^{-1}, because it converted to be NH$_4$-zeolite by immersing the zeolite in NH$_4$Cl overnight, 1645 to 1647 cm^{-1} attributed to the typical of observed H$_2$O.
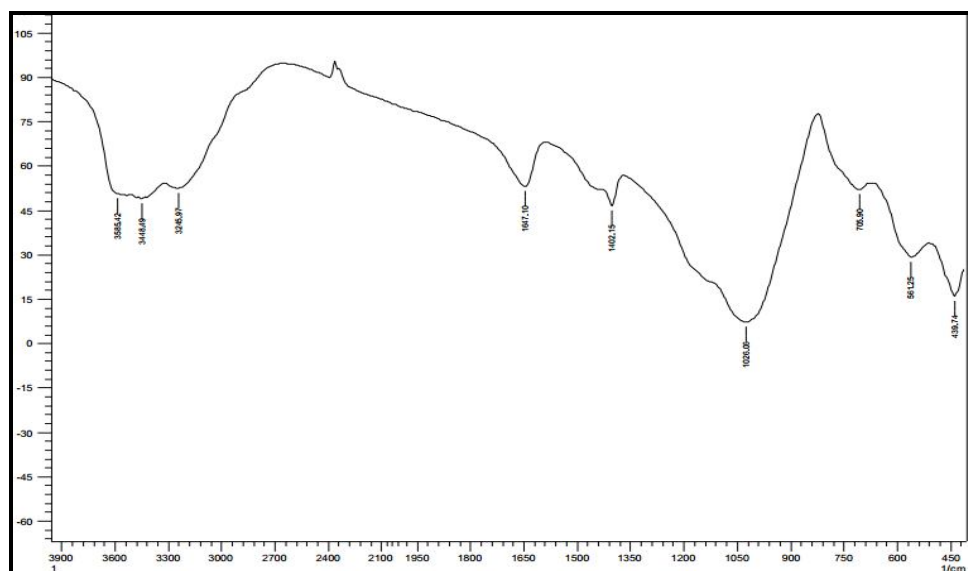

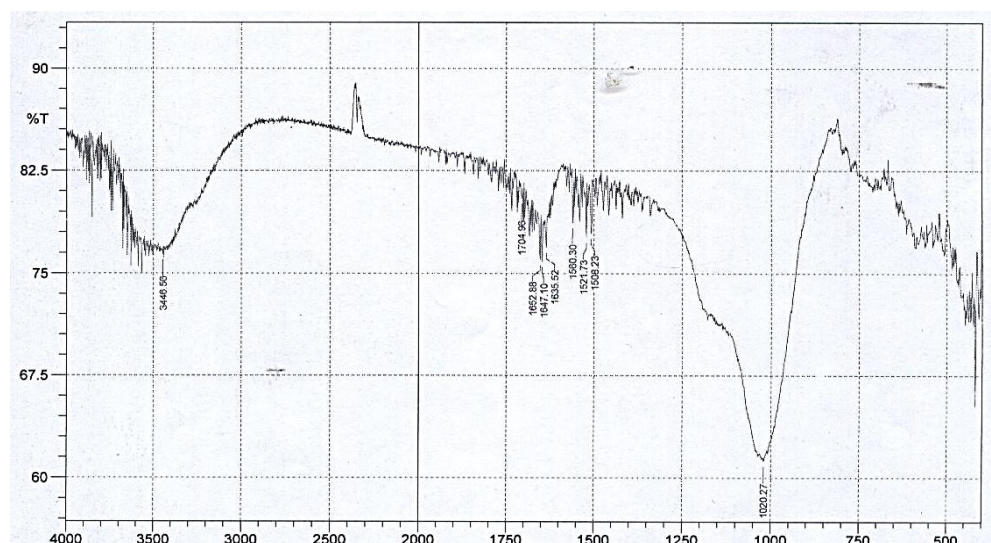**Fig 4.1 IR Spectra of ZeoliteSample 1 (ZN1)**

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Fig 4.2 IR Spectra of NH4-Zeolitesample 2 (ZN2)

4.3.3   X-ray Fluorescence

In order to characterize the WADKALLY natural zeolite X-ray fluorescence method was used as presented previously. The obtained results from chemical analysis of the samples are shown through Table (4.2) and (4.3) respectively. This study showed that natural zeolites1 contained a complement of exchangeable sodium, and calcium ions. The zeolite contained high percentage of SiO_2, followed by Al_2O_3, CaO, and negligible percentage of Na_2O, MgO, and Fe_2O_3. While natural zeolite 2 relatively has the same results expect has very low MgO value.

Table 4.2 Chemical and Physical Composition of Natural Zeolitesample 1 (ZN1)

Component	%
SiO_2	62.94
Al_2O_3	19.81
CaO	9.12
MgO	2.71
NaO_2	2.12
Fe_2O_3	2.28

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Table 4.3 Chemical and Physical Composition of Natural Zeolitesample 2 (ZN2)

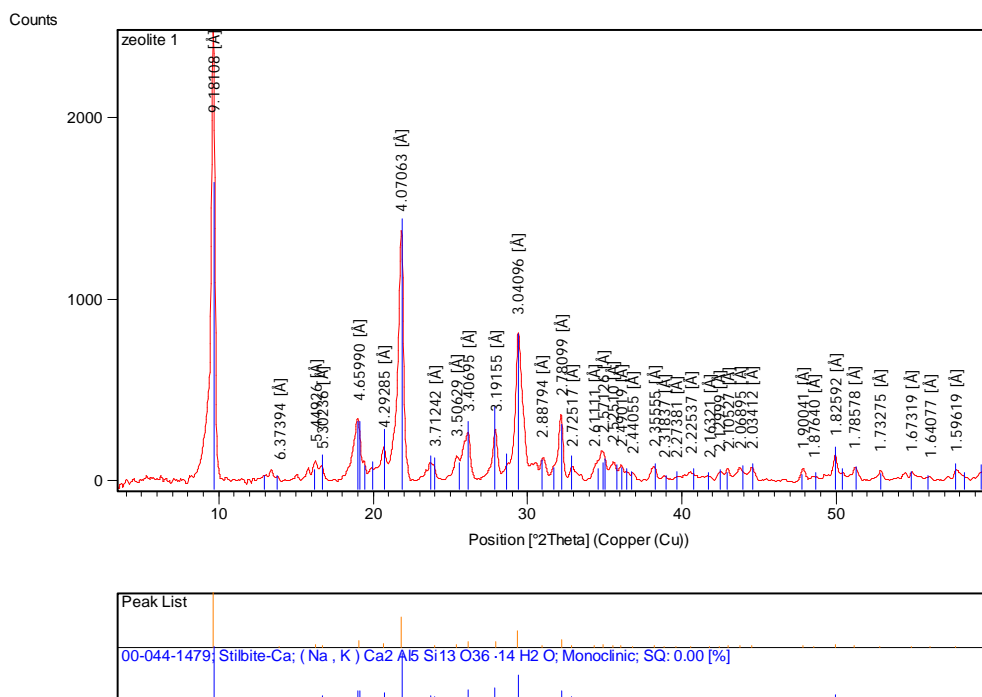| Component	%
SiO$_2$	64.36
Al$_2$O$_3$	21.74
CaO	10.16
MgO	0.929
NaO$_2$	1.482
Fe$_2$O$_3$	0.597

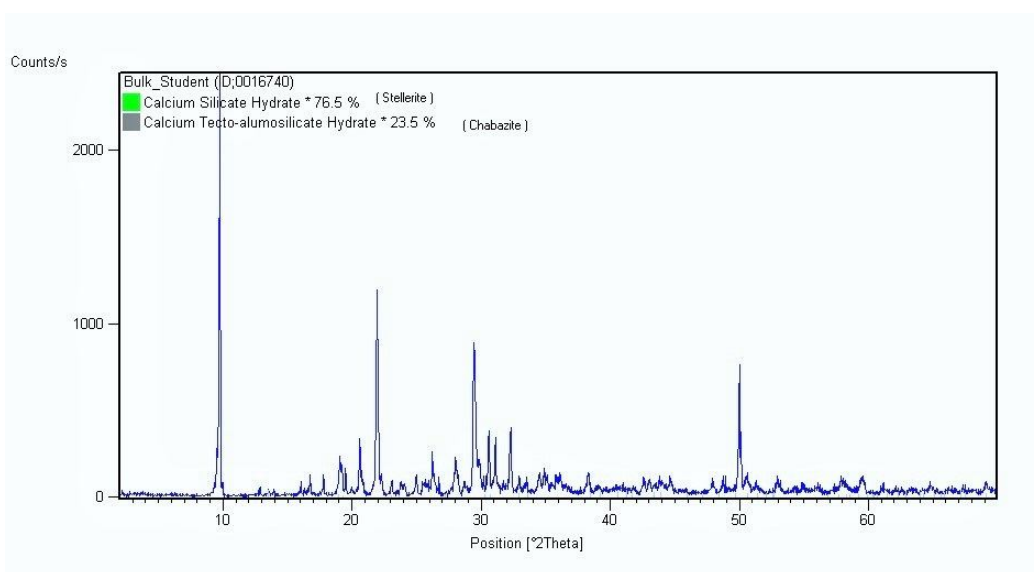**Fig 4.3 XRD Pattern of ZeoliteSample 1 (ZN1)**

Fig 4.4 XRD Pattern of ZeoliteSample 2 (ZN2)

4.4   Metals Adsorption on Natural Zeolites

4.4.1   Iron Removal with Na-Zeolite

Table (4.4) presented the effect of iron adsorptionon water conductivity; the decrement of the water conductivity after the treatment ensure that iron cations was removed from the water with the two type of zeolite;so it is possible to use the two types of zeolite for removing iron. The following Tables represent adsorption capacity using the two types of zeolite and their proportion. As can be seen from Table (4.5) no adsorption on zeolitesample No.1 (ZN1) was observed at pH less than 3.0. Additionally, the color of the zeolite at below pH 3.0 changed to an orange, which is a strong evidence for the precipitation of iron hydroxide/oxide. During adjustment of the pH to 3, a slight opacification occurred, which was already due to beginning precipitation of iron. However, Table (4.6) presented an opposite results with ZN2.

Table: 4.4 The Effect of Iron Adsorption on Water Conductivity

Zeolite Type	pH		Conductivity	
	Initially	After Treatment	Initially	After Treatment
zeolite 1 ZN1	8.77	n.d.	2.04	2.01
zeolite 2ZN2	8.77	n.d.	2.04	2.02

Table: 4.5 Adsorption Rates of Iron on Na-Zeolite 1(ZN1)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration before ZN1 treatment mg/l	Concentration after zeolite treatment mg/l	% adsorption on ZN1
Element: Iron	1	4.790	1.050	78.07
	2	4.660	1.003	78.74
	3	4.560	2.454	46.18
	4	4.233	4.231	0.047
	5	3.232	3.148	0.026
	6	3.212	3.211	0.0311
	7	2.254	2.002	11.18
	8	2.102	2.000	4.850
	9	3.121	3.111	0.320

Table: 4.6 Adsorption Rates of Iron on Na-Zeolite2(ZN2)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration before ZN2 treatment	Concentration after ZN2	%Adsorption on ZN2
Element: **Iron**	1	5.23	0.023	99.5
	2	5.07	0.802	84.1
	3	6.25	1.23	80.3
	4	5.69	1.08	81.0
	5	4.98	2.56	48.6
	6	4.97	2.01	59.6
	7	4.54	1.09	76.0
	8	4.02	2.07	48.5
	9	3.55	2.00	43.7

4.5 Adsorption Results with NH₄- Zeolites

4.5.1   Synthetic Solution

The efficiency of the ion exchange processes for different metal ions depends on the size and charge of cations as well as the zeolite structure [Inglezakisetal, 2002] However, the pH value is a significant parameter for metal ions removal using zeolite as it can influence the characteristic of the exchangeable ions and of the zeolite [Santos et al, 1989].

The metal ions removal from synthetic solution at pH of: 1, 2, 3, 4, 5, 6, 7, 8 and 9 values were presented through Fig. (4.5) and Fig (4.6); whileFig (4.7) and Fig (4.8) presented the iron removal from produced water.

It was observed that the amount of metal ions adsorbed by studied ZN1and ZN2 is dependent of pH, and increases with the decrement of the solution pH.Fig. (4.5) presented that the higher removal of metal ions achieved at pH equal to 1 forboth ZN1 and ZN2; the figure presented that, calcium and magnesium ions were removed by 70% and 50% respectively, while approximately about 50% of the other ions such as potassium and sodium were removed at pH value of 1 usingZN1; lower removal for sodium was achieved at pH 3, 4, and 9; while low removal for potassium was achieved at pH 4, 5 and 6.
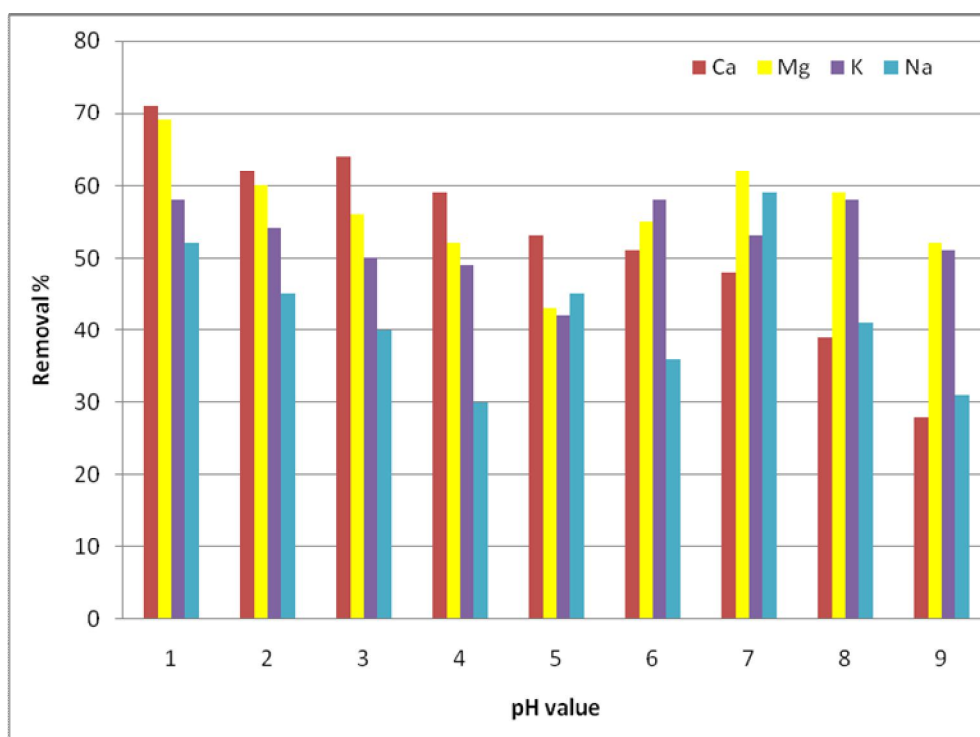
Fig 4.5 Metal Ions Removal from Synthetic Solution at pH Values for Zeolite1 (ZN1)
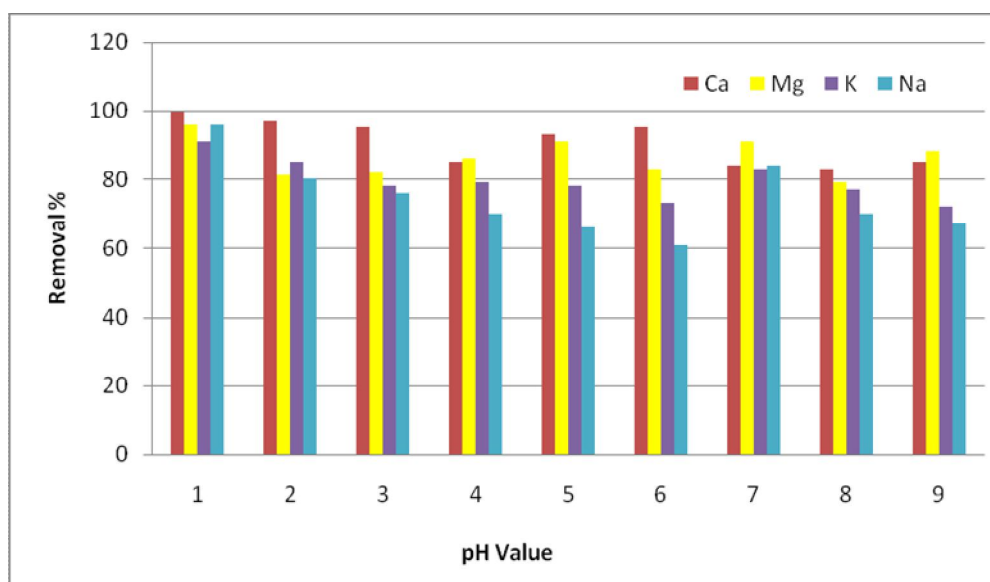

Fig 4.6 Metal Ions Removal from Synthetic Solution at pH ValuesZeolite 2 (ZN2)

For ZN2 the results were presented in Fig 4.6, at pH 1the removal of calcium, sodium, magnesium and potassium are almost 100%, 95%, 92% and 80% removed respectively. This result suggests that there is no competition between protons and those ions for zeolite sites; at pH equal to 2, the removal of irons was achieved 90% for Calcium and more than 70% for

other ions; Magnesium has similar value at pHequal to 1 and 7; while Calcium generally has approximately more than 80% irons removal for all pH values. In contrast, the lowest removal for Potassium and Sodium ions was obtained at pH equal to 5 and 6; this is due to the effect of competition with H+.

4.5.2   Produced Water (Untreated Sample)

The results obtained for produced water and synthetic solution at pH equal to 1 are shown in Table 4.15. It can be observed that, the metal ions removal was greater for Calcium and Magnesium ions. The removal of Sodium and Potassium ions is about more than80% for the same pH. Investigations with the produced water at pH 2 to 9 were carried out, despite, data experimental obtained from synthetic solutions showed a better metal ions removal at pH 1for ZN1and ZN2. From The comparative results between synthetic solution and produced water are shown in Table 4.18. It can be observed that zeolite (ZN2) has a greater efficiency for the metal ions removal from synthetic solution. This can be attributed to the matrix effect from produced water, due to presence of several dissolved solutes, which increase the ionic strength from solution as well the ions competition by the zeolite adsorption sites.

Table: 4.7Adsorption of Calcium on NH$_4$-Zeolite1 (ZN1)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN1
Element Ca 50 mg/l	1.00	0.4104	0.2011	50
	2.00	0.4020	0.1958	51
	3.00	0.2409	0.1002	58
	4.00	0.2378	0.1103	54
	5.00	0.2370	0.1350	43
	6.00	0.2210	0.1112	49
	7.00	0.3120	0.1991	36
	8.00	0.1650	0.1214	24
	9.00	0.1600	0.1363	14

Table: 4.8 Adsorption of Calcium on NH4-Zeolite2 (ZN2)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN2
Element Ca 50 mg/l	1.00	0.4104	0.0013	99.6
	2.00	0.4020	0.0224	94
	3.00	0.2409	0.0231	90
	4.00	0.2378	0.0657	72
	5.00	0.2370	0.0312	87
	6.00	0.2210	0.0220	90
	7.00	0.3120	0.1120	64
	8.00	0.1650	0.0110	93
	9.00	0.1600	0.0033	98

Table 4.9 Adsorption of Magnesium on NH4-Zeolite1 (ZN1)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN1
Element Mg50 mg/l	1.00	0.3524	0.1610	54
	2.00	0.3557	0.1504	58
	3.00	0.3598	0.2336	35
	4.00	0.3599	0.1932	46
	5.00	0.3613	0.2223	38
	6.00	0.3554	0.1765	50
	7.00	0.3525	0.1699	52
	8.00	0.3583	0.1766	51
	9.00	0.3592	0.1898	47

Table 4.10 Adsorption of Magnesium on NH4-Zeolite2 (ZN2)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN2
	1.00	0.3524	0.0235	93
	2.00	0.3557	0.1033	71
	3.00	0.3598	0.1354	62
	4.00	0.3599	0.1169	68
Element Mg50 mg/l	5.00	0.3613	0.1033	71
	6.00	0.3554	0.1265	64
	7.00	0.3525	0.0334	91
	8.00	0.3583	0.1115	69
	9.00	0.3592	0.1121	69

Table 4.11 Adsorption of Potassium on NH4-Zeolite1 (ZN1)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN1
	1.00	1.8627	0.7621	59
	2.00	1.844	0.9652	48
	3.00	1.6342	0.8551	48
	4.00	1.599	0.9643	40
Element K 50 mg/l	5.00	1.4582	0.9212	37
	6.00	1.4461	0.8896	39
	7.00	1.4282	0.8351	42
	8.00	1.3911	0.6545	53
	9.00	1.3867	0.6544	53

Table 4.12 Adsorption of Potassium on NH4-Zeolite2 (ZN2)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN2
	1.00	1.8627	0.3562	81
	2.00	1.844	0.465	75
	3.00	1.6342	0.455	72
	4.00	1.599	0.364	77
Element K 50 mg/l	5.00	1.4582	0.4621	68
	6.00	1.446	0.389	73
	7.00	1.4282	0.5351	63
	8.00	1.3911	0.454	67
	9.00	1.3867	0.554	60

Table 4.13 Adsorption of Sodium on NH4-Zeolite1 (ZN1)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN1
	1.00	0.4781	0.2624	45
	2.00	0.4822	0.3254	33
	3.00	0.4661	0.3662	21
	4.00	0.4888	0.3998	20
Element Na 50 mg/l	5.00	0.4853	0.3214	34
	6.00	0.4791	0.3456	28
	7.00	0.4686	0.2001	57
	8.00	0.4669	0.3211	31
	9.00	0.4635	0.3666	21

Table 4.14 Adsorption of Sodium on NH4-Zeolite2(ZN2)

Dilution: 1:100 Resulting In 0.5 Mg/L Maximum	pH	Concentration Before ZN1 Treatment Mg/L	Concentration After Zeolite Treatment Mg/L	% Adsorption On ZN2
	1.00	0.4781	0.0228	95
	2.00	0.4822	0.1003	79
	3.00	0.4661	0.1364	71
	4.00	0.4888	0.1658	66
Element Na50 mg/l	5.00	0.4853	0.2114	56
	6.00	0.4791	0.2331	51
	7.00	0.4686	0.1225	74
	8.00	0.4669	0.1854	60
	9.00	0.4635	0.1993	57

4.6 Study of pH Effect on Adsorption Capacity

The efficiency of the ion exchange processes for different metal ions depends on the size and charge of cations as well as the zeolite structure [Inglezakisetal, 2002] However, the pH value is a significant parameter for metal ions removal by zeolite as well as it can influence the characteristic of the exchangeable ions and of the zeolite [Santos et al, 1989].

It was observed that the amount of metal ions adsorbed by ZN1and ZN2studied is dependent of pH, and which increases with decrease of pH solution. Presented thatin Fig. 4.7 the higher removal for metal ions achieved at pH 1 for ZN1 and ZN2 which indicate that calcium and magnesium ions were removed by almost 70% and 50% respectively, while for other ions such as potassium and sodium was around 50% at value of pH 1by ZN1. Lowest removal for Na at pH 3, 4, 9 and at pH 4, 5, 6 for potassium.

For ZN2 the results were presented in Fig 4.8, at pH 1the removal of calcium, sodium, magnesium and potassium are almost 100%, 95%, 92% and 80% respectively. This result suggests that there is no competition between protons and those ions for zeolite sites.at pH2 the removal almost 90% for calcium and more than 70% for other ions. Magnesium has similar value at pH1, 7 calcium generally has approximately more than 80% for all pH values.

In contrast, the lowest removal for potassium and sodium ions was obtained at pH 5 and 6, probably due to the effect of competition with H^+.

Table 4.15 Metal Ions Removal for the Synthetic Solution and Produced Water Sample at pH1.0

Metals / Samples	Ca	Mg	K	Na
Synthetic solution (ZN1)	71	69	58	52
Synthetic solution (ZN2)	99.8	96	91	96
Produced water (ZN1)	50	54	59	45
Produced water (ZN2)	99.6	93	81	95
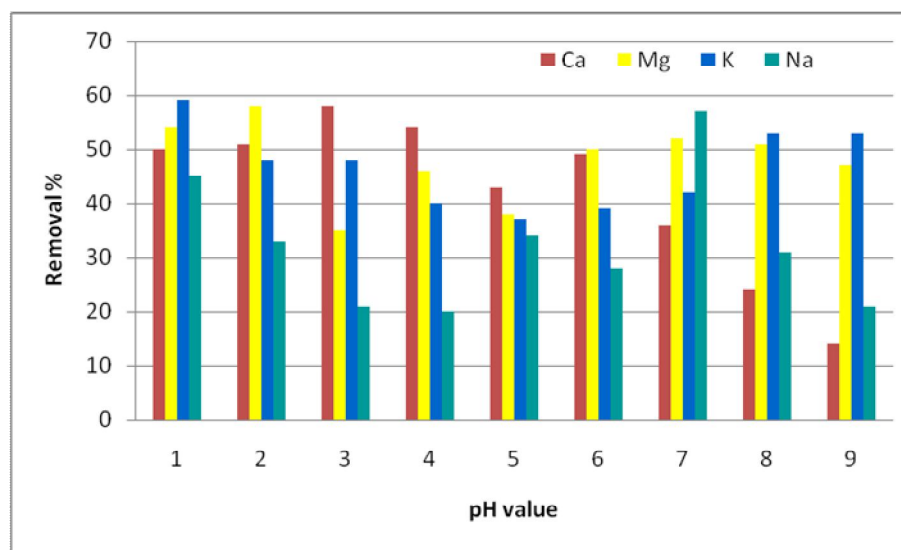
Fig 4.7 Metal Ions Removal from Produced Water at Different pH (ZN1)
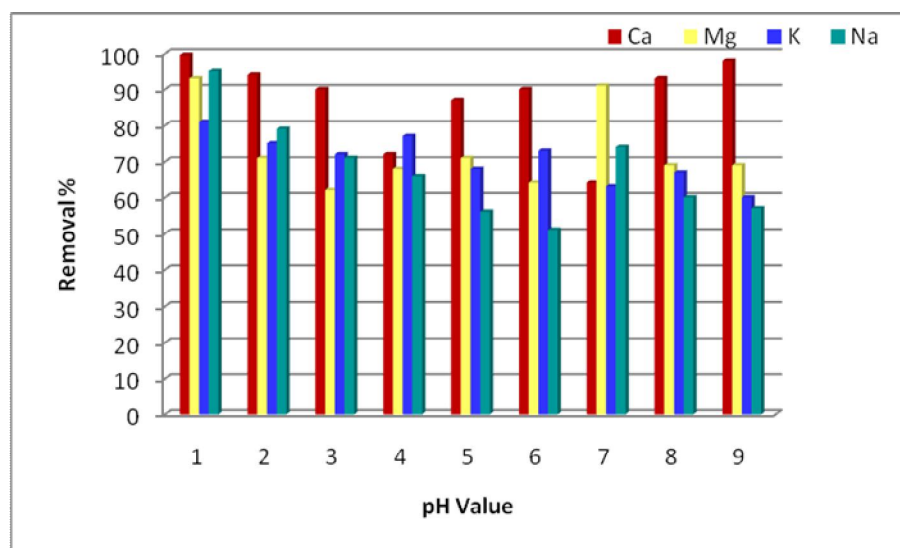
Fig 4.8 Metal Ions Removal from Produced Water at Different pH (ZN2)

4.7 **Fracturing Fluid Rheology at Different Conditions**:

The fracturing fluid was formulated with oilfield produced water before and after treatment. The rheological properties of fracturing fluid tested are evaluated at various expected treating temperatures, shear rates and pH. A viscosity performance of cross linked-HEC, CMHEC designed with typical oilfield produced formation water at temperature range of 10 to 80°C and shear rates range of 300 to 1000 sec^{-1} the results are reported which follow.

4.7.1 Fluid Stability with Time

The first test was conducted from 10 to 120 minutes to study the effect of the time in formulation started with HEC linear polymer and four types of water sample were used**.** The results showed that more stability was achieved with samples without metals. The same procedures were repeated for CMHEC the results are which follow.

Table 4.16   Fluid Stability with Time

Time (min)	Viscosity (Pa.s) untreated sample	Viscosity (Pa.s) treated sample	Viscosity (Pa.s) treated sample by natural zeolite	Viscosity (Pa.s) deionized water sample
10	0.536	0.469	0.698	0.723
20	0.324	0.402	0.6	0.659
30	0.339	0.339	0.577	0.612
40	0.222	0.3	0.532	0.555
50	0.222	0.296	0.486	0.513
60	0.277	0.277	0.425	0.426
70	0.288	0.233	0.363	0.375
80	0.288	0.201	0.342	0.346
90	0.233	0.156	0.326	0.33
100	0.111	0.133	0.304	0.318
110	0.111	0.133	0.283	0.288
120	0.111	0.133	0.271	0.277
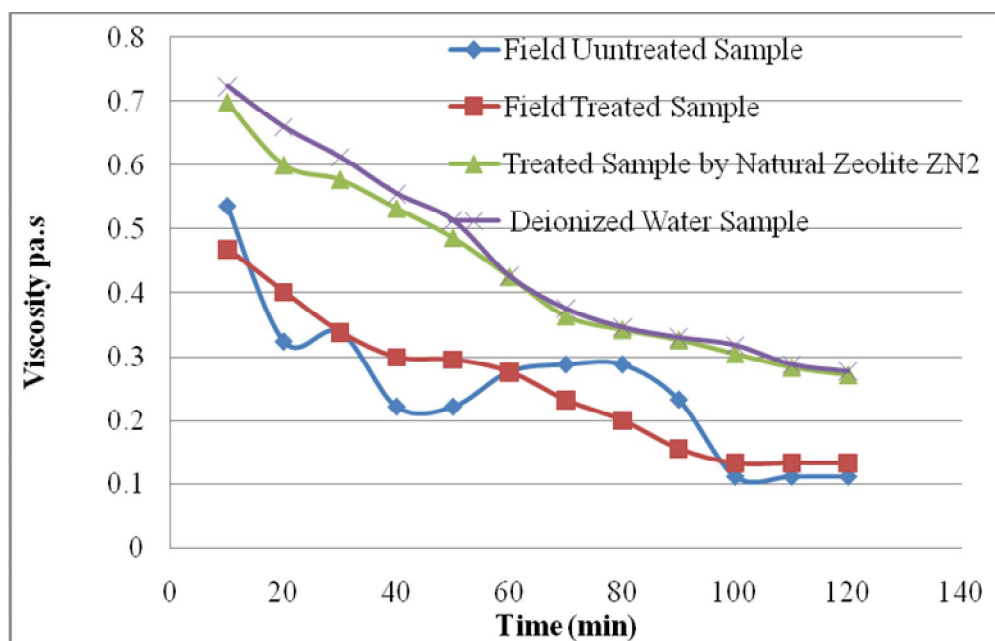
Fig 4.9 Rheology Studies of 5g HEC Using Four Samples of Water, Ph7.2, Ambient Temperature and 300sec^{-1}
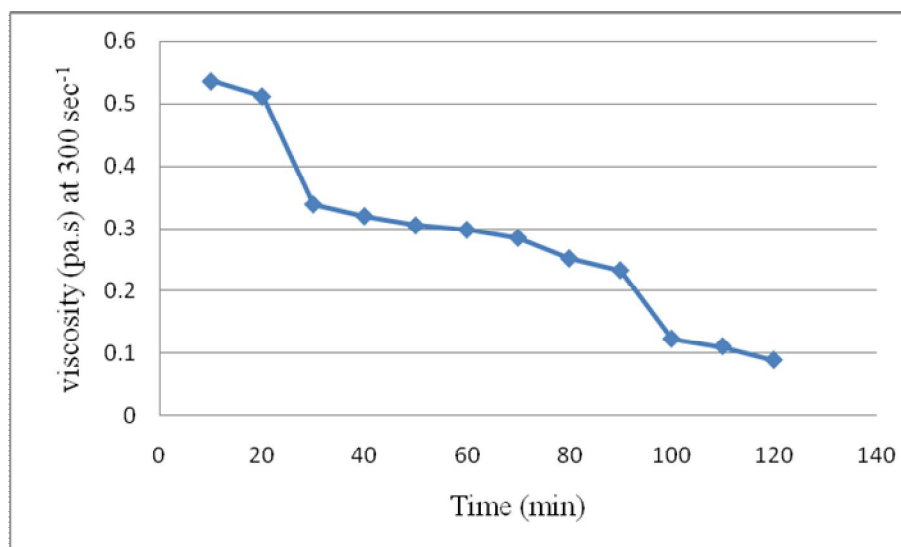
Fig 4.10 Rheology Study of HEC at Ambient Temperature and 300/Sec^{-1} 100% Untreated Formation Water, pH 8.5

4.7.2   Effect of HEC Concentrations at Different Temperature
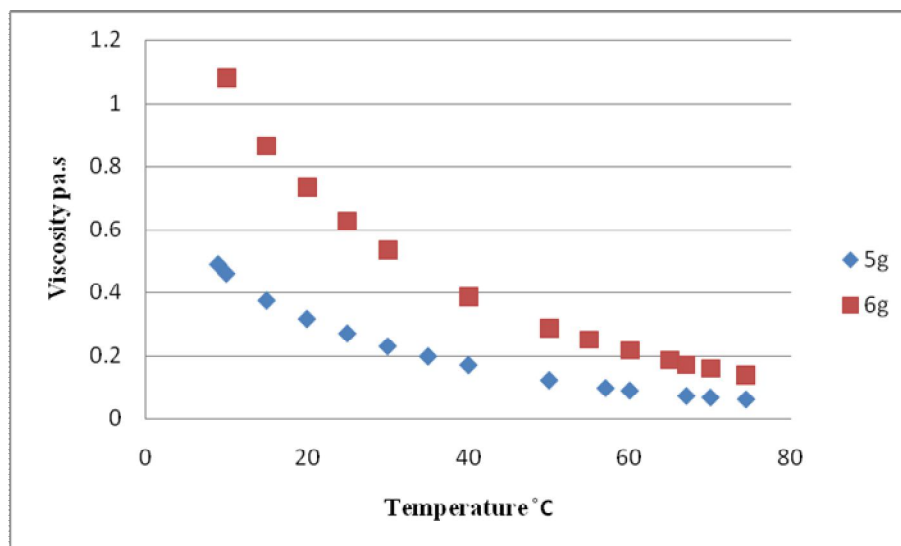
Fig 4.11 HEC Viscosity at Different Temperature without Cross-linker
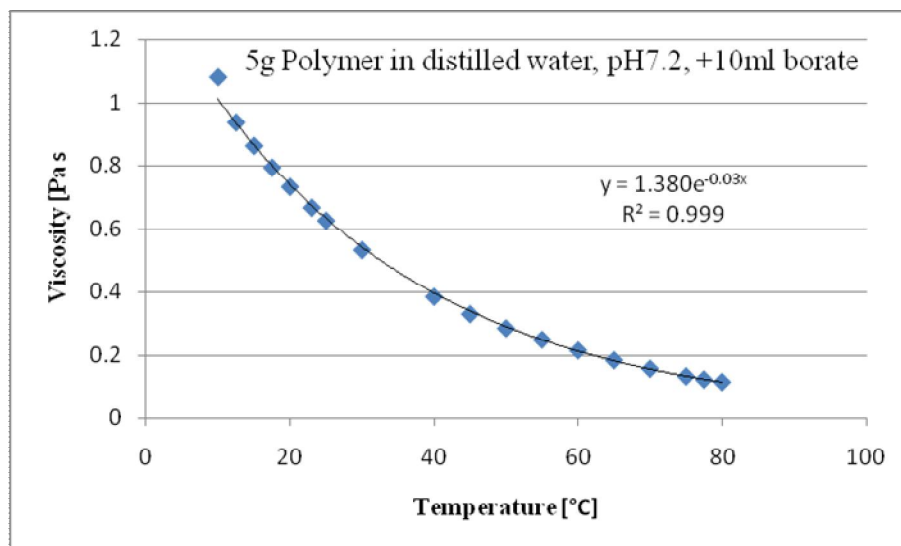
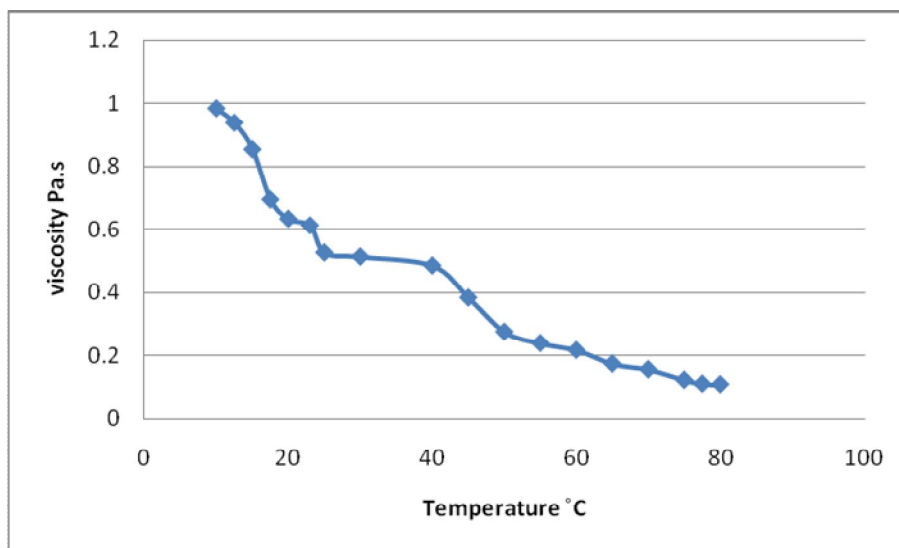**Fig 4.12The Effect of Cross-linker on HEC at Different Temperature**

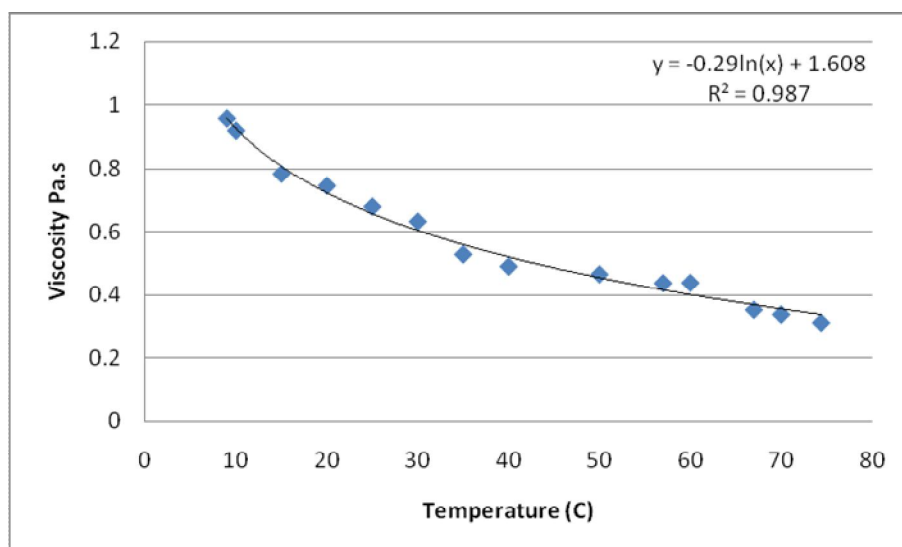**Fig 4.13: The Of Effect of Crosslinked on HEC at Different Temperature Using Treated Water by Natural Zeolite2**

The plotted trendline equation shows $y = -0.29\ln(x) + 1.608$ with $R^2 = 0.987$. Axes: Viscosity Pa.s (y-axis) versus Temperature (C) (x-axis).

Fig 4.14: The of Effect of Cross-linker on CMHEC at Different Temperature Using Treated Water by Natural Zeolite2.

As can be seen that from Fig (4.8) and fig (4.9) and Fig (4.10) the same results were achieved and a bit different was observed. Fig (4.9) showed that increase in the viscosity by adding crosslink, however the same degradation with increasing temperature. So this result confirmed that HEC group it doesn't crosslink and has less thermal stability. It can be clear from fig CMHEC is more thermal stable than HEC.

4.7.3   Effect of pH On Fluid Formulation

The pH of polymer solution is very important for the cross-linker characteristics of any metals, some metal form effective cross-linked fluid over a wide range of pH.The experimental were conducted for different samples of water to study the effect of pH on gelling formulation.   The following Figures represent gelling formulation with HEC and CMHEC cellulose derivatives.

4.7.3.1   **With HEC**

Rheology plot of HEC with 100% of produced formation water (untreated sample) at ambient temperature is presented in table 4.10 and Fig. 4.4. The Figure revealed that the hydrated gel polymer at different pH. As can be clear from the figure higher viscosities were achieved with pH 6-8, while the results at pH10 better than pH9. Figure 4.5 and Table 4.11 are shown the results of 100% treated sample (site the field) there is no significant difference between two figurers, despite treated sample having low value of oil & grease.

Figure 4.6, Table 4.12 and Figure 4.7, Table4.13 rheology study of 100% treated sample by natural zeolite and deionized water sample respectively. As can be clear that there is significant increasing in the fluid viscosity and a bit stability at 2-h.
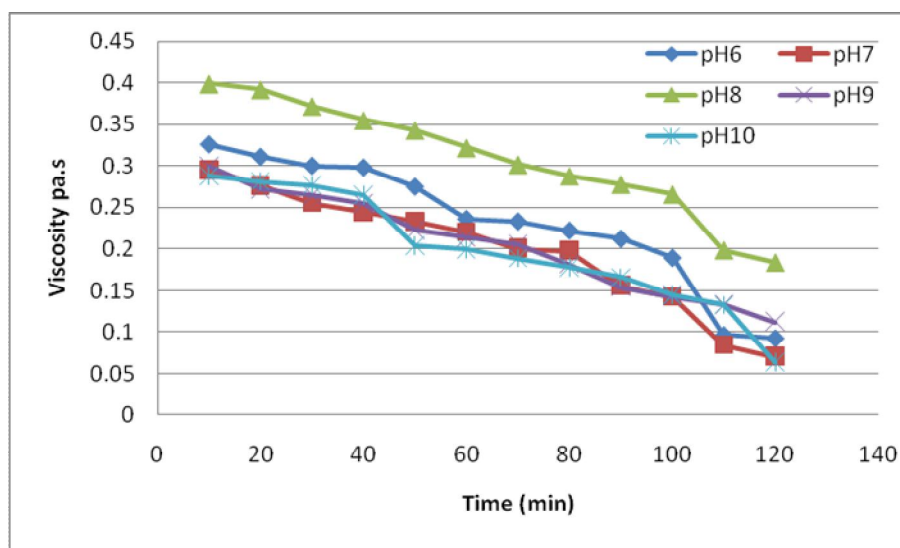
Fig 4.15 Rheology Study of HEC at Ambient Temperature and 300/Sec 100% Untreated Water
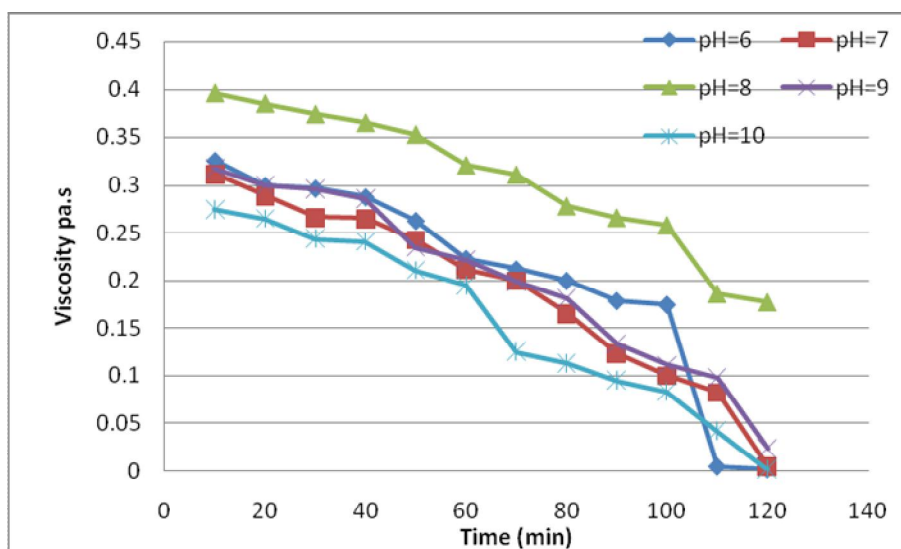
Fig 4.16 Rheology study of HEC at ambient temperature and 300/sec 100% treated water (on site the field)
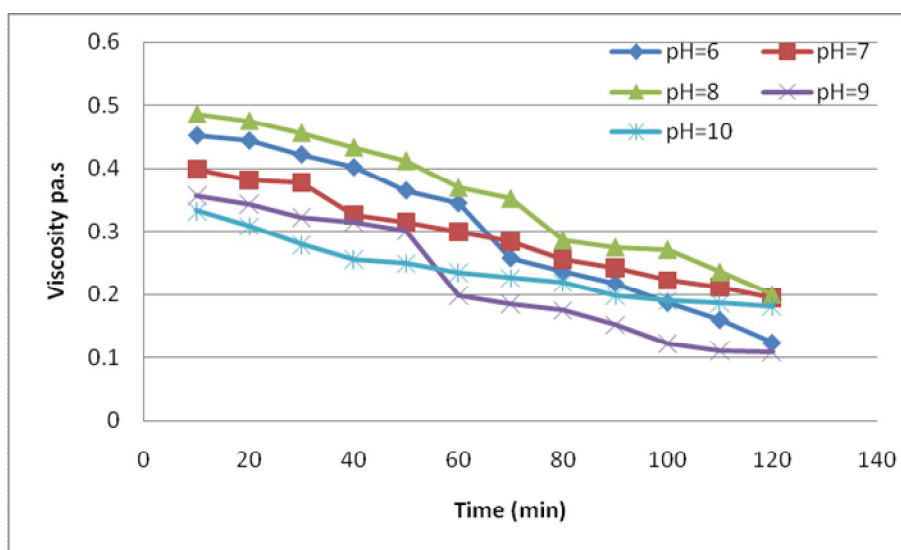

Fig 4.17 Rheology Study of HEC at Ambient Temperature and 300/Sec 100% Treated Water by Natural Zeolite2.
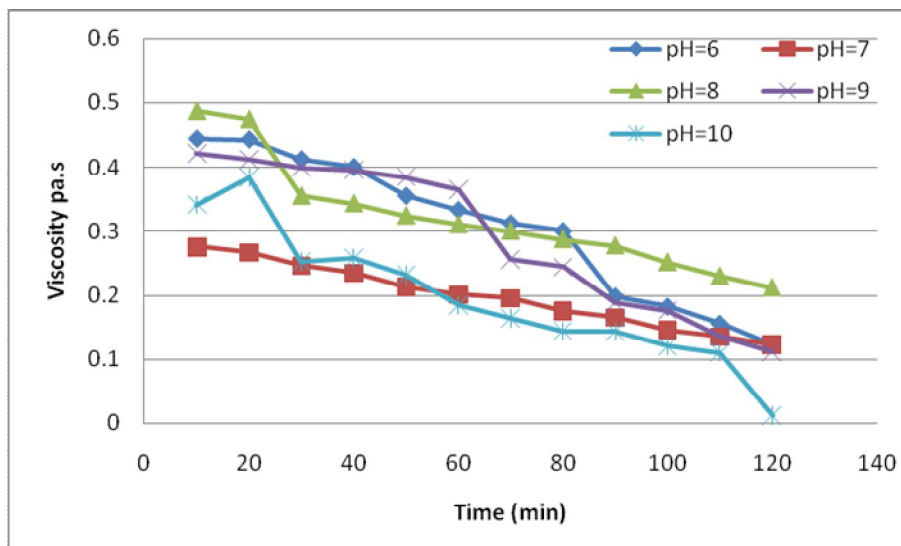
Fig 4.18 Rheology Study of HEC at Ambient Temperature and 300/Sec 100% Deionized Water

From the above tables and figures: The results of studying the effect of pH on viscosity and fluids formulation showed that higher viscosities were achieved at pH from 6 and 8. These values relatively high and the higher pH levels further contribute to better proppant handling.

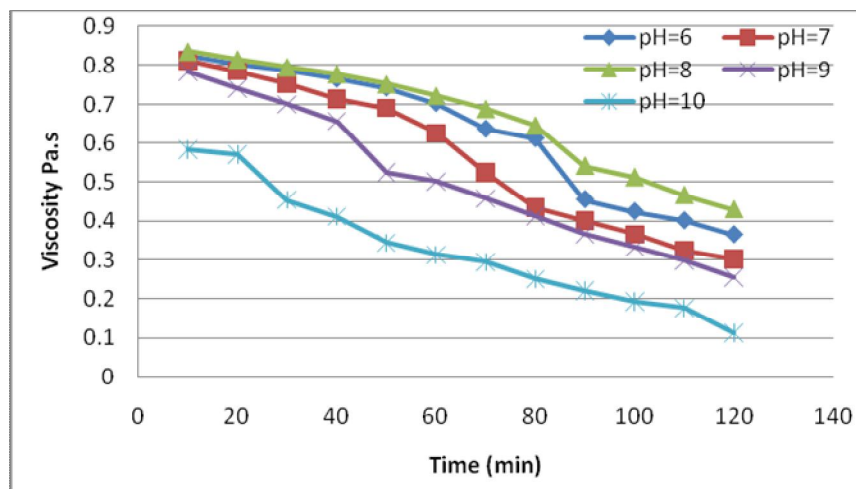**4.7.3.2   With Cross-linked**
**   CMHEC**

Fig 4.19 Rheology Study of Cross-linked CMHEC at Ambient Temperature and 300/Sec 100% Untreated Water.
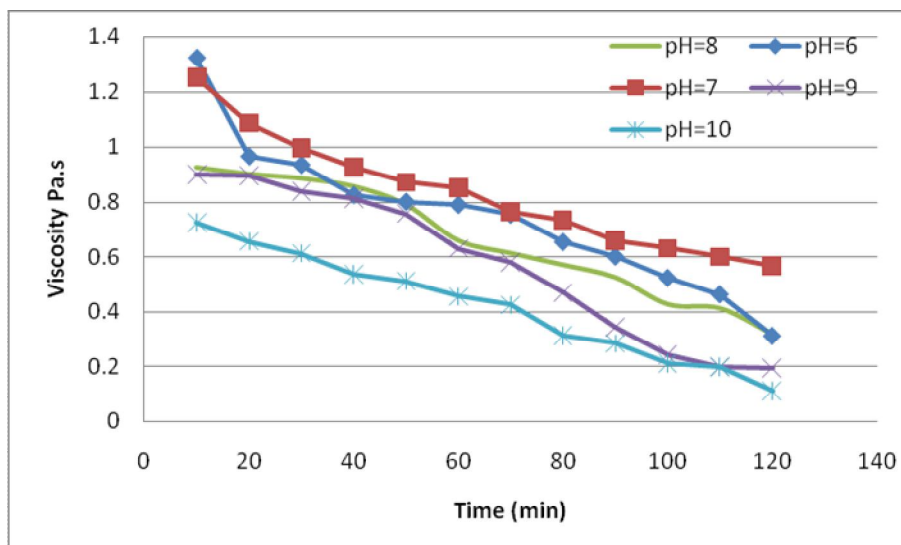
Fig 4.20 Rheology study of cross-linked CMHEC at ambient temperature and 300/sec 100% treated water (on site of the field)
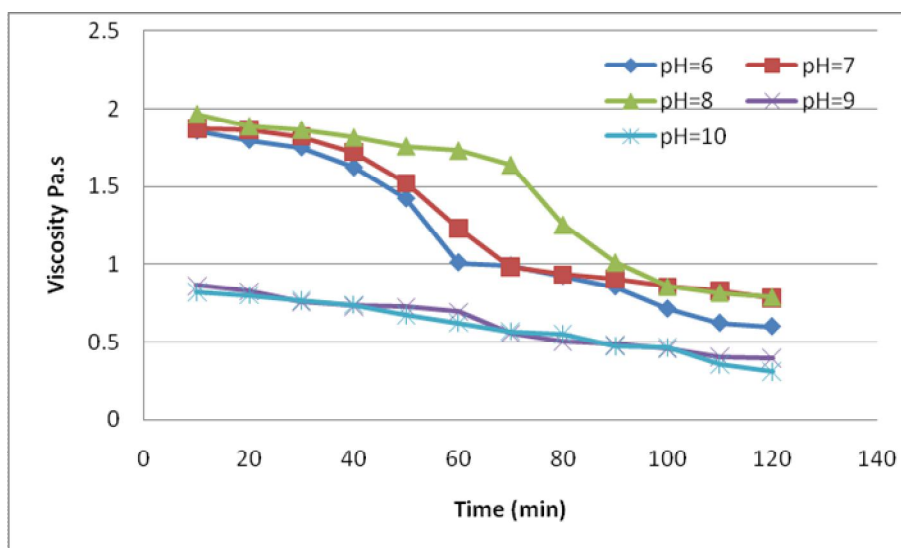

Fig 4.21 Rheology study of cross-linked CMHEC at ambient temperature and 300/sec 100% treated water by natural zeolite2 (ZN2).

As seen from Fig. 4.10, 4.11, 4.12 the fluids designed with cross-linked CMHEC to study fluid stability when tested over 2-h. The effect of the polymer was noticed on the fluids. The fluids formulated with three type of water samples and varied pH , as can be clear that for all cases the fluids were stable and degraded to below about 85-min.

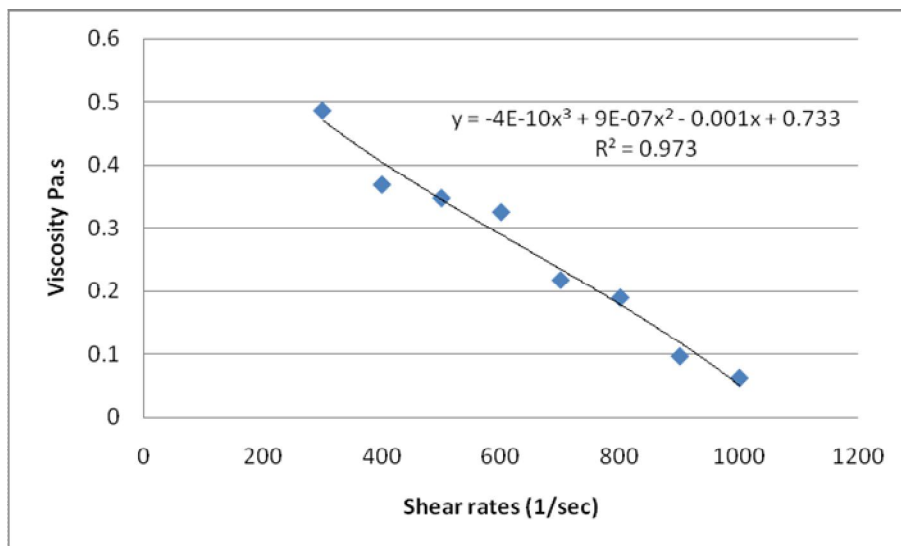**4.7.4**   **The Effect of Shear Rate**

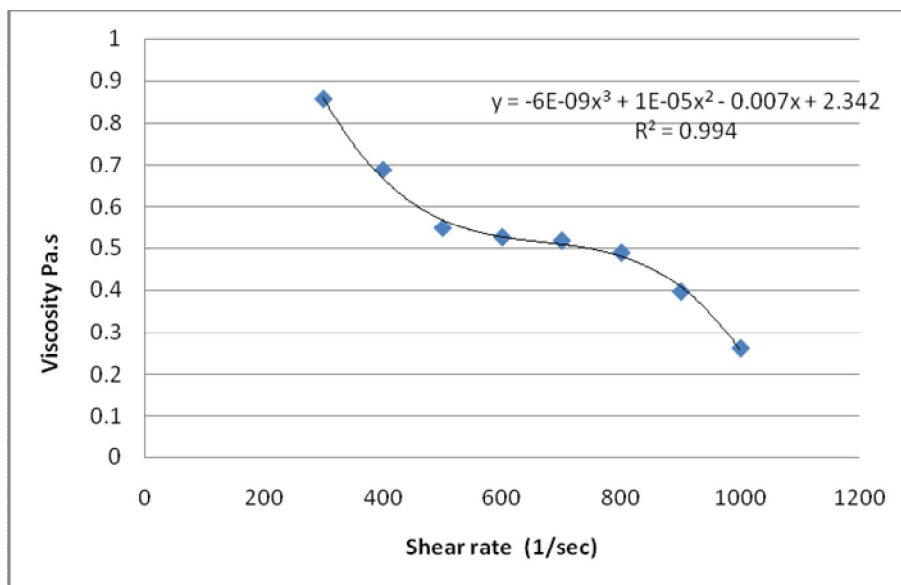The equation shown: $y = -4E{-}10x^3 + 9E{-}07x^2 - 0.001x + 0.733$, $R^2 = 0.973$

Fig 4.22: The Effect of Shear Rates at Ambient Temperature Using Treated Sample by Natural Zeolite and HEC, pH8.

The equation shown: $y = -6E{-}09x^3 + 1E{-}05x^2 - 0.007x + 2.342$, $R^2 = 0.994$

Fig4. 23: The Effect of Shear Rates at Ambient Temperature Using Treated Sample by Natural Zeolite and CMHEC, pH8.