Dissolution Kinetics of Different Inorganic Oilfield Scales in Green Formulations

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ABSTRACT: Scale mineral deposition is a critical problem that hinders the daily production of oil and gas fields. Chemical removal of these scales, based on the scale type, is common. In this paper, borax and diethylene tremaine penta acetic (DTPA) acid-based formulations are used for the removal of sulfides, carbonates, and sulfate scales. In particular, the dissolution rates of sulfide (pyrite, pyrrhotite, and galena), sulfate (celestite and barite), and carbonate (calcite) scales were investigated in a rotating disc apparatus at typical well conditions. Scanning electron microscopy–energy-dispersive X-ray and X-ray diffract analyses were performed for characterizing scale composition and type. The effect of temperature, scale type, and formulation on the dissolution rate is studied. Even though borax formulation has been developed for the sulfide scale removal, it showed a high dissolution rate for the carbonate scale ($7.23 \times 10^{-7}$ mol·L$^{-1}$·s$^{-1}$·cm$^{-2}$). For the sulfide scale, the highest dissolution in borax formulation was obtained with galena (lead sulfide, PbS), followed by pyrrhotite, and the lowest dissolution was reported for pyrite ($1.55 \times 10^{-8}$ mol·L$^{-1}$·s$^{-1}$·cm$^{-2}$). Borax formulation was found to be inefficient in the removal of sulfate scales with a dissolution rate lower than carbonate and sulfide scales by 3 and 2 orders of magnitude, respectively. Similarly, DTPA-based formulation has yielded the highest dissolution for the carbonate scale ($7.98 \times 10^{-6}$ mol·L$^{-1}$·s$^{-1}$·cm$^{-2}$). However, for sulfate, DTPA-based formulation showed better performance than borax. The increase in temperature leads to an increase in the dissolution rate for almost all types of scales; however, DTPA-based formulation showed improved performance with temperature. Both formulations are efficient in removing sulfate- and sulfide-rich scales. The experimental results of DTPA have been validated by density functional theory calculations of binding energies between DTPA and metal ions present in the mixed scale.

1. INTRODUCTION

Scale formation is a critical problem that affects the optimal exploitation of oil and gas fields. After the startup of production, the system thermodynamic stability is interrupted, as the pressure declines with time in the reservoir. Gases such as CO$_2$ and H$_2$S will be present when producing from sour wells. In addition, some fields might need water injection for pressure maintenance inside the reservoir; injection of incompatible water also leads to scale formation. This could cause a significant flow assurance problem that costs the oil and gas producer more than USD 1.4 billion annually.$^1$ Buildup of scale inside the oil and gas tubing system leads to the reduction in its inner diameter and consequentially chokes the hydrocarbon production. At the extreme cases, the flow will completely have choked with the formed scale.

Inorganic scales can form at any point of the production system including reservoir, wellbore, production tubings, downhole pumps, and surface facilities.$^2$ Technical problems associated with scale formation include but are not limited to fluid flow obstruction, heat transfer impedance, metal parts wearing, reduced equipment life, localized corrosion, reduced performance of corrosion inhibitor, and unanticipated equipment shutdown.$^3$ The common types of inorganic scales found in the oil field are carbonate scales such as calcite (CaCO$_3$) and siderite (FeCO$_3$) and sulfates such as barite (BaSO$_4$) and celestite (SrSO$_4$) in addition to sulfides like pyrite (FeS$_2$) and pyrrhotite (Fe$_7$S$_8$).

1.1. Scales in Qatar Oil and Gas. Chemical treatment is the common solution for the scale buildup problem in oil and gas fields. Recently, our research group has studied the removal of iron sulfide scales using green formulations. Both theoretical and experimental approaches have been used to develop effective formulations and provide insights on the mechanisms of sulfide scale dissolution.$^4$ A new formulation based on a chelating agent and converter, particularly (DTPA + K$_2$CO$_3$),$^6$
is introduced. Also, another formulation composed of an oxidizing agent (borax) has shown better dissolution capability for iron sulfide scales.\(^7\)\(^,\)\(^8\) HCl is the conventional chemical treatment used to remove oilfield scales. Unfortunately, this method leads to corrosion of the pipes and equipment and also produces the toxic gas hydrogen sulfide as a byproduct. Hence, there is the need for better formulations. Both formulations (DTPA + K\(_2\)CO\(_3\) and the use of an oxidizing agent borax) have shown a very low corrosion rate and no hydrogen sulfide production unlike HCl.\(^9\)\(^,\)\(^10\)

Our earlier work has studied the removal of the single type of inorganic scales, mainly, iron sulfide; yet in the field, scale is found as a mixture of different types of inorganic scales.\(^11\)\(^−\)\(^14\) Therefore, the main objective of this study is to extend the application of the developed formulations to other types of scales, in particular, carbonate, sulfide, and sulfate scales. The dissolution of the most common oilfield inorganic scales, particularly carbonate (CaCO\(_3\)), sulfate (SrSO\(_4\) and BaSO\(_4\)), and sulfides (FeS\(_2\) and Fe\(_7\)S\(_8\)), in borax and diethylene triamine penta acetic (DTPA) formulations are investigated. The effect of scale type, temperature, and formulation on the dissolution rate is investigated at typical downhole conditions of high temperature and high pressure. This work aims to study the effect of DTPA + K\(_2\)CO\(_3\) and borax formulation on the removal of mixed scales, as this is more practical in what is observed in oil fields, where different scales are found together. The results obtained from this work provide oil and gas professionals with the dissolution kinetic data needed to design chemical formulations for the scale removal. In addition, the data obtained herein will help in selecting the suitable type of
formulation required for the removal based on scale composition.

2. RESULTS AND DISCUSSION

2.1. Scale Characterization. XRD (X-ray diffraction) analysis was performed using powder samples. For the sulfate scales shown in Figure 1, the orange and green curves show the measured XRD peaks for barite and celestite, respectively. Herein, all the peaks observed in the orange curve were attributed to the barite sample in agreement with previous reports. Similarly, the results for celestite (shown in green) are supported by previous literature reports. With regard to sulfide scales, XRD confirmed that the sample used herein is pure PbS. All the peaks, shown in purple at 2 theta of 26, 30, 43.5, 51, 63, 69, and 71° are for PbS. Pyrite sample results are given elsewhere, whereas the four peaks at 30, 34.5, 44, and 53.5° (in red color) are for pyrrhotite. Finally, carbonate scales are studied using the CaCO3 sample with the XRD peaks illustrated in black and are in agreement with the published literature. All samples were pure minerals as confirmed by the XRD results.

2.2. Effect of Formulation on Scale Dissolution. The dissolution rate of carbonate, sulfide, and sulfate scales using DTPA + K2CO3 and borax formulations has been investigated in 12 experiments. The optimum formulation concentration that yields the maximum scale dissolution is used. Herein, the dissolution rates for the three types of inorganic scales are revealed in Figures 2–4. The percentage error for the dissolution experiment is detailed in Table S1 of the Supporting Information. The dissolution of sulfide and sulfate scales using borax formulation is shown in Figure 2, whereas Figure 3 illustrates the dissolution rate of carbonate scales in borax. Even though borax formulation was developed for the sulfide scale removal, it showed a relatively higher dissolution rate for the carbonate scale (1.37 × 10−6 mol·L−1·s−1·cm−2). The measured calcite scale dissolution as shown in Figure 3 is 2 orders of magnitude higher than sulfide and 3–4 orders of magnitude higher than sulfates (Figure 2). For the sulfide scale, the higher dissolution in borax formulation was obtained with lead sulfide (galena), followed by pyrrhotite, and the lowest dissolution was reported for pyrite 1.55 × 10−8 (mol·L−1·s−1·cm−2). Borax formulation was found to be inefficient in removing the sulfate scale, with the dissolution rate being lower than that of carbonate and sulfide scales by 2–3 orders of magnitude, respectively. In summary, the borax formulation has shown high dissolution for the carbonate scale, moderate dissolution for the sulfide scale, and almost no dissolution for sulfates. Accordingly, it is recommended to use the borax formulation for the removal of mixed scales dominated by carbonate and sulfide scales.

Figure 3 shows that the calcite dissolution rate in DTPA is about six times the dissolution in borax formulation. Similar to the borax formulation, DTPA-based formulation has yielded the highest dissolution for carbonate scales (7.98 × 10−6 mol·L−1·s−1·cm−2) compared to sulfide and sulfate scales, as shown in Figures 3 and 5. However, for the sulfate and sulfide scales, sulfates showed better dissolution in DTPA formulation than sulfides. The highest dissolution for sulfite was obtained with celestite, which was five times higher than barite dissolution. Therefore, the DTPA formulation has shown the best performance with carbonates, followed by sulfate scales, and then the lowest dissolution was obtained for sulfides. Hence, it is recommended to use the DTPA-based formulation for sulfate- and carbonate-dominated mixed scales.

2.3. Effect of Temperature on the Dissolution Rate. Because scales can form in both shallow and deep wells, where temperatures are different, accordingly, the dissolution rate measurement using the two formulations was obtained at different temperatures of 100 and 150 °C. Figures 5–7 indicate that the overall dissolution rate is enhanced, in general, with temperature. The increase of temperature leads to increase in the dissolution rate for almost all types of scales; however, the significant increment with temperature was observed with DTPA-based formulation as shown in Figures 6 and 7.

2.4. Theoretical Binding Affinities. Density functional theory (DFT) was used to study the binding affinities of Fe2+, Ca2+, Ba2+, and Pb2+ to DTPA. Equation 1 was used to calculate the binding energies. The optimized structures (Figure 8) of DTPA binding to different metals show that they all form six coordinated bonds with DTPA. The calculated binding energies using eq 1 are in agreement with the experimental stability constants (Table 1) from the literature. The stability constants just like the calculated binding energies denote the binding affinity of DTPA to the metal ions. The calculation for strontium (Sr) was not done to save computational cost. However, because Ca2+, Sr2+, and Ba2+ are group 2 metals, which go down the group, Ca2+ and Ba2+ were calculated leaving out Sr2+. The stability constants of Ca2+, Sr2+, and Ba2+ are 10.9, 9.7, and 8.7, respectively, showing that the binding affinity of DTPA decreases down the group. The same trend is observed in the calculated binding energies, as Ca-DTPA is greater than Ba-DTPA. The stability constant of Pb-DTPA is 19.1, which is the highest among the studied complexes and is in agreement with the binding energy. The negative values of all the binding energies correlated with the experimental result show that the formulation involving DTPA is effective for all different mixed scales studied.

\[ E_{\text{metal-complex}} = E_{\text{compound}} - E_{\text{metal}} \] (1)

3. CONCLUSIONS

In this paper, the kinetics of the most common types of inorganic scales, particularly, carbonate (CaCO3) and sulfate (SrSO4, BaSO4) in addition to sulfides (FeS2, Fe7S8, PbS) using two newly developed green formulations, was investigated using a high-pressure high-temperature (HPHT)-rotating disc apparatus (RDA) reactor. The first formulation
is composed of DTPA and K2CO3, and the second one is formed from borax. The effect of scale type, temperature, and formulation on dissolution was addressed at typical downhole conditions. The following are the main conclusions:

- The dissolution rate of carbonate, sulfide, and sulfate scales has been investigated using two newly developed formulations of borax and DTPA + K2CO3 in a RDA.
- Both borax and DTPA formulations have shown the best dissolution rate for the carbonate scale (CaCO3), yet the DTPA-based formulation shows six times higher dissolution with calcite.
- The DTPA formulation has shown the best performance with carbonate, followed by sulfate scales, and then the lowest dissolution was obtained for sulfides; therefore, it is recommended to use the DTPA-based formulation for removing sulfate– and carbonate-rich scales.
- The borax formulation is effective for the removal of carbonate and sulfide scales, but it is not recommended with sulfate scales such as barite and celestite.
- Unlike borax, the DTPA-based formulation has shown good performance for all types of scales; however, slightly lower dissolution was obtained for sulfide scales except galena.
- The increase of temperature leads to increase in the dissolution rate for almost all types of scales; however, the significant increment with temperature was observed in DTPA-based formulation.
- DFT calculations of the binding energies of Fe2+, Ca2+, Ba2+, and Pb2+ with DTPA have supported experimental observations.

Figure 4. Dissolution of different inorganic scales using DTPA + K2CO3 formulation (T = 150 °C).

Figure 5. Effect of temperature on the dissolution of different inorganic scales using borax.

Figure 6. Effect of temperature on calcite dissolution in both formulations.
The use of DTPA + K2CO3 formulation can be applied to the mixed scale removal in the oil and gas industry, hence boosting production.

4. METHODOLOGY

4.1. Materials. Different types of rock samples were obtained from Geology Superstore Company, UK. Sulfide, sulfate, and carbonate scale samples were used in this study. Sulfide scales used were pyrite (FeS2), pyrrhotite (Fe7S8), and galena (PbS); the sulfates were celestite (SrSO4), barite (BaSO4), and calcite (CaCO3). In addition, Advanced Technology & Industrial Co. Ltd., Hong Kong has supplied potassium tetraborate tetrahydrate (K2B4O7·4H2O, borax) with 99.5% purity. AkzoNobel, Netherlands provided the chelating agent (DTPA pentapotassium, DTPAK5) with the stock concentration of 40 wt % and pH of 13. Figure 9

Table 1. Calculated Binding Energies of DTPA Complexed to the Metal Ions Present in Different Scales

| complex  | metal   | B.E. (Hartrees) | B.E. (kcal/mol) |
|----------|---------|----------------|-----------------|
| Fe-DTPA  | Fe2+    | −1263.58       | −900.69         |
| Ca-DTPA  | Ca2+    | −676.70        | −1234.43        |
| Ba-DTPA  | Ba2+    | −25.11         | −913.50         |
| Pb-DTPA  | Pb2+    | −191.55        | −1487.36        |

The energy of DTPA = −1460.51 Hartrees.

The use of DTPA + K2CO3 formulation can be applied to the mixed scale removal in the oil and gas industry, hence boosting production.
illustrates the type of scale samples used in this work. The dimensions and porosity of the scale discs are shown in Table 2. To measure the porosity, the samples were dried overnight and then weighed before being inserted into the reactor of the RDA. They were vacuumed for 2 h, and then, a brine solution of KCl (potassium chloride) was transferred to the sample at the atmospheric pressure. The pressure was stabilized and steadily increased to 136 bar. Thereafter, the samples were left at this condition for about 22 h. The pressure was then decreased gradually, the samples were removed, and then, their weights were measured after. The porosity was calculated using the formula (eq 2) reported by Sayed and Nasrabaedi:

$$A_0 = \frac{A_C}{(1 - \Phi)}$$

where $A_0$ is the initial surface area of the pyrite disc (cm$^2$), $A_C$ is the cross-sectional area (cm$^2$), and $\Phi$ is the disk porosity in the volume fraction. The calculation of the porosity is detailed in Table S2 of the Supporting Information.

The procedure used for scale sample preparation is given in previous publications.$^{6,7}$ XRD was used for mineralogy identification of the scale sample.

4.2. Experimental Section. A HPHT-RDA reactor was used for reaction rate measurements. The equipment was designed locally at Qatar University and manufactured by Top Industrie, France. The equipment is capable of conducting experiments at conditions that simulate oil and gas wells. The pressure and temperature can go up to 400 bar and 250 $^\circ$C, respectively. Also, the experiment can be performed under static or dynamic conditions with a disc rotational speed of up to 1500 rpm. In addition to the RDA, an ICP–OES (inductively coupled plasma optical emission spectrometry) model Optima 7300 DV was also used for cation concentration measurements. Sample mineralogy identification was performed using XRD Rigaku MiniFlex II made in Japan. The dissolution rate was measured at 100 and 150 $^\circ$C using the HPHT-RDA reactor (Figure 10). All experiments were conducted at 1200 rpm and 1000 psi for 30 min, similar to a previous work for the purpose of comparison.$^{6,7}$ First, the rock samples were loaded into the reactor, while the desired formulation is prepared and loaded into the fluid tank (see Figure 10). Then, both the reactor and tank temperature were set to the desired temperature and pressure of the experiment with a 30 psi decrease in pressure difference to enable the fluid flow. After the temperature is stabilized in both the reactor and fluid tank, the fluid in the tank is transferred to the reactor by opening the pneumatic valve. Effluent samples (5 ml) were automatically withdrawn from the reactor every 5 min. These samples were then diluted and analyzed using ICP–OES.

The procedure used for the dissolution rate measurement and the description of the RDA were explained in previous publications.$^{6,7}$ The dissolution rate is calculated as the slope (ppm/min), as shown in Figure 11. Finally, weight-loss measurements were used for calculating the dissolution rate. However, weight-loss results have shown up to 16% deviations from the HPHT-RDA results (Table S1 in Supporting Information). The procedure used for the dissolution rate measurement and the description of the RDA were explained in previous publications.$^{6,7}$ The

![Figure 10. Schematic of the HPHT-RDA equipment showing the main parts of the setup (Photograph courtesy of “Musa Ahmed et al.”. Copyright 2020).](https://dx.doi.org/10.1021/acsomega.0c04357)
detailed description of the experiments performed herein is given in Table 3.

Table 3. Experimental Details Showing Scale Type, Formulation Used, Rotations per Minute (rpm), Temperature (°C), and Pressure (psi)

| #  | rock            | formulation | RPM   | T, °C (±1) | P, psi (±5) |
|----|-----------------|-------------|-------|------------|-------------|
| 1  | SrSO₄           | 20% DTPAK₅ + 9% K₂CO₃ | 1200   | 150        | 1000        |
| 2  |                |             | 100   |            |             |
| 3  | FeS₂            | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 4  |                |             | 100   |            |             |
| 5  | BaSO₄           | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 6  |                |             | 100   |            |             |
| 7  | PbS             | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 8  |                |             | 100   |            |             |
| 9  | Fe₇S₈           | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 10 |                |             | 100   |            |             |
| 11 | CaCO₃          | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 12 |                |             | 100   |            |             |
| 13 | CuSO₄          | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 14 |                |             | 100   |            |             |
| 15 | Al₂O₃          | 20% DTPAK₅ + 9% K₂CO₃ | 150    | 100        |             |
| 16 |                |             | 100   |            |             |

4.3. Computational Details. The Gaussian 09 program was employed for all DFT calculations. B3LYP (Becke, 3-parameter, Lee−Yang−Parr) and DefTZVP were used as the level of theory and basis set, respectively. All calculations were done using water as an implicit solvent using the polarizable continuum model-self-consistent reaction field approach. Vibrational frequencies were calculated to ensure that there were no imaginary frequencies. The basis set superposition error was corrected using the counterpoise method. The Chimera software V1.13 was used for the visualization of the results.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04357.

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Notes

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