Study of Barium Sulfate Scale Dissolution into Ethylenediaminetetraacetic acid (EDTA)

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Abstract. Barium sulfate (barite) scale deposition may cause the problem in surface and subsurface production equipment resulting in reduced production, decrease in pressure, and premature failure of down holes equipment. One of the barite scale management is by using dissolver. There are many chelating agents that can be used to dissolve this scale including ethylenediaminetetraacetic acid (EDTA). In this work, EDTA is used to dissolve the laboratory-reproduced barium sulfate scale. Barite scale was reproduced in the laboratory by mixing barium chloride (BaCl₂) solution and sodium sulfate (Na₂SO₄) solution at 25°C. The sensitivity analysis was performed to determine the optimum parameters/conditions in which EDTA dissolution is optimum through Inductively Coupled Plasma Optical Emission Spectrometry (ICP-EOS) analysis and characterization study using Field Emission Scanning Electron Microscope (FESEM). This includes the effect of agitation, temperature, pH, catalyst used, and the presence of oxalate ion. These laboratory tests showed that the solubility of barite increased as it was agitated; at high pH of 11 to 13; and at elevated temperature of 95°C. Potassium chloride (KCl) at high elevated temperature was used as synergy/activator to improve the dissolution of barium sulfate with EDTA. As a conclusion, this project sets a framework to identify the best EDTA formulation and estimate its dissolution profile to ensure a more informed treatment design for barite scale removal.

Introduction
There are many problems that can occur during handling oil and gas production operations. One of them is the depositional of the mineral scales such as barium sulfate (BaSO₄)[1]. The major contribution of BaSO₄ formation is because the formation water contains high concentration of Ba²⁺ and the injection water usually contain high concentration of SO₄²⁻ and these two come into contact in region of the well bore[2][3][4][5]. Thus, this scale will block production tubing, reduce porosity and permeability of the reservoir because barite is highly insoluble minerals (2.5mg/L) and has low solubility product Ksp=10⁻⁹.⁹⁹[5][6].

A various study has been done in the past in removing barium sulfate mechanically or chemically. Most practices in the industry utilized chelating or completing agents. Aminopolycarboxylic acid, such as diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA) can be used to dissolve barite scale [7][8]. EDTA was chosen in this dissolution test because it is inherently biodegradable[9] as compared to DTPA. Even though DTPA is the strongest chelating agent in dissolution of barium sulfate, it not readily biodegradable[10].

EDTA is hexadentate ligand that consists of four carboxylic acid groups and two nitrogen atoms for coordination with metal ions (Figure 1)[11]. EDTA thermally degrades to hydroxyethyl iminodiacetic acid (HEIDA) and iminodiacetic acid at pH 9.5 and 500°F in 30 minutes[12]. Further hydrolyze of HEIDA creates ethylene glycol and iminodiacetic acid. EDTA can degrade even though it has low biodegradability by using certain strains of bacteria [9]. Other than being used as barium sulfate dissolver, EDTA can also be used to remove carbonate, calcium sulfate and a mixture of calcium scale. EDTA chelating agent has been utilized to remove barium sulfate (barite) scales from oil and gas wells. EDTA is the most widely used metal ion control agent in the industry. It has 6 to 8 complexing sites, respectively, enabling one molecule to interact with all the reactive centres of a metal ion, forming a stable ring complex (Figure 1).
In this study, the dissolution of barite has been investigated where the active solvent, EDTA is known to be a strong cation chelating agent. Of particular interest is the way in which a compound known to complex strongly with Ba$^{2+}$ ions in solution behaves on the surface of crystalline BaSO$_4$; the dissolution rate of barium sulfate by EDTA solution has been studied in this work.

![Molecular structures of ethylenediaminetetraacetic acid EDTA.](image)

**Figure 1** Molecular structures of ethylenediaminetetraacetic acid EDTA.

### Methodology

#### Materials

The barium sulfate scale used in this project was prepared by reacting sodium sulfate (Na$_2$SO$_4$) with barium chloride (BaCl$_2$). The barite sample for the dissolution process was based on the assumption that the dissolved solid samples are of nearly the same particle size and shape. The chelating agents based on the aminocacetate group formed effective scale dissolver which is EDTA. Next, oxalic acid (H$_2$C$_2$O$_4$) was used as oxalate ions and potassium chloride (KCl) was used as catalyst.

**Preparation of BaSO$_4$**

Doubly deionized water was used to prepare BaCl$_2$ and Na$_2$SO$_4$ solutions for each experiment. BaSO$_4$ crystals were prepared by pouring aqueous barium chloride (BaCl$_2$) solution (0.1 mol/L, 500 mL) quickly into a 1500mL beaker containing aqueous sodium sulfate (Na$_2$SO$_4$; 0.1 mol/L, 500 mL), which was stirred continuously with a magnetic stirrer. In the process of precipitation and incubation, the system was kept at 25°C and left to react for 24 hours [13]. The produced BaSO$_4$ crystals were then filtered and subsequently washed with abundant doubly deionized water, following by drying in an oven at 70°C for at least 24 hours. The barite was crushed in an agate mortar and these barite were ready for the dissolution test and FESEM analysis [14].

If the concentrations of Ba$^{2+}$ and SO$_{4}^{2-}$ become sufficiently high i.e. supersaturation condition is achieved, barite will precipitate as crystal growth by the following reaction,

$$\text{Ba}^{2+} + \text{SO}_{4}^{2-} \rightarrow \text{BaSO}_4(s) \quad (1)$$

It was assumed that only barite was produced and no other mineral phases (other than barite) were synthesized under that mixed brine condition set up [5].

#### Dissolution

The dissolution experiment was carried out using 3g of the prepared barite sample in 50 ml of 0.1M EDTA with pH of 12.3. The same test condition was maintained for dissolution of barium sulfate using potassium formate and oxalic acids. At a strong alkaline condition at pH of more than 12, the dissolvers were progressively deprotonated and became negatively charged. This is based on the concept that the ligand (L), EDTA has a strong affinity for barium in solution. This shifts the reaction shown below to the right and promotes the dissolution of barite.

$$\text{BaSO}_4(s) + \text{L}_m^- \rightarrow (\text{BaL})_{2-m} + \text{SO}_{4}^{2-} \quad (2)$$
The real-time dissolution experiment was then conducted in a beaker with EDTA solution in the static and dynamic conditions. The dissolution test was carried out on five various dissolving times i.e. 1 hour, 2 hours, 3 hours, 4 hours and 5 hours. Both static and dynamic (stirred modes) conditions were applied to the dissolution test.

The effect of temperature towards barium sulfate dissolution was investigated by varying the test temperature of 25°C, 40°C, 60°C, 80°C, and 95°C accordingly [21]. The dissolution test was also conducted at varying pH conditions i.e. pH 9, pH 10, pH 11, pH 12 and pH 13 to see the dissolution profile.

The stirring rate was kept constant in all experiments and was ensured sufficiently for a smooth, non-turbulent circulation of the suspended barium sulfate particles. The assumption of the stirred system with a constant stirring rate is to eliminate the interference of transport on the surface for the dissolution process. Therefore, the dissolution reaction under a stirred system can mostly depend on the surface reaction without much interference on mass transport [5].

The chelation products of the dissolution test were analyzed by an inductively coupled plasma (ICP) analyzer from Thermo Scientific Inductive Coupled Plasma ICAP 6000 Series [5].

Characterization

The FESEM analysis was performed on crystal surfaces that had been previously etched in EDTA solutions and dried before mounting on a specimen holder. FESEM can be used to observe the morphology changes of crystal and the etch pits on the surfaces. Compared with convention scanning electron microscopy (SEM), field emission scanning electron microscopy (FESEM) produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nanometers – three to six times better. However, the FESEM only tolerates specimens that are perfectly dry. Field emission scanning electron microscopy (FESEM) provides topographical at magnifications of 10x to 300,000x, with virtually unlimited depth of field. A Zeiss SUPRA 40VP FESEM was used for this investigation [15].

![Figure 2 Scanning electron micrographs (SEM) of distinct crystal morphologies of synthetic barite. The scales on the images are 2 μm. (A) Rosette crystals (B) well-rounded crystals [16].](image)

Figure 2 shows rosette-like barite crystals had a flower-like habit and were the dominant morphologies. The rosette crystals formed under temperatures of 5°C, 20°C, and 40°C in the absence of organics i.e EDTA. Well-rounded, spherical barite crystals were observed formed under temperature of 5°C, 20°C, 40°C in the presence of 0.01M EDTA [16].

Results and Discussion

A. Dissolution Test

Dissolution proceeds preferentially at the lower energy surfaces in the barite crystal. Chelating agents form strong complexes with metal ions in solution and are known to promote the dissolution of inorganic compounds. In this work, EDTA was used to study the dissolution of barite crystal.
It was observed that as barite was added into EDTA solution, the solution immediately turned cloudy. As time increased, there were no color changes observed as barite was white in color and EDTA solution was a clear solution. This was also observed for other conditions/parameters tested in this experiment.

1. The effects of agitation

In agitated condition, the barite was observed to be suspended. As time proceeded, the chelating agent was dissolving the solid barite, i.e. concentration of solid powder was decreasing, and the amount of barite in the solution was increasing. Thus, all barite particles were floating in the solution and were thus accessible to the EDTA molecules. Figure 3 shows the dissolution of barium sulfate due to agitation, this shows that the agitation increases accessibility of barite to EDTA and this leads to increase in dissolution.

When there was no agitation, the barite particles settled at the bottom of the beaker. Thus, at any given time, only the top layer is exposed to EDTA. Thus, dissolution occurs in that layer only [17].

Previews study by Putnis, 2008[11] and Lakatos, 2002[7] reported on using paddle stirrers and shakers towards the dissolution of barite. If paddle-type stirrers [11] were used, lower values have been observed possibly because paddles only stir the solution, and not the barium sulfate powder. If shakers were used [7], the amount of dissolved barite was about the same but took longer time to achieve equilibrium than the dissolution test using magnetic stirrer. Again, this can be attributed to more accessibility of suspended barite particles as compared to static particles that are periodically shaken. Thus, dissolution of barite strongly depends on accessibility of barite scale.

![Figure 3 Effect of agitation on barium sulfate solubility in 0.1M EDTA, pH=12.3, 25°C](image)

2. Effect of temperature

Figure 4 shows the effect of temperature on the barite solubility in the formulation EDTA at the following temperatures; 25, 40, 60, 80 and 95°C [21]. These solubility experiments were performed using the hot plate with a magnetic stirrer for 1h.

It was found that the solubility of BaSO₄ increases with increasing temperature since the rate of BaSO₄ precipitation decreases [18]. Increasing the temperature enhances the diffusion of EDTA to the barite particles surfaces and increases the reaction rate [19]. Increasing the temperature from 25 to 95°C increases the barite solubility from 26.81 mM to 97.26 mM after 1h.
3. Effect of pH

Figure 5 shows the effect of pH on barium sulfate dissolution. At pH 11, the dissolution of barium sulfate started to achieve a plateau which obviously proved that the barite dissolution is favorable at high pH. At high pH conditions, EDTA became progressively deprotonated and the affinity for barium ions increased [20]. The dissolution enhancement caused by NaOH is highly concentration-dependent. At low concentrations, when only partial neutralization takes place, the positive effect is negligible. At high NaOH concentrations, when full neutralization of the acidic groups is reached, the dissolution of barite extremely high compared to the level characteristic in distilled water, or NaOH free systems [7]. Therefore, the pH of the EDTA solution was kept above 11 [8][17][19][10].

\[
\text{EDTA + 4NaOH} \rightarrow \text{EDTA-4Na + 4H}_2\text{O} \quad (3)
\]

4. Effect of catalyst (Potassium Chloride – KOH)

Ten dissolution experiments at 25 °C were carried out using barium sulfate sample that already been prepared. Five experiments were performed using 0.1M EDTA and five using 0.1M EDTA + 0.1M KCl at the same temperature and pressure (25 °C and 1 atm). The experiment was conducted in...
constant rotation for each of the two-fluid. Figure 6 shows that the dissolution using EDTA alone was higher than barite dissolution in the EDTA + KCl. Supposedly, the dissolution profile using EDTA + KCl must be higher than using EDTA alone. This is because potassium chloride will convert barium sulfate to barium chloride in the presence of high pH Na-EDTA (pH above 11) [3]. The chemical equation below shows the reaction of barium sulfate with potassium chloride.

\[
\text{BaSO}_4(s) + 2\text{KCl} \rightarrow \text{BaCl}_2 + \text{K}_2\text{SO}_4
\]  

Figure 6 Effect of potassium chloride on barium sulfate solubility in 0.1M EDTA, pH=12.3, 25°C.

5. Effect of synergies (Oxalic acid)

These experiments were performed using 0.1M EDTA with 0.1M and 0.2M oxalic acid [17] at 25°C and pH of 12.3. The experiment was conducted in constant rotation. Figure 7 shows the dissolution profile was constant for 0.1M oxalic acid when it was added into the solution. For 0.2M of oxalic acid, the dissolution profile was slightly increased as time increased. Given the sensitive nature of the dissolution test, the measurement system was ensured to be precise and accurate to minimize errors.

Figure 7 Effect of synergy (oxalic acid) on barium sulfate solubility in 0.1M EDTA, 0.5M Oxalic acid, pH=12.3, 25°C.
B. Characterization of Barite Scale

Figures 8 and 9 show the images obtained by FESEM and it was Rosette crystals which had a flower-like habit (Figure 8) and well-rounded crystals (Figure 9) of barium sulfate. The EDTA caused the dissolution of cleavage steps which receded with time. The shape of barite changes from Rosette crystals to well-rounded crystal because the presence of organic substance which is EDTA[16].

Figure 8 – FESEM image of barium sulfate (1 μm) at 25°C
Figure 9 – FESEM image of barium sulfate (10K X) at 0.1M EDTA, pH=12.3, 95°C

Conclusion

Based on the results obtained from evaluating the dissolution rate of the barium sulfate in EDTA as a chelating agent, it can be concluded that:-

- It needs to be agitated in order to increase the accessibility of barium sulfate in EDTA.
- The dissolution process must be in high temperature, starting from 80°C.
- The recommended pH of EDTA should be greater than 11 to achieve the maximum solubility of barite.
- The catalyst must be conducted at a high temperature in order to reach its maximum capacity.
- The concentration of EDTA and EDTA + Oxalic acid must be equal to get the optimum reaction and the pH must be in the range 11 to 13.

Other type of chelant can be studied using the same framework to determine the best chelant with the best optimum conditions.

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