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To cite this article: Mian Umer Shafiq *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **217** 012023

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Investigation of Changing Pore Topology and Porosity During Matrix Acidizing using Different Chelating Agents

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Abstract. Core flooding acidizing experiments on sandstone/carbonate formation are usually performed in the laboratory to observe different physical phenomena and to design acidizing stimulation jobs for the field. During the tests, some key parameters are analyzed such as pore volume required for breakthrough as well as pressure. Hydrochloric acid (HCl) is commonly used in the carbonate matrix acidizing while Mud acid (HF: HCl) is usually applied during the sandstone acidizing to remove damage around the well bore. However, many problems are associated with the application of these acids, such as fast reaction, corrosion and incompatibility of HCl with some minerals (illite). To overcome these problems, chelating agents (HEDTA, EDTA and GLDA) were used in this research. Colton tight sandstone and Guelph Dolomite core samples were used in this study. The experiments usually are defined in terms of porosity, permeability, dissolution and pore topology. Effluent samples were analyzed to determine dissolved iron, sodium, potassium, calcium and other positive ions using Inductively Coupled Plasma (ICP). Meanwhile Nuclear Magnetic Resonance (NMR) was employed to determine porosity and pore structure of the core sample. Core flood experiments on Berea sandstone cores and dolomite samples with dimensions of 1.5 in $\times$ 3 in were conducted at a flow rate of 1 cc/min under 150oF temperature. NMR and porosity analysis concluded that applied chemicals are effective in creating fresh pore spaces. ICP analysis concluded that HEDTA showed good ability to chelate calcium, sodium, magnesium, potassium and iron. It can be established from the analysis that HEDTA can increase more amount of permeability as compared to other chelates.
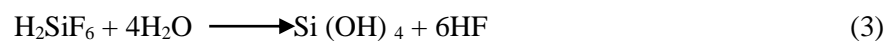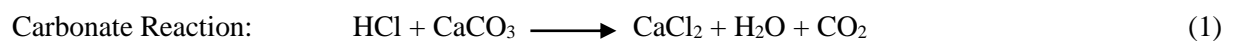
1. Introduction

Acids play a key role in boosting production or increasing injectivity in hydrocarbon fields. Aboud [1] predicted that 40% more energy resources will be required in 2020 than in the present because the world demand for energy is increasing. In order to fulfill this demand, acidizing of high temperature reservoirs gain importance because the new reserves explores are much deeper and hotter reservoirs [2]. In the process of acidizing, acids have been injected to react with sandstone and carbonate formations. The injection of different acids cause reaction of acids with the minerals present in the rock. Different minerals like quartz, carbonates and feldspar can be dissolved by the injection of acids, thus increasing the permeability of the reservoir around wellbore, which ultimately increases the flow rate of hydrocarbon fluid from to the wellbore [3] and [4, 5]. These reactions can cause dissolution of

rock matrix and formation of precipitates, which might bring about changes in the permeability and porosity of a reservoir. Therefore, the main goal of sandstone acidizing is to remove the formation damage while for carbonate is to create new wormholes [6].

The mixture of hydrofluoric acid (HF) and hydrochloric acid (HCl), known as mud acid [7] is normally applied during the sandstone acidizing process to remove the damage around the wellbore while hydrochloric acid has been injected to create new wormholes in case of carbonate acidizing. Sandstone formation has been acidized using mud acid by [7, 8] and hydrochloric acid has been applied on carbonate formation by [9, 10] to dissolve carbonates and other positive ions. Stimulating carbonate rocks typically involves a reaction between an acid and the minerals like calcite ($CaCO_3$) or dolomite $CaMg(CO_3)2$. The primary reaction of carbonate with acid is presented in equation 1 [11].

Carbonate Reaction: $HCl + CaCO_3 \longrightarrow CaCl_2 + H_2O + CO_2$ (1)

Sandstone reactions [12]: $SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$ (2)

$H_2SiF_6 + 4H_2O \longrightarrow Si(OH)_4 + 6HF$ (3)

However, using hydrochloric acid is not successful in some cases, even some field studies reported damages [11]. First is the presence HCl sensitive mineral of (illite), this may choke the pore throat and thus decreasing the permeability and porosity which is a serious issue. Secondly, corrosion rate is higher, also the reaction rate will be high at high-temperature conditions which may cause other problems like precipitation.

Because of mentioned problems faced using HCl acid, other approaches have been studied and used as an alternative to HCl acid in carbonate and sandstone acidizing. [13, 14] performed experimental study with different acid combinations, replacing conventional mud acid. HCl acid has been replaced with organic acid to acidize sandstone formation. Chunming [15] applied novel emulsified acid to acidize Chinese oil fields and discovered that the increase in permeability of oil saturated cores by 96.1% while by only 10.1% for water saturated cores. [12, 16] applied Organic-HF to overcome the problems faced during sandstone matrix acidizing. Different chelating agents have been used at high temperature conditions i.e., Hydroxyethylenediaminetetraacetic acid (HEDTA) and Ethylenediaminetetraacetic acid (EDTA) used at high temperature without the use of HF-containing fluids resulted in the increase of gas production. EDTA and HEDTA created wormholes at 400°F explained by [17] and discovered the significance of chelating agent Na_3HEDTA compared to mud acid. Various stimulating studies on sandstone formation using HEDTA chelating agent have been conducted at higher temperatures by [17, 18, 19] and showed its significance in increasing permeability compared to mud acid. [20] compared the use of different acids developed for sandstone acidizing. Slow reaction rate and less corrosivity have allowed the petroleum industry to apply formic and acetic acids for many years as alternatives to HCl in carbonate acidizing. The rapid HCl spending prevents deep penetration of acid into the formation [11].

The main aim of this study is to overcome the problems related to the presence hydrochloric acid. While the advantages of hydrochloric acid presented by McLeod [21] should be maintained. In this study different methods such porosity and NMR measurements and ICP analysis has been performed to monitor rock and fluid alterations at different stages of acidizing process. NMR analysis have been applied by [22] for the very first time on sandstone samples. This technique proved to be very useful in determining the pore space topology after acidizing.

2. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has proved its significance in different fields like chemistry, physics, and biomedicine. The same principle used in these fields can also be applied for the imaging of reservoir rock. "NMR logging is a subcategory of electromagnetic logging [23], that can measure the induced magnet moment of hydrogen nuclei (protons) contained within the fluid-filled pore space of porous media (reservoir rocks)". Conventional logging measurements respond to both rock matrix and fluid properties and are mineralogy dependent while NMR-logging respond to the presence of hydrogen protons. Information related to the quantities of fluids present, the properties of these fluids, and the sizes of the pores containing these fluids can be obtained using NMR analysis. From this information, it is possible to infer or estimate.

- The volume (porosity) and distribution (permeability) of the rock pore space
- Rock composition
- Type and quantity of fluid hydrocarbons
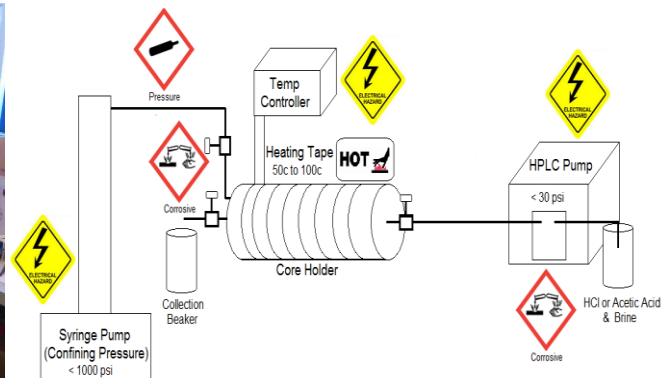- Hydrocarbon producibility

Cutoff-BVI (CBVI) model is used to determine the moveable fluids (large pores) and immobile fluid (capillary pores) based on a fixed-T2 value (T2cutoff) which divides the free-fluid index (FFI) and BVI. The T2 signal from the rock matrix is actually very rapid, even modern logging tools cannot detect it. Accordingly, the recorded T2 distribution only represents the porosity occupied by immovable BVI, movable (FFI) water and clay-bound-water (CBW) components. This value (T2cutoff) is used to divide the T2 distribution into movable (i.e., producible or free fluids and FFI) and immovable (i.e., bound-fluid, BVI, and CBVI) components.

3. Experimental studies

3.1 Core Flood Setup

Figures 1a and 1b shows the core-flooding experimental setup and schematic diagram respectively, which were used for the core flooding of Berea sandstone and Guelph dolomite core samples with chelates. This core flooding setup is capable of handling a pressure up to 10,000 psi and a temperature up to 200°F. The wetted parts of the apparatus are made of corrosion resistive material (e.g., hastelloy), which makes this system rust free even at higher concentrations of acids. The experimental setup consists of five basic parts which are explained below with detailed function.

- Core holder is used to confine the core sample at desired pressure and temperature. The material of this core holder is hastelloy. It has two inlets and one outlet. The confining pressure applied during the experiments is 1000 psi while the temperature is 150°F.
- The High Performance Liquid Chromatography pump as shown in Figure 1a and 1b, is used to inject the acid into the core holder at desired and controlled rate. It can inject liquid at a maximum rate of 6000 cc/min. The injection rate for this research is 1 cc/min. The less injection rate is used in order to avoid high back pressure during the experiment.
- The Temperature controller (Figure 1a) with a tape is used to heat the core holder at desired temperature value. The maximum temperature attained using this controller is 500°F.
- The syringe pump (Figure 1a) is used to create a high pressure inside the core holder. It uses fresh water to create a high pressure and can create up to 20,000 psi pressure.
- Collection beaker is used to collect the reacted acid sample at the collection point as seen in Figure 1a.
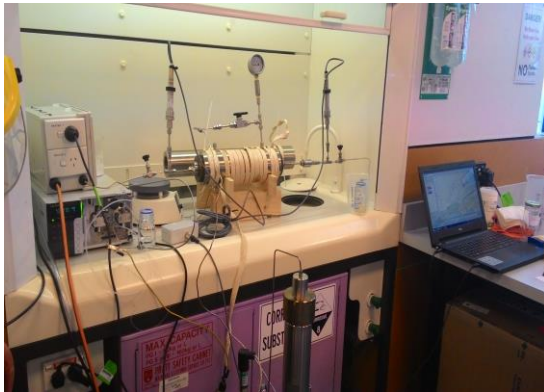
Figure 1a. Core Flood Setup   **Figure 1b.** Schematic Diagram

3.2 Core flood experiments

The core plug were weighed initially and dimensions were obtained using Vernier calliper. The core was put inside the core holder and core flood instrument was setup as shown in Figure 1a. The core was then confined under pressure of 1,000 psi using the syringe pump as shown in Figure 1a. The core holder was then heated to 150°F using the temperature controller and tape. The chelate was injected using HPLC pump at a rate of 1 cm^3/min where the pressure variation was monitored at pressure transducers. The constant pressure value at HPLC pump and transducer shows the completion of the reaction. Injection of acid is terminated and one hour residence time was allowed to complete the reaction of the chelate with the core sample. Distilled water is injected to remove the remains of the acid present in the core sample.

Table 1. Sample name and composition

Sample Name	Type of rock	Chelate
Sample A		EDTA
Sample B	Colton Sandstone	HEDTA
Sample C		GLDA
Sample A		EDTA
Sample B	Guelph Dolomite	HEDTA
Sample C		GLDA

3.3 Laboratory Measurements / Procedures

Apart from the core flooding experiments, there were variety of other measurements and preparation work carried out as well, which included:

- Measuring permeability, porosity of the core samples before and after core flooding experiments.

- Drying of core samples before and after each test at 80°C for 24 hours.

- Weight of all dry core samples was measured before and after core flooding experiments.

- Saturation of core samples using brine (5% NaCl) for NMR analysis using manual saturator.

- Running NMR tests on the brine saturated samples before and after each core flooding test.

- The reacted acid was collected from the core flood test and was analyzed for various ions using ICP analysis.

4. Result and Analysis

4.1. Porosity and Permeability Analysis

The porosity is defined as the measure of empty spaces in the rock and it provides information about the storage capacity of the reservoir rock. It is considered as one of the most critical parameter for the determination of oil and gas initial in place. It can be measured or determined in different ways i.e., manually and automatically. In this research Automatic Porosity Permeability Apparatus (Figure 2) is used to measure both porosity and permeability. Permeability and porosity values before and after acidizing are presented in table 2.
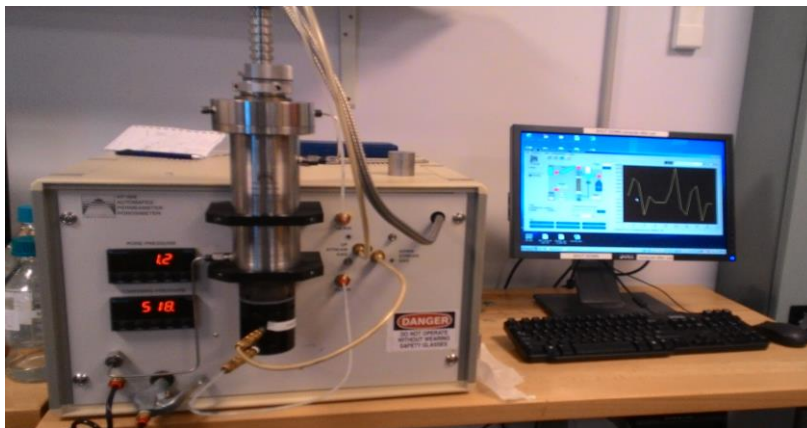

Figure 2. Automatic Porosity permeability apparatus

The main purpose of acidizing is to remove the damage around the wellbore and to create new channels in the reservoir rock. The main purpose of the application of HCl is to remove calcium, potassium, sodium, magnesium and iron minerals. Creating new pores by dissolving these minerals increase the porosity and permeability. Usually, sandstone samples contain very less amount of sodium, potassium and calcium ions, therefore; as a result, the change in porosity is also less. The removal of these ions is very necessary in order to get better acidizing results because these minerals can cause precipitation later during the main acid stage of sandstone acidizing.

Table 2. Porosity (∅) and Permeability (K) results

	Sample Name	Chelate used	Initial ∅ %	Final ∅ %	% change
Tight sandstone	Sample A	EDTA	10.74	11.66	8.50
	Sample B	HEDTA	11.49	12.65	10.10
	Sample C	GLDA	12.13	13.01	7.25
Carbonate	Sample A	EDTA	16.80	16.82	0.11
	Sample B	HEDTA	14.19	15.09	6.30
	Sample C	GLDA	21.20	21.63	2.03
	Sample Name		Initial K (md)	Final K (md)	% change
Tight sandstone	Sample A	EDTA	0.7118	0.6379	-10.30
	Sample B	HEDTA	0.4633	0.9542	105.67
	Sample C	GLDA	0.8069	0.7842	-2.80
Carbonate	Sample A	EDTA	104.27	93.76	-10.07
	Sample B	HEDTA	9.80	18.11	84.79
	Sample C	GLDA	405.55	399.41	-2.00

HEDTA proved to be very useful chelating agent as compared to EDTA and GLDA for both sandstone and carbonate samples. The increase in permeability is almost double when HEDTA was allowed to react with sandstone and carbonate samples. Although other chelates were also very effective in increasing porosity of tight sandstones but the permeability increment is not in favour. This maybe attributed towards the formation of precipitate and residing of these precipitates in the larger pores which choke the pore spaces. Also, these chelates are soluble in water at very high temperature ranges, decrease in temperature can cause formation of precipitates and settling of solid particles present in chelate.

4.2 NMR measurements

NMR measurement has been applied on all core samples before and after acidizing to investigate the change in pore size distribution and change in pore topology. Figure 3 represent the T2 spectrum for each dolomite core sample reacted with chelates while figure 4 represent the spectrum analysis of each sandstone core sample. Change in pore size distribution can be seen clearly in spectrum of sample C and B, it means that the new pores have been created while spectrum of sample A represents decrease in pore sizes. The reduction of pore space sizes can be attributed to dissolution of minerals and re-precipitation in the pores. These precipitates can be formed due to ineffective acidizing by chelate and can reduce the porosity. Sample B (reacted with HEDTA) spectrum showed maximum increase in number of large pore spaces, validating permeability and porosity results discussed in table 2.
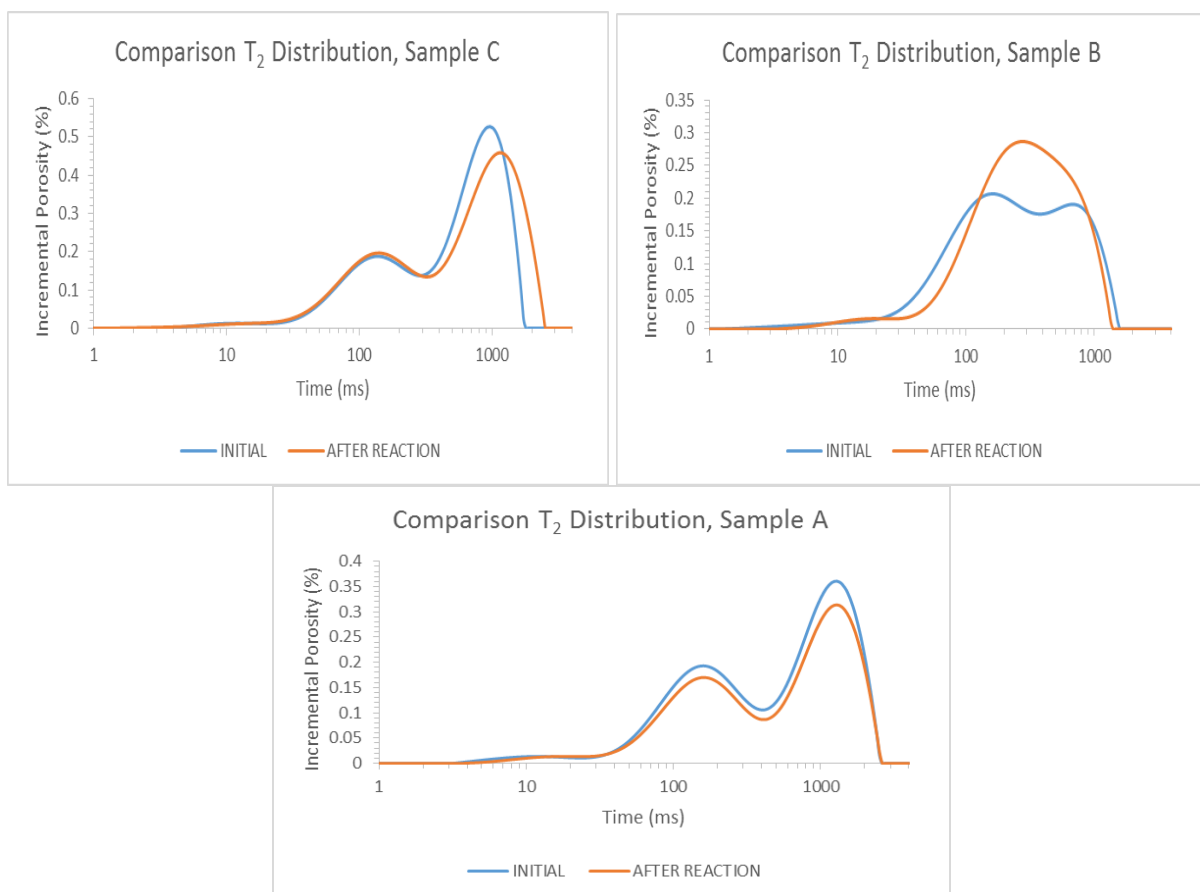

Figure 3. T2 spectrum of carbonate samples

The spectrum in figure 4 clearly represents the increase in the total amount of pore spaces in the sandstone core samples after acidizing, where maximum change in number of pore spaces has been

observed in sample B reacted with HEDTA, validating porosity and permeability results (Table 2). The increase in porosity after acidizing can be attributed to the effective action of chelate on the core sample. Sample A reacted with EDTA and there is decrease in porosity which can be attributed to the ineffectiveness of EDTA on sandstone core sample. HEDTA proved to be very effective in creating more spaces in both sandstone and carbonate samples.
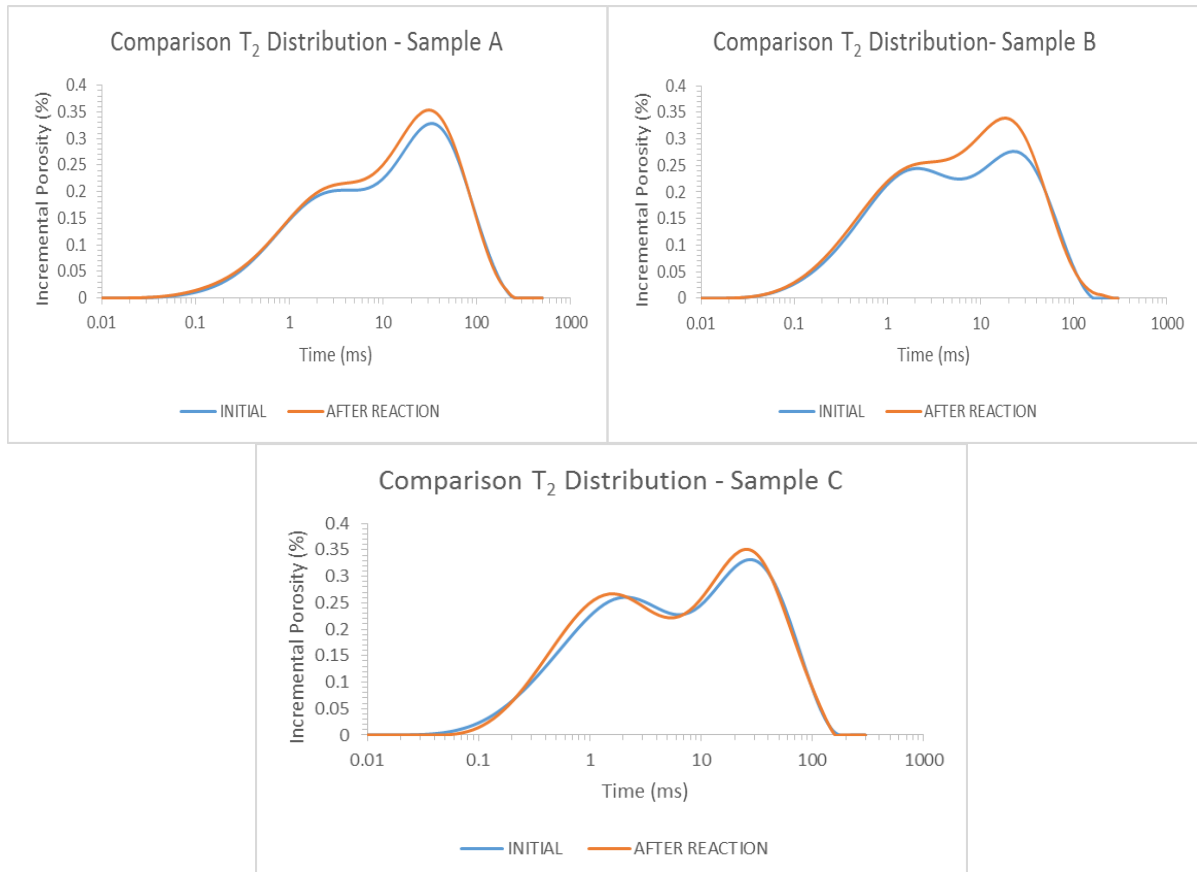

Figure 4. T2 spectrum of sandstone samples.

Table 3 explains the porosity results obtained from NMR analysis. Figures 3 and 4 are based on these results. These results are validating the porosity results obtained previously mentioned in Table 2; where the maximum change in the porosity has been observed when carbonate sand sandstone samples were reacted with HEDTA. The advantage of NMR porosity measurement over general porosity measurement is the knowledge of pore distribution which has been explained and analysed using Figures 3 and 4.

Table 3. Porosity Results using NMR.

	Sample Name	Chelate used	Initial ø %	Final ø %	% change
	Sample A	EDTA	11.75	12.49	6.30
Tight sandstone	Sample B	HEDTA	12.63	14.13	11.90
	Sample C	GLDA	14.02	14.39	2.60
	Sample A	EDTA	18.02	15.59	-0.13
Carbonate	Sample B	HEDTA	14.66	16.02	9.30
	Sample C	GLDA	21.33	22.35	4.80

4.3 Inductively Coupled Plasma (ICP) Analysis

Inductively Coupled Plasma analysis is used to investigate the concentration of different ions dissolved by the acid during the reaction. During the core flooding experiments effluent samples (reacted acid) were collected at regular intervals of time and utilized to determine the concentrations of Si, Ca, Na, K, Fe and Mg present in the reacted chelate. The results presented are in parts per million (ppm). From the analysis presented in Table 4, it can be seen clearly that the maximum amount of each mineral is dissolved when HEDTA has been applied. All samples are collected after 20 minutes of core flood experiments.

Table 4. Concentration of dissolved ions (ppm)

	EDTA		HEDTA		GLDA	
Element	**Sandstone**	**Carbonate**	**Sandstone**	**Carbonate**	**Sandstone**	**Carbonate**
Sodium	3710	4930	4290	4440	2870	2090
Magnesium	614	198	1370	2570	900	962
Aluminium	0.432	2.27	136	6.65	0.962	39.1
Silicon	4.47	0.954	97.9	0.684	0.1	42.1
Phosphorous	0.1	0.1	2.85	0.1	0.1	0.1
Sulphur	105	111	67.7	133	26.6	17
Potassium	869	1970	313	2310	130	2610
Calcium	1090	178	4600	4320	2640	2010
Titanium	0.1	0.1	0.319	0.150	0.1	0.1
Chromium	0.1	0.1	0.269	0.1	0.1	0.1
Manganese	1.33	0.522	155	5.73	1.6	141
Iron	0.285	7.81	207	54.9	3.28	145
Cobalt	0.1	0.1	0.524	0.121	0.1	1.31
Zinc	31.6	4.32	101	12.1	1.39	22.8

Table 4 represents that HEDTA can dissolve dissolves more amount of sodium, magnesium, aluminium, silicon and calcium. That's why increase in porosity and permeability is quite significant when HEDTA was applied on sandstone samples. While EDTA removed more amount of sodium, sulphur and potassium from carbonate samples as compared to HEDTA and GLDA. GLDA removed more amount of magnesium and calcium from sandstone samples as compared to EDTA. From ICP analysis it can be concluded that HEDTA id effective in removing positive ions as compared to other chelates applied.

5. Conclusion

It can be concluded that HEDTA chelate had significant effect on the porosity and permeability of the core sample and removed positive ions efficiently. Moreover, NMR analysis concluded that fresh large pore spaces has been created using the chelates especially HEDTA results were quite significant. HEDTA can be recommended for tight sandstone and carbonate acidizing.

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