Dissolution of Barium Sulfate Scale by Using Ethylenediaminetetraacetic Acid (EDTA)

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***Abstract*—Barium sulfate ($BaSO_4$) scale is one of the major problems that cause equipment breakdown consequently decline the oil recovery. In order to remove the scale, a chelating agent ethylenediaminetetraacetic Acid (EDTA) is used as a scale remover. The objective of this experiment is to identify the effect of temperature and concentration of EDTA to the dissolution of $BaSO_4$ scale. Different temperature and concentration of EDTA are varied to find the optimum effectiveness. Based on the results obtained from Inductively Coupled Plasma Mass Spectrometry (ICP-MS) 0.005M EDTA solution at 80°C is the most optimum condition as the solubility of barium sulfate was found to be 110.5 ppm. This study showed that EDTA at high concentration and low temperatures are not potent for $BaSO_4$ dissolution.**

Keywords*— *Barium sulfate, Ethylenediaminetetraacetic Acid, scale, dissolution, scale remover, chelating agent.

I. INTRODUCTION

Scales deposition that forms a sturdy layer on the internal surface of the pipelines, equipment and systems has long been a major and common problem in oil and gas industries. This issue might influence the optimum operating of equipment and normally cause breakdown. These scales arise due to the fluids incompatibility or changes of thermodynamic conditions which will lead to accumulation and precipitation that cause blockage to the pipelines and might decline the oil recovery[1]. The scale deposition within the oil field are sulfates such as barium sulfate (barite), strontium sulfate (celestite) and calcium sulfate (anhydrite, gypsum), calcium carbonates, iron, silica and variant insoluble[2]. Barium sulfate or also called as barite is a common scale in the oil and gas production and its low solubility in regular solvents like hydrochloric acid (HCl), make it as one of the toughest scales to be removed[3].

Chemical dissolution creates a way in controlling the scale deposits by using chelating agents. Chelating agents have the properties as natural biogenic compounds and anthropogenic compounds have an important role in influencing and controlling dissolution of the scale, precipitation and promoting metals release of into solution[4]. Chemical dissolvers that classified under amino carboxylic acids group is a strong chelating agent to remove sulfate scales. Ethylenediaminetetraacetic acid (EDTA) are known as the two common chelating agents and barium sulfate dissolver used for the dissolution experiments as these agents are all strong metal ion chelators and forms a strong complex with metal ions in solution[5].

It is essential to understand the barite scale dissolvers to develop a treatment which can dissolve the barite solids formed and to understand the relationship between dissolver concentration and temperature to a great extent. Recent study shows that there are many chelating agents that have been used to study solubility of barium sulfate as the scale remover. However, the dissolution rate of scale deposition is dissimilar as different organic substances with variant molarity and concentration are being used and but the optimum conditions for dissolution have not totally been addressed[6]. In addition, it is acknowledged that temperature change features an important impact on the solubility of barium sulfate that successively affects its scaling tendency. As temperature decreases, the tendency of scaling will increase and will continue to form in the wellbore as temperature fall[2].

This study aims at exploring the optimum condition of chelating agent EDTA as scale dissolver by identifying the effect of concentration and temperature of the solvent to the dissolution of $BaSO_4$ scale.

II. METHODOLOGY

2.1 Preparation of acid solution

The stock solution of EDTA (1,000 mg/L) was prepared. EDTA powder with molecular weight of 292.24 g/mol was weighted to 186.1 g. It was then placed into 1000 ml beaker before 800 ml distilled water is added to make a standard 0.5M EDTA solution. The solution is stirred vigorously on a magnetic stirrer. The pH is adjusted by the addition of 20 g sodium hydroxide (NaOH) pellets since EDTA will not go into solution until the pH of the solution is adjusted to approximately 8. Then, filled the beaker with distilled water to the 1000ml mark. The solution is transferred into Schott bottle and sterilized by autoclaving for 20 minutes at 121°C on liquid cycle. Working solutions were obtained by appropriate dilution in the range of concentration 0.5M to 0.0001M based on the previous study by[4].

2.2 Dissolution Studies

2.2.1 Effect of concentration

Standard 0.5M EDTA solution is diluted to the concentration 0.05M, 0.01M, 0.005M and 0.001M in 100ml beaker. The temperature will remain at room temperature (27°C). 1g of $BaSO4$ was then merged with 100ml EDTA solution. The stirring rate kept constant at 200 rpm in all experiments to ensure an undisturbed non-turbulent circulation of the suspended barite grains. Samples are taken on 15 minutes. The solution is filtered by filter paper and centrifuged to eliminate suspended particles. 4ml of the solution is extracted and a syringe is used to make a sampling. The samples then were analyzed using ICP-MS.

2.2.2 Effect of temperature

To study the effect of temperatures of the acid solution to the dissolution of barium sulfate, the concentrations of acid solution will be kept constants at 0.005M throughout the experiment as the previous experiment showed that at that concentration, highest dissolution of barium sulfate occurred. This experiment also required 1g of barite in 100ml acid solution and the samples is taken with the similar way it was taken in the previous experiment at the varies temperature from 22, 40, 60 and 80 °C also being analyzed using ICP-MS. Parallel experiments were conducted where the $BaSO_4$ particles residue from the experiments which has the highest dissolution is analyzed by Fourier Transform Infrared Spectroscopy (FTIR).

2.3 Weight Loss

The weight of the barite at the initial and final of the experiment was weighed. $BaSO_4$ scale on the plate is weighted before it is put into 100 ml of the most optimum concentration and temperature of EDTA solution. After 1 hour, the $BaSO_4$ scale is again weighted to measure its weight before and after being placed in acid solution. The solubility of the barite was determined using the following equation:

$$\text{Solubility (\%)} = \frac{\text{dissolved barite weight}}{\text{initial barite weight}} \text{ x } 100$$

where, the initial barite weight is 1 g in 100 ml of solvent; the dissolved barite weight is the difference between the initial barite (before the test) and the remaining barite (after the test). A parallel experiment was conducted where the surface of plate with barium sulfate before and after dissolution with EDTA solution is observed using Geology Microscope.

III. RESULTS AND DISCUSSION

3.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis

3.1.1 The effect of concentration of EDTA solution to the dissolution of $BaSO_4$

Table 1: Concentration of barium sulfate dissolved in different concentration of EDTA solution.

Concentration of EDTA Solution (M)	Concentration of Barium Sulfate Dissolved (ppm)	Amount of Barium Sulfate Dissolved (g/L)
0.001	32.4	0.0324
0.005	36.6	0.0366
0.01	22.5	0.0225
0.05	16.4	0.0164
0.5	5.5	0.0055

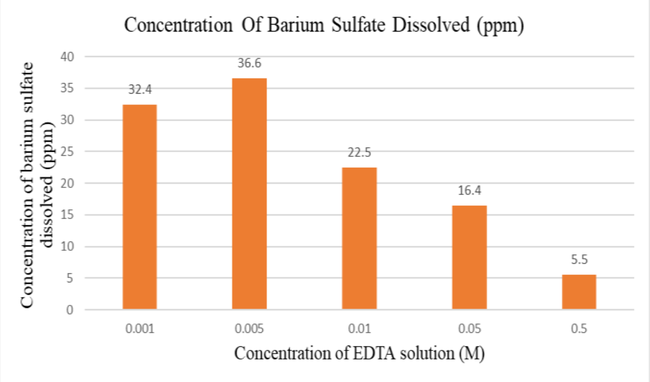

Fig. 1: Concentration of barium sulfate dissolved in different concentrations of EDTA solution

Samples of 1g barium sulfate in different concentrations of EDTA solution in the range of 0.001 to 0.5 M is analyzed using ICP-MS to figure out the concentration of barium sulfate that dissolved in 100 ml of EDTA solution. As presented in Table 1, the amount of barium sulfate dissolved by increasing concentration of EDTA solution was slightly increased at 0.001 M to 0.005M and decrease gradually from 0.005M to 0.5M. It can be seen in Figure 1 that 0.005M EDTA solution attained a much greater dissolution of barium sulfate as a solvent. Theoretically, it was expected that the lower the concentration of acid solution, the lesser the dissolution of the scale[4].

However, results show the contrary to the expectations, dissolution increases as the EDTA concentration is reduced. Inadequate EDTA molecules exist in solution to correlate with the available Ba^{2+}. Based on the graph, it can be observed that a 0.005 M EDTA solution provide the maximum barium sulfate dissolution capacity which is 36.6 ppm or equivalent to 0.0366 g/L $BaSO_4$ for 15 minutes. This must be due to saturation of the solution with unreacted chelant and barium-chelant complex. A greater concentration of EDTA higher than 0.005 M leads to a declination in the rate of dissolution due to arising in competitive adsorption of EDTA on the barite surface, thereby reducing the rate of desorption of Ba^{2+} into the solution. Moreover, when the concentration is increased by more than 0.005 M of EDTA the viscosity rises, and the reaction is retarded[7].

3.1.2 The effect of temperature of EDTA solution to the dissolution of $BaSO_4$

Table 2: Concentration of barium sulfate dissolved in different temperature of EDTA solution.

Temperature of EDTA Solution (°C)	Concentration of Barium Sulfate Dissolved (ppm)	Amount of Barium Sulfate Dissolved (g/L)
27	36.6	0.0366
40	56.6	0.0566
60	84.5	0.0845
80	110.5	0.1105

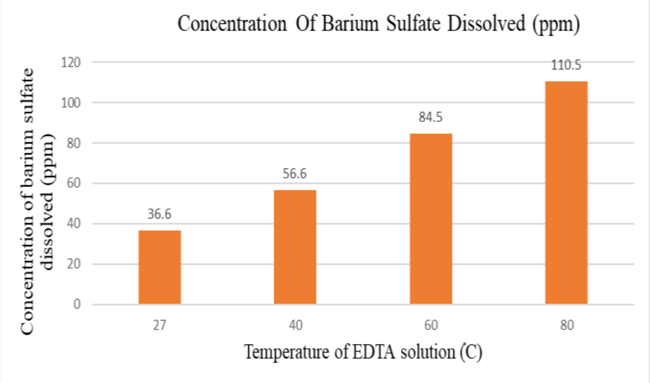

Fig.2: Concentration of barium sulfate dissolved in different temperatures of EDTA solution

To study this parameter similar concentration of EDTA solution is used in which is 0.005M. Temperature of EDTA solution differed from room temperature, 40°C, 60°C, and 80°C. Temperature is kept constant for 15 minutes and stirred at 120 rpm before the sample of 1g barium sulfate in 100 ml of EDTA solution is taken and analyzed using ICP-MS to figure out the concentration of barium sulfate dissolved. The results presented in Table 2 show that the dissolution rate is a temperature dependent as the concentration of barium sulfate dissolved increased significantly as the temperature of EDTA solution increased.

As might be expected, the dissolution is improved at raised temperatures. Figure 2 followed the general trend and showed the relationship between temperature and dissolved barium sulfate is directly proportional. A temperature rises from 27°C to 80°C causes an increase in BaSO4 solubility since the temperature is one of the major parameters that affect the solubility. At the highest temperature of EDTA solution which is 80°C, concentration of barium sulfate dissolved is also the highest which is 110.5 ppm or equivalent to 0.1105 g/L. This is parallel with the study by [8], that increasing the temperature of scale dissolvers has the positive effects to accomplish disintegration and boosted scale dissolution. As greater temperatures are available downhole because at higher formation depths higher existing pressures will lift up the boiling point of the aqueous solution, hence greater scale removal rates may be obtained [9].

3.2 Fourier-transform infrared spectroscopy (FTIR) Analysis

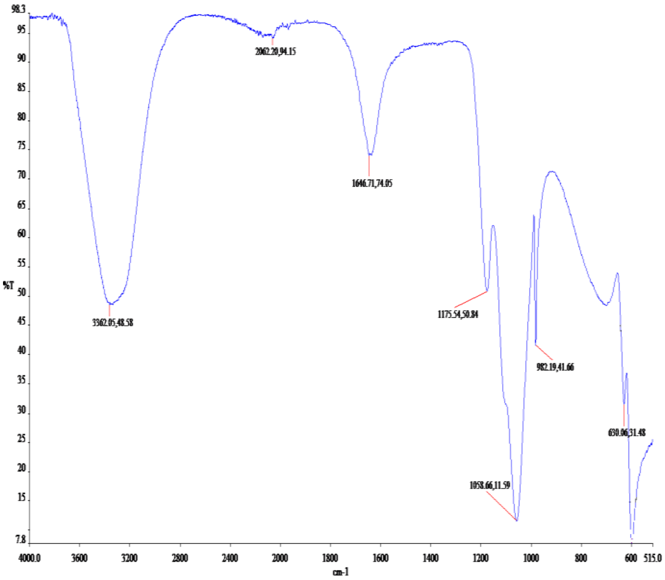

Fig 3: FTIR analysis for $BaSO_4$ before dissolution with EDTA solution

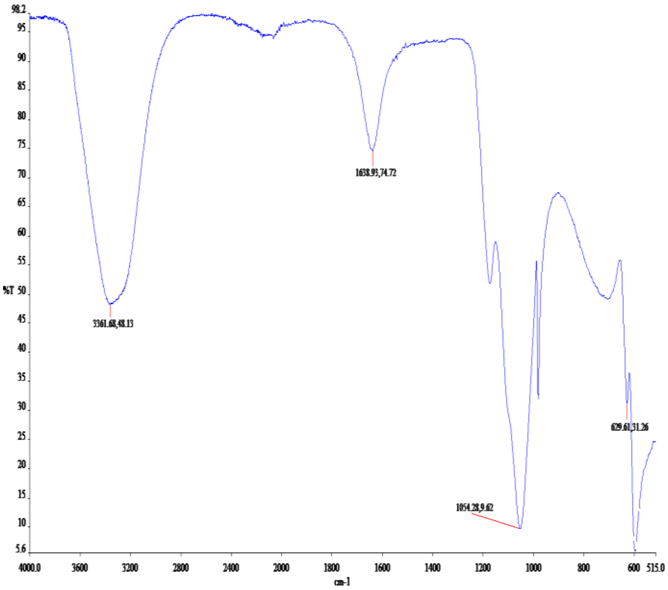

Fig 4: FTIR analysis for $BaSO_4$ after dissolution with 0.005M EDTA solution at 80°C.

Table 3: Infrared band positions of the studied barium sulfate.

Wave number (cm^{-1})			Assignments
Peak Group	Before	After	
A	3362.02	3361.68	H-O-H stretching
B	2062.20	------	CH stretch
C	1646.71	1638.93	H-O-H bending of water
D	1175.54 1058.66 ------ 982.14	------- ------- 1054.28 ------	(*v3*) sulfate vibrational modes (*v3*) sulfate vibrational modes (*v3*) sulfate vibrational modes (*v1*) sulfate vibrational modes
E	630.06	629.61	(*v4*) sulfate vibrational modes

FTIR spectroscopy for the barite solids before the dissolution and FTIR for the residual barite solid after the dissolution with EDTA solution is shown in Figure 3 and Figure 4 respectively. Table 3 shows five group of main FTIR absorption bands relying on the different frequencies of the band position. The comparisons between the FTIR peaks for barite solids before dissolution (BD), and after dissolution (AD) with their assignments for each peak are presented in the Table 3.

There are four fundamental vibrational modes of sulfate bands which are nondegenerate (v1), one doubly degenerate (v2), and two triply degenerate (v3 and v4). For sulfate in a solid state, the internal vibrational features normally become visible at ~1050–1250 (v3), ~1000 (v1), ~500–700 (v4), and ~400–500 (v2) cm^{-1}

FTIR analysis for the BD and AD of barium sulfate showed that the bands position and the absorbance intensity changed after the dissolution of barite particles in EDTA. Group A indicates the presence of hydroxyl groups O–H stretching mode and absorbed water[10]. In group-B, the peaks at 2062.20 cm-1 appeared in BD with low intensity and disappeared after the dissolution, which is related to CH stretch[11]. In group C, the peak 1646,71 cm-1 BD peak shifted to 1638.93 cm-1 AD indicated that small amount of water in barium sulfate and capability of barium sulfate to absorb water during dissolution with EDTA.

In group D, the peaks at 1175.54 and 1058.66 cm-1 in BD are associated with the v3 of sulfate and the peak at 982.19 cm-1 is related to the v1 of sulfate[12]. These peaks were disappeared, and a new peak arose at 1054.28 cm-1 in AD due to the dissolution of barite in EDTA. The peak is attributed to v3 sulfate vibrational mode and indicated that some of the sulfate functional groups were eliminated caused by the dissolution. The peak at 630.06 cm-1 in BD, was relocated to 629.61 cm-1 in AD with the similar intensity and showed that the v4 of sulfate was though to break during the dissolution of barite.

3.3 Weight Loss

Table 4: Weight of barite before and after the dissolution

Weight Before (g)	Weight After (g)	Weight Dissolved (g)	Solubility (%)
1.62	0.1944	1.4256	88

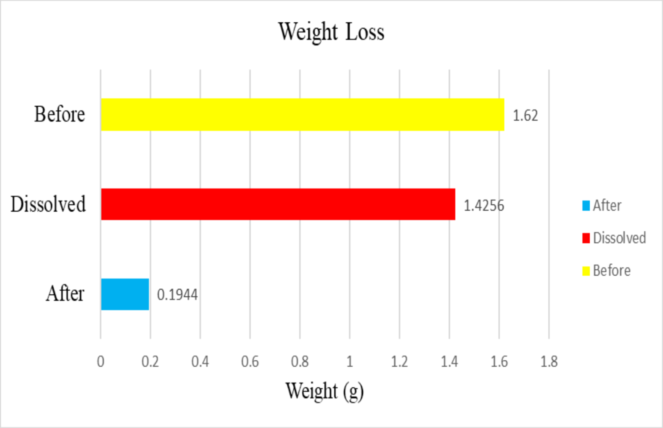

Figure 5: Weight of barium sulfate scale before and after dissolution.

The experiment was carried out at 80°C using 0.005 M EDTA solution as in previous experiments showed that at this temperature and concentration, the amount of barium sulfate dissolved is the highest. Barium sulfate scale on a plate is weighted before placed in scale dissolver. The solutions were left undisturbed for 1 hour to let the dissolution process to occur as the solution is not stirred. As can be seen, the weight of barium sulfate scale on the plate after being put in EDTA solution decrease from 1.62 g to 0.1944 g. Dissolved barium sulfate weight is the subtraction of initial weight at the beginning of the experiment and the residual barium sulfate weight at the end of the experiment which is 1.4256 g. By using the solubility formula, value of initial weight subtracts the final weight of the barium sulfate scale divided by the initial weight[13], it can be concluded that the solubility of barium sulfate scale in 0.005 M EDTA solution at 80°C reached 88%. As the dissolution process occurred, it is predictable that the weight of the barium sulfate scale is reduced after being placed in the acid solution as some particles of barium are dissolved into the acid solution.

Figure 7: Surface of barium sulfate scale plate before dissolution.

Figure 8: Surface of barium sulfate scale plate after dissolution.

The same barium sulfate scale plate which is used to determine the weight loss is used in this experiment parallelly. Figure 6 and Figure 7 shows the surface of barium sulfate scale on a plate before and after dissolution with EDTA solution respectively. The first image displays that the scale was not yet being dissolved as the white surface appeared with no pattern. As being placed in EDTA solution for 1 hour, the barium sulfate plate is again being observed using Geological Microscope. It can clearly be seen that image after the dissolution process occurred has the pattern. This pattern showed that some of the barium sulfate scales is dissolved in EDTA solution.

The morphology and particle size of the barite solid is impossible to be observed using Geological Microscope as its lens only possible to magnify 10 times and give the overall enlargements possible at 40 X with the scanning lens[14]. It is recommended to use Scanning Electron Microscope to determine the grain size and any surface dissolution effects and to study the morphology of barite grains before and after dissolution. SEM can produce a 3D, black and white image on a computer screen since the energy source employed in the electron microscope is a beam of electrons. The beam has a short wavelength and strikes most objects in its path as well as increases the resolution of the microscope[15].

IV. CONCLUSION

Generally, through the proposed experimental procedures, it was feasible to study the dissolution of $BaSO_4$ by varied the parameters of EDTA concentration and temperature. The dissolution study denotes that under low temperatures in high EDTA concentration, dissolution is incompetence for $BaSO_4$ and increasing the temperature give positive factors to achieve disintegration and enhanced scale dissolution. 0.005 M EDTA concentration at 80 °C was found to be the most optimum condition 110.5 ppm or 0.1105 g/L of barium sulfate is dissolved which is the highest dissolution compare to others concentration and temperature. It is essential to investigate the effect of concentration and temperature of scale remover to the dissolution of the scale to formulate the treatment. Thus, the proposed methodology represents a wide study about the $BaSO_4$ dissolution by EDTA. For future study, different parameters can be investigated such as the effect of pH of the scale remover to the dissolution of $BaSO_4$ and the effect of catalyst to improve the dissolution of the scale.

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